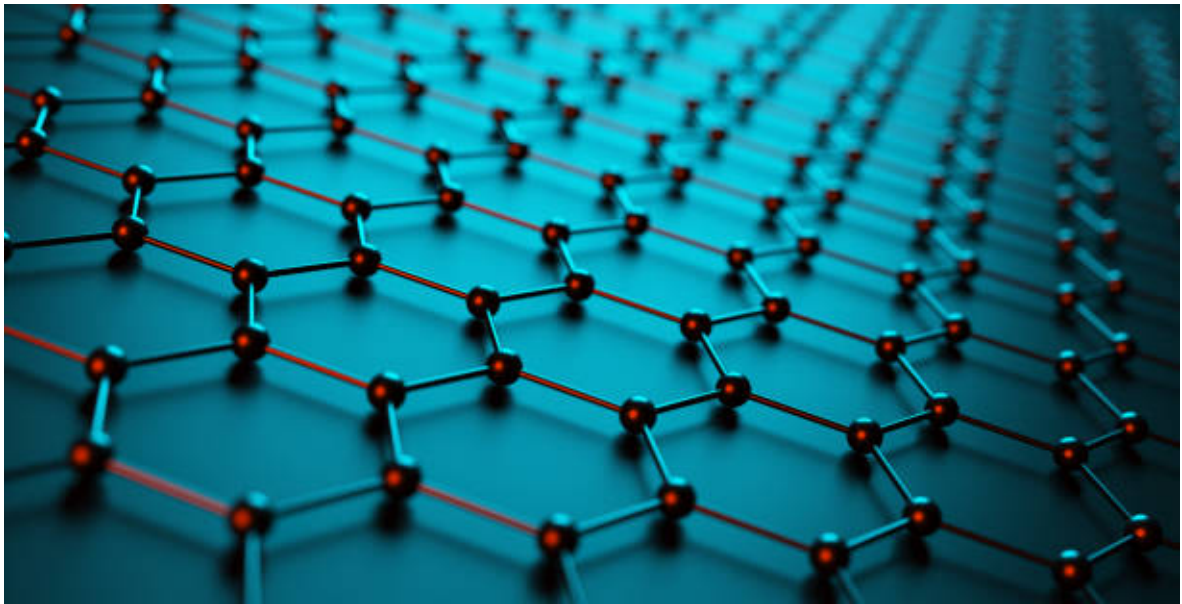


Calculating Band structure of graphene using Tight-Binding model

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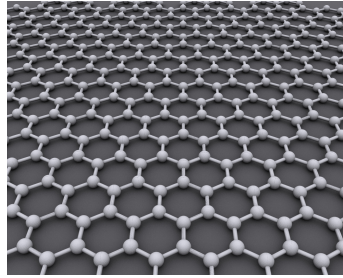


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1 Introduction

Solid state physics deals with the study of Electrical, Magnetic, Thermal, Mechanical, Optical and other such properties of solid materials. Crystal structure of materials affects their properties. The structure is determined using techniques such as x-ray crystallography, neutron diffraction, electron diffraction etc. A serious study of solid state physics began with discovery of x ray diffraction by crystals. Graphene is a single layer of carbon allotrope graphite. It has a hexagonal honeycomb lattice. Graphene is the thinnest material known to man. It is one atom thick. Fields in which use of graphene looks possible in near future include biological engineering, photovoltaic cells, optical electronics, ultrafiltration, etc.



Structure of graphene

Reference: Graphene-Wikipedia

1.1 Crystal

A crystal is a solid formed by periodic arrangement of atoms, ions or molecules. Not all solids are crystals. Crystals occur everywhere in nature ranging from table salt (NaCl) to valuable gemstones such as emerald, ruby, sapphire.

1.2 Important terminologies

1. Unit cell: The smallest unit which can be periodically repeated to form a crystal is called unit cell.
2. Basis: It is the arrangement of atoms associated with each lattice point. For e.g., Na and Cl are the basis of NaCl crystal.
3. Lattice: The set of mathematical points to which the basis is attached is called lattice. Arrangement of basis on lattice gives crystal.
4. Primitive lattice cell: A cell containing only one lattice point.

1.3 Lattice Translation Vectors

Suppose we consider a point P in the lattice of a crystal. If another point Q in lattice has same surrounding arrangement of atoms as that of P, then we say that Q is translated with respect to P. This is mathematically represented using lattice translational vectors. Suppose point P is located

at \vec{r} , then position of point Q is represented by:

$$\vec{r'} = \vec{r} + u_1\vec{a}_1 + u_2\vec{a}_2 + u_3\vec{a}_3 \quad (1)$$

where u_1, u_2, u_3 are integers. The lattice is primitive if for any two points, the above equation is satisfied with suitable choice of u_1, u_2, u_3 . Here, $\vec{a}_1, \vec{a}_2, \vec{a}_3$ are the primitive lattice translational vectors.

The number of atoms in a basis can be one or more than one. So, the position of atoms in a basis is determined by:

$$\vec{r}_i = x_i\vec{a}_1 + y_i\vec{a}_2 + z_i\vec{a}_3 \quad (2)$$

Origin(also known as associated lattice point) is chosen such that $0 \leq x_i, y_i, z_i \leq 1$. Atoms can then be arranged and lattice is formed.

Index system is used to identify the orientation of a plane in crystal. It is determined using following steps:

1. We choose lattice translational vectors(which may be primitive or non-primitive). Let us assume it to be $\vec{a}_1, \vec{a}_2, \vec{a}_3$.
2. Find the intercepts of plane on these axes. Suppose it has intercepts as $1\vec{a}_1, 2\vec{a}_2, 3\vec{a}_3$.
3. Take the reciprocal of co-efficients i.e. $1, \frac{1}{2}, \frac{1}{3}$.
4. Reduce it to three integers having same ratio. Here, it will be (6,3,2).

2 Fourier analysis of crystal

2.1 Index system

Indexes in general are denoted by (hkl). If a plane cuts negative side of axes it is denoted by bar over that index, for e.g. $(\bar{h}kl)$

We know that crystal is invariant under any translation of the form $\vec{T} = u_1\vec{a}_1 + u_2\vec{a}_2 + u_3\vec{a}_3$. So electron number density, charge concentration and other such properties remain invariant under such transformations. Electron number density $n(\vec{r})$ is the most important of them i.e $n(\vec{r} + \vec{T}) = n(\vec{r})$. We now expand $n(\vec{r})$ as Fourier series:

$$n(\vec{r}) = n_o + \sum_{p=1}^{\infty} \left[C_p \cos\left(\frac{2\pi p x}{a}\right) + S_p \sin\left(\frac{2\pi p x}{a}\right) \right] \quad (3)$$

where C_p and S_p are Fourier co-efficients. We could clearly see that it has periodicity of a . So, $n(x + a) = n(x)$. Writing this in Euler's form makes our further task easier. So, in 1-D we rewrite it as:

$$n(x) = \sum_p n_p e^{i2\pi p x/a} \quad (4)$$

where the sum is over all integral values of p . To ensure that $n(x)$ is real, we need $n_{-p}^* = n_p$. Fourier co-efficients is given by:

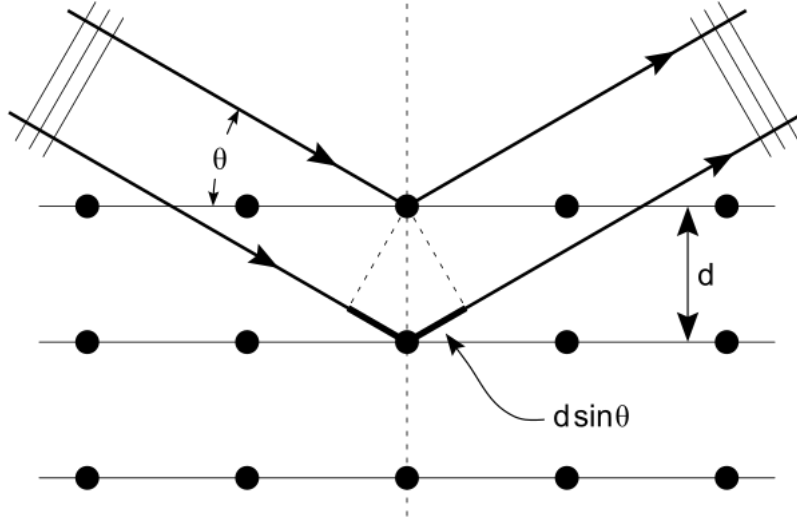
$$n_p = \frac{1}{a} \int_0^a n(x) \exp(-i2\pi p x/a) dx \quad (5)$$

In 3-D, we need vectors \vec{G} such that $n(\vec{r}) = \sum_{\vec{G}} n_{\vec{G}} \exp(i\vec{G} \cdot \vec{r})$. Here, the Fourier co-efficients is given by:

$$n_{\vec{G}} = \frac{1}{V_c} \int_V n(\vec{r}) \exp(-i\vec{G} \cdot \vec{r}) dV \quad (6)$$

where V_c is volume of crystal.

2.2 Bragg's law



Lower light beam travels an extra length of $2d \sin \theta$

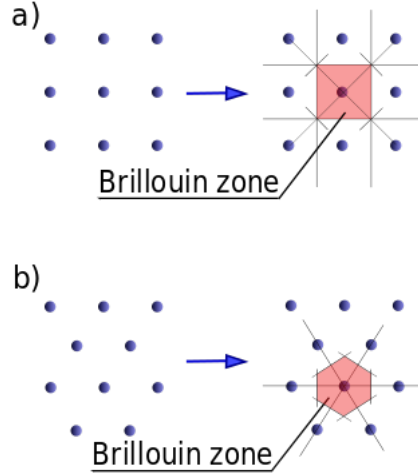
Reference: Bragg's law-Wikipedia

Bragg's law is a simple relation which gives condition for constructive interference when radiation is incident on lattice. Consider two parallel planes which are d distance apart. Radiation is incident on this plane. Then, the path difference between light falling on two adjacent planes is $d \sin \theta + d \sin \theta = 2d \sin \theta$. For constructive interference, it should be an integral multiple of λ . So, $n\lambda = 2d \sin \theta$. Let us now define reciprocal translational vectors. Consider b_1, b_2, b_3 as axes for reciprocal lattice vectors. Then:

$$\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3}; \vec{b}_2 = 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3}; \vec{b}_3 = 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3} \quad (7)$$

\vec{G} is defined as $v_1 \vec{b}_1 + v_2 \vec{b}_2 + v_3 \vec{b}_3$. $\vec{a}_i \cdot \vec{b}_j = 2\pi$ if $i = j$ else it is equal to 0. Reciprocal vectors have unit $1/[\text{length}]$.

2.3 Brillouin zone



Brillouin zone of (a) square lattice and (b) hexagonal lattice

Reference: Brillouin zone-Wikipedia

Brillouin gave a geometrical interpretation of diffraction conditions which is widely used in solid state physics:

$$2\vec{k} \cdot \vec{G} = G^2 \quad (8)$$

This condition can be rewritten as:

$$\vec{k} \cdot \frac{1}{2}\vec{G} = \left(\frac{1}{2}G\right)^2 \quad (9)$$

Select a vector \vec{G} from reciprocal space. Draw a plane perpendicular to it at its midpoint. Any vector whose tail coincides with tail of \vec{G} and whose head terminates on this plane satisfies the diffraction equation. The smallest volume enclosed by such planes is called the first Brillouin zone. The following are calculations for Brillouin zones of few lattices:

1)**Simple cubic lattice:** For simple cubic lattice, the primitive translational vectors are:

$$\vec{a}_1 = a\hat{x}, \vec{a}_2 = a\hat{y}, \vec{a}_3 = a\hat{z} \quad (10)$$

The corresponding reciprocal translational vectors are:

$$\vec{b}_1 = \frac{2\pi}{a}\hat{x}, \vec{b}_2 = \frac{2\pi}{a}\hat{y}, \vec{b}_3 = \frac{2\pi}{a}\hat{z} \quad (11)$$

The boundaries for first Brillouin zones are midpoints of $\pm\vec{b}_1, \pm\vec{b}_2, \pm\vec{b}_3$. They enclose a cube of volume $(2\pi/a)^3$. Thus, the reciprocal lattice of simple cubic cell is a simple cubic cell itself.

2)**Body centred cubic lattice:** For bcc lattice, the primitive translational vectors are:

$$\vec{a}_1 = \frac{1}{2}a(-\hat{x} + \hat{y} + \hat{z}), \vec{a}_2 = \frac{1}{2}a(\hat{x} - \hat{y} + \hat{z}), \vec{a}_3 = \frac{1}{2}a(\hat{x} + \hat{y} - \hat{z}) \quad (12)$$

The corresponding reciprocal translational vectors are:

$$\vec{b}_1 = \frac{2\pi}{a}(\hat{y} + \hat{z}), \vec{b}_2 = \frac{2\pi}{a}(\hat{z} + \hat{x}), \vec{b}_3 = \frac{2\pi}{a}(\hat{x} + \hat{y}) \quad (13)$$

These vectors are in fact the primitive translational vectors of face centred cubic lattice. Therefore, the reciprocal lattice of bcc lattice is fcc lattice. The volume of primitive cell is $2(2\pi/a)^3$. The first Brillouin zone in this case is defined by the planes drawn at the midpoints of:

$$\frac{2\pi}{a}(\pm\hat{y} \pm \hat{z}), \frac{2\pi}{a}(\pm\hat{z} \pm \hat{x}), \frac{2\pi}{a}(\pm\hat{x} \pm \hat{y}) \quad (14)$$

These 12 planes enclose a dodecahedron.

3)**Face centred cubic lattice:** For fcc lattice, the primitive translational vectors are:

$$\vec{a}_1 = \frac{1}{2}a(\hat{y} + \hat{z}), \vec{a}_2 = \frac{1}{2}a(\hat{z} + \hat{x}), \vec{a}_3 = \frac{1}{2}a(\hat{x} + \hat{y}) \quad (15)$$

The corresponding reciprocal translational vectors are:

$$\vec{b}_1 = \frac{2\pi}{a}(-\hat{x} + \hat{y} + \hat{z}), \vec{b}_2 = \frac{2\pi}{a}(\hat{x} - \hat{y} + \hat{z}), \vec{b}_3 = \frac{2\pi}{a}(\hat{x} + \hat{y} - \hat{z}) \quad (16)$$

These vectors are the primitive translational vectors of body centred cubic lattice. Therefore, the reciprocal lattice of fcc lattice is bcc lattice. The volume of primitive cell in reciprocal space will be $4(2\pi/a)^3$. The first Brillouin zone in this case is defined by the planes drawn at the midpoints of:

$$\frac{2\pi}{a}(\pm\hat{x} \pm \hat{y} \pm \hat{z})$$

These planes form an octahedron.

3 Electrons in solids

3.1 Drude model

Drude's model is a semi-classical model of electrons in a solid. Drude applied kinetic theory of gas to electrons. As this model was developed around 1900, it considered electrons as classical particles and hence quantum effects were not considered. Drude tried to explain the following things through his model:

- Differentiate between conductors and insulators
- Electrical conductivity in metals
- Thermal conductivity in metals

The following were assumptions made by Drude:

- Electrons move in straight line between collisions. This assumption is known as free electron approximation.
- Time between subsequent collisions is τ . This time does not depend on path or velocity of electrons.
- Long range interactions between electrons and other electrons or ions is ignored. It is known as independent electron approximation.

- After each scattering, the average momentum of electron $\langle \vec{p} \rangle = 0$.

Let us denote the Lorentz force by \vec{F} . The time between consecutive collisions is τ , so the probability of collision in any unit time is $\frac{1}{\tau}$. Suppose we consider momentum of electron at time t and $t+dt$. So, the probability of scattering after collision in infinitesimal time dt is dt/τ . In this derivation, let us denote average velocity $\langle \vec{v} \rangle$ by \vec{v} (same goes for \vec{p} and \vec{F} also). For the electrons which undergo scattering, the average momentum after scattering is 0. For electrons which don't undergo scattering, the average momentum is $m\vec{v}(t+dt) = m\vec{v} + \vec{F}dt$. To calculate net average momentum, we take weighted average:

$$\begin{aligned} m\vec{v}(t+dt) &= (1 - \frac{dt}{\tau})(m\vec{v} + \vec{F}dt) + \frac{dt}{\tau} \cdot 0 \\ &= m\vec{v} + \vec{F}dt - \frac{dt}{\tau}m\vec{v} - \frac{dt^2}{\tau}\vec{F} \end{aligned}$$

Ignoring $(dt)^2$ and rearranging equation, we get:

$$\frac{d\vec{p}}{dt} = -\frac{m\vec{v}}{\tau} + \vec{F} \quad (17)$$

We see that there is $-\frac{m\vec{v}}{\tau}$ term which is drag force. In equilibrium, average electron velocity is constant and so $\frac{d\vec{p}}{dt} = 0$. So, $\frac{m\vec{v}}{\tau} = \vec{F}$. For the time being, let us consider only electrical forces. So, $\vec{F} = -e\vec{E}$. Average velocity of electron comes out to be $\frac{-e\vec{E}\tau}{m}$. Current density \vec{j} is given by:

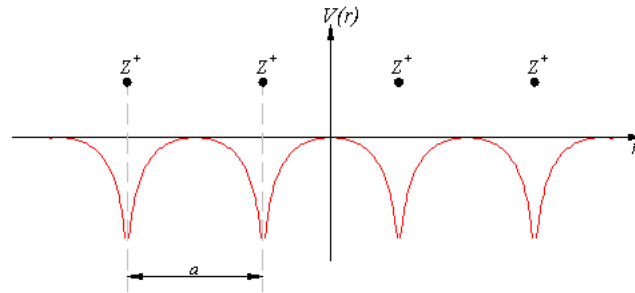
$$\vec{j} = -en\vec{v} = \frac{ne^2\tau}{m} \quad (18)$$

Resistivity ρ is equal to:

$$\rho = \frac{1}{\sigma} = \frac{m}{ne^2\tau} \quad (19)$$

We could write τ as $\frac{l}{v}$ where l is mean free path and v is thermal velocity of electrons obtained above. Putting this, we see that resistivity is proportional to square root of temperature. However, experimentally there is linear temperature dependence which is one of the limitations of Drude's model.

3.2 Free electron model



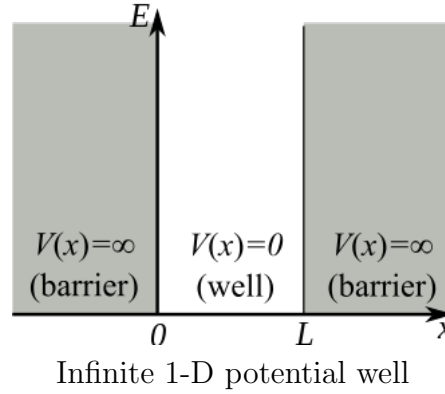
Small bumps in periodic lattice

Reference: Particle in a one-dimensional lattice-Wikipedia

The problem with Drude's model is that it has given electrons a classical treatment. We need to include wave nature of electron to create a better model. Suppose for example we consider a sodium atom. The potential energy due to Coulombic attraction between electron and protons in nucleus is $\frac{-Ze^2}{4\pi\epsilon_0 r}$. This energy shoots up to infinity as $r \rightarrow \infty$. When many such atoms are kept side by side, the potential energy reduces drastically and there are small bumps periodically as shown in the figure. In free electron model, we ignore such small bumps and assume potential to be an infinite well and then apply time independent Schrodinger's equation which is:

$$\hat{H}\psi_n = \left[\frac{-\hbar^2}{2m} \nabla^2 + V(r) \right] \psi_n = E_n \psi_n \quad (20)$$

Let us derive the wavefunction for 1-D infinite potential well. For an infinite potential well, potential energy is:



Reference: Particle in a box-Wikipedia

$$V(x) = \begin{cases} 0, & 0 \leq x \leq L \\ \infty, & x < 0 \text{ or } x > L \end{cases}$$

Therefore, the above equation reduces to:

$$\frac{d^2}{dx^2} \psi_n(x) = -\frac{2mE}{\hbar^2} \psi_n(x) \quad (21)$$

The general solution for $\frac{d^2 y}{dx^2} = -k^2 y$ is given by $y = A \sin kx + B \cos kx$ where A and B are constants. Let the wavefunction in the region $0 \leq x \leq L$ be ψ_n where n is an integer whose dependency we'll derive in a moment. On comparing, our differential equation for 1-D infinite potential well with standard equation, we get:

$$k = \sqrt{\frac{2mE}{\hbar^2}}$$

Since electron is trapped inside the potential well, wavefunction for $x < 0$ and $x > L$ is 0. Since wavefunction is continuous:

$$\psi_n(x=0) = 0 \text{ and } \psi_n(x=L) = 0$$

$\psi_n(x=0) = 0$ gives $B = 0$ and $\psi_n(x=L) = 0$ gives $\sin kL = 0$ which means:

$$\begin{aligned}
kL &= n\pi \\
k &= \frac{n\pi}{L}
\end{aligned}
\tag{22}$$

So, the wavefunction for 1-D infinite potential well in region $0 \leq x \leq L$ is given by:

$$\psi_n(x) = A \sin\left(\frac{n\pi x}{L}\right) \tag{23}$$

In quantum mechanics, $|\psi(x)|^2$ represents probability density of a particle in 1-D (this idea can be extended to 3 dimensions as well). We now integrate $|\psi_n|^2$ over whole space and equate it to 1 and this is known as normalization of wavefunction. So,

$$\int_0^L A^2 \sin^2\left(\frac{n\pi x}{L}\right) dx = 1$$

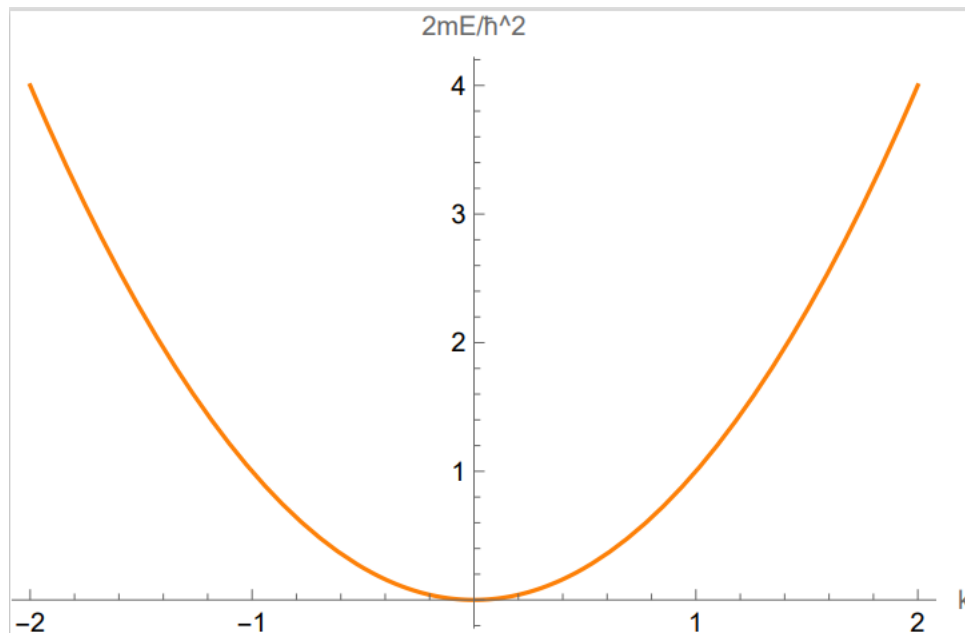
which on solving we get $A = \sqrt{\frac{2}{L}}$. Therefore, the wavefunction is:

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \tag{24}$$

To calculate energy, we use equation (22)

$$\begin{aligned}
k &= \frac{n\pi}{L} \\
\sqrt{\frac{2mE}{\hbar^2}} &= \frac{n\pi}{L} \\
E &= \frac{n^2 \hbar^2 \pi^2}{2mL^2}
\end{aligned}$$

We have plotted E v/s k plot below:



k is plotted on x axis and $\frac{2mE}{\hbar^2}$ is plotted on y axis

For practical purposes, we need a model to describe the electron behaviour in 3 dimensions. The above model can be extended to 3 dimensions and the solution of which is given by:

$$\psi_n(x, y, z) = A \sin\left(\frac{n_x \pi x}{L}\right) \sin\left(\frac{n_y \pi y}{L}\right) \sin\left(\frac{n_z \pi z}{L}\right) \quad (25)$$

and energy is given by:

$$E_{n_x, n_y, n_z} = \frac{\pi^2 \hbar^2}{2mL^2} (n_x^2 + n_y^2 + n_z^2) \quad (26)$$

Wavefunctions which satisfy free particle Schrodinger's equation and periodicity conditions are of the form:

$$\psi_K(\vec{r}) = \exp(i\vec{k} \cdot \vec{r}) \quad (27)$$

which can be derived for 1-D case as follows. We can extend it to 3-D case by replacing $k_x x$ by $\vec{k} \cdot \vec{r}$.

$$\begin{aligned} \left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right) \psi_k(x) &= E \psi_k(x) \\ -\frac{\hbar^2}{2m} \frac{\partial^2 \psi_k(x)}{\partial x^2} &= (E - V(x)) \psi_k(x) \end{aligned}$$

Considering potential to be constant equal to V_o everywhere,

$$\begin{aligned} -\frac{\hbar^2}{2m} \frac{\partial^2 \psi_k(x)}{\partial x^2} &= (E - V_o) \psi_k(x) \\ \frac{\partial^2 \psi_k(x)}{\partial x^2} &= -\frac{2m(E - V_o)}{\hbar^2} \psi_k(x) \end{aligned}$$

Considering $\sqrt{\frac{2m(E - V_o)}{\hbar^2}} = k$,

$$\frac{\partial^2 \psi_k(x)}{\partial x^2} = -k^2 \psi_k(x)$$

The general solution of which can be given by

$$\psi_k(x) = Ae^{ikx} + Be^{-ikx} \quad (28)$$

where A and B are constants to be normalized. If the wave is travelling from left to right, $B = 0$ as $-k$ term represents the wave travelling from right to left. So, for wave travelling from left to right, the wavefunction finally becomes:

$$\psi_k(x) = Ae^{ikx} \quad (29)$$

We could write a similar wavefunction in 3-D case as mentioned above. It represents a travelling plane wave subjected to conditions:

$$k_x = 0, \pm \frac{2\pi}{L}, \pm \frac{4\pi}{L}, \dots \quad (30)$$

Similiarly for k_y and k_z . In a system of N electrons, occupied energy levels (which we call as orbitals) can be represented as points in \vec{k} space. The energy at the surface of the sphere is Fermi energy and the wavevector associated with it is denoted by k_F . From the above condition, we see that there exists a single triplet of k_x, k_y, k_z in volume of $(\frac{2\pi}{L})^3$. Therefore, in volume of sphere of radius k_F , we have:

$$2 \cdot \frac{\frac{4\pi k_F^3}{3}}{(\frac{2\pi}{L})^3} = N \quad (31)$$

number of orbitals where factor of 2 comes due to Pauli's exclusion principle. So, the value of k_F comes out to be:

$$\left(\frac{3\pi^2 N}{V} \right)^{\frac{1}{3}} \quad (32)$$

Energy E_F of the Fermi level comes out to be:

$$E_F = \frac{\hbar^2 K_F^2}{2m} = \frac{\hbar^2}{2m} \left(\frac{3\pi^2 N}{V} \right)^{\frac{2}{3}} \quad (33)$$

4 Bloch function

For free electron model, we ignored the small bumps in potetnial between the atoms and solved the time independent Schrodinger equation. In, reality these bumps exists and have finite value. For a better model, we need to consider these small bumps. It is easy to see that these bumps are periodic, i.e.

$$V(x) = V(x + a)$$

where a is the distance between two atoms in lattice. Without solving Schrodinger equation, we could make two important observations. We could see that wavefunction should be periodic.

$$\psi(x) = \psi(x + Na)$$

Also, since crystal consists of large number of atoms, by symmetry we could say that time averaged electron density in every unit cell should be same. All cells are identical and so they must have same average electron density.

$$|\psi(x)|^2 = |\psi(x + Na)|^2$$

which on simplifying gives

$$\psi(x + Na) = e^{i\theta} \psi(x)$$

The wavefunctions satsifying above conditions are called Bloch functions and they are of the form:

$$\psi_K(x) = u_K(x) e^{iKx} \quad (34)$$

where $u_K(x)$ is of the form

$$u_K(x + Na) = u_K(x)$$

5 Tight binding model for 1D lattice

In free electron model, we ignored small bumps in potential energy between two atoms. In tight binding model, we consider the finite potential energy between the atoms. We assume electrons of atom to be localised and then delocalise them using Linear Combination of Atomic Orbitals (LCAO) rule. As usual, we consider the 1-D case first and will extend it to higher dimensions. Using Linear Combination of Atomic Orbitals (LCAO) rule, we write the wavefunction for tight binding approximation as:

$$\psi_k(x) = \sum_{n=-\infty}^{\infty} \phi(x - na) e^{ikna} \quad (35)$$

where ϕ is the orbital wavefunction as we have considered electrons to be localized in atom. We now show that the wavefunction satisfy Bloch's theorem:

$$\begin{aligned} \psi_k(x) &= \sum_{n=-\infty}^{+\infty} \phi(x - na) e^{ikna} \\ \psi_k(x + ma) &= \sum_{n=-\infty}^{+\infty} \phi(x + ma - na) e^{ikna} \\ &= e^{ikma} \sum_{n=-\infty}^{+\infty} \phi(x + ma - na) e^{ik(n-m)a} \\ &= e^{ikma} \sum_{n=-\infty}^{+\infty} \phi(x + (m - n)a) e^{ik(n-m)a} \end{aligned}$$

Since integral is from $-\infty$ to $+\infty$, replacing $n-m$ by l ,

$$\begin{aligned} \psi_k(x + ma) &= e^{ikma} \sum_{l=-\infty}^{+\infty} \phi(x - la) e^{ikla} \\ &= e^{ikma} \psi_k(x) \end{aligned}$$

Therefore, the wavefunction satisfies Bloch's theorem. Before proceeding, we normalise the wavefunction. We introduce a normalization constant C_N .

$$\begin{aligned} \int_{-\infty}^{+\infty} |C_N|^2 \psi_k^*(x) \psi_k(x) dx &= 1 \\ |C_N|^2 \sum_m \sum_n e^{ik(n-m)a} \int_0^L \phi^*(x - ma) \phi(x - na) dx &= 1 \end{aligned}$$

Since the electron wavefunction is localised, the overlap integral is very small and so,

$$\int_0^L \phi^*(x - ma) \phi(x - na) dx \approx 0$$

So, for all $m \neq n$, the above integral is equal to 0. When $m = n$, $e^{(ik(n-m)a)} = 1$.

$$\int_0^L \phi^*(x - ma)\phi(x - na)dx = \int_0^L \phi^*(x - ma)\phi(x - ma)dx = 1$$

because we consider normalised wavefunction of electrons. We have n such terms. Finally, we get

$$\begin{aligned} \int_{-\infty}^{+\infty} |C_N|^2 \psi_k^*(x) \psi_k(x) dx &= 1 \\ |C_N|^2 \sum_m \sum_n e^{(ik(n-m)a)} \int_0^L \phi^*(x - ma)\phi(x - na)dx &= 1 \\ |C_N|^2 N &= 1 \\ C_N &= \frac{1}{\sqrt{N}} \end{aligned}$$

Therefore, the wavefunction is given by

$$\psi_k(x) = \frac{1}{\sqrt{N}} \sum_n e^{ikna} \phi(x - na) \quad (36)$$

To calculate energy, we use Hamiltonian operator.

$$\sum_m \sum_n \langle \phi(x - ma) | \hat{H} | \phi(x - na) \rangle$$

For our convenience, we split this into two terms: $m = n$ and $m \neq n$. So,

$$\begin{aligned} \sum_m \sum_n \langle \phi(x - ma) | \hat{H} | \phi(x - na) \rangle &= \sum_m \sum_{n,n=m} \langle \phi(x - ma) | \hat{H} | \phi(x - na) \rangle \\ &+ \sum_m \sum_{n,n \neq m} \langle \phi(x - ma) | \hat{H} | \phi(x - na) \rangle \end{aligned}$$

We first evaluate $m = n$ term. For $m = n$ term, the Hamiltonian approximately gives values of energy of electron in an orbital. Note that we write approximately because we are not neglecting the interaction of electrons with other atoms. Let us denote it by E_{atomic} . Generally, the atomic orbitals are exponentially decaying, so

$$\frac{\partial^2 \phi}{\partial x^2} \approx e^{-x}$$

So contribution of $-\frac{\hbar^2}{2m} \nabla^2$ term is nearly 0. Now, the only term left to evaluate is $V(x)$ in $m \neq n$ case. In free electron model, we considered it to be zero and then derived the energy expression. Here, we considered potential energy to be of finite value between the atoms and so, $\phi^*(x - ma)V(x)\phi(x - na)$

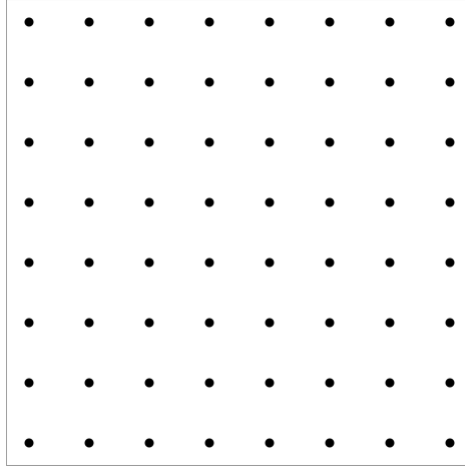
is not zero between the atoms. Since this contribution is significant only in regions between the atoms and its next nearest neighbours, it is known as nearest neighbour approximation. Using this,

$$\begin{aligned} \sum_m \sum_{n, n=m\pm 1} e^{ik(n-m)a} \langle \phi(x-ma) | \hat{H} | \phi(x-na) \rangle &= \sum_m (e^{ik(m-1-m)a} + e^{ik(m+1-m)a}) \\ &\quad \langle \phi(x-ma) | \hat{H} | \phi(x-na) \rangle \\ &= 2\cos(ka)\gamma \end{aligned}$$

where we consider $\langle \phi(x-ma) | \hat{H} | \phi(x-na) \rangle$ is approximately constant (which has contribution mostly due to potential term between the atoms) and equal to γ . So finally, the expression for energy comes out to be

$$E_k = E_{atomic} + 2\gamma \cos(ka) \quad (37)$$

6 Tight binding model for 2D square lattice



2D square lattice

Reference: Square lattice-Wikipedia

In case of 1D lattice we had 2 nearest neighbouring atoms. For 2D square lattice, we have 4 nearest neighbouring atoms, 2 along x axis and 2 along y axis. Wavefunction of electron in k space is given by:

$$\psi_{k_x, k_y}(x, y) = \sum_{n=-\infty}^{\infty} \sum_{m=-\infty}^{\infty} e^{i\vec{k} \cdot \vec{r}} \phi(x-ma, y-na) \quad (38)$$

Where $\vec{k} = k_x\hat{x} + k_y\hat{y}$ and $\vec{r} = ma\hat{x} + na\hat{y}$, m and n are integers. Putting this in the above equation,

$$\begin{aligned}
\psi_{k_x, k_y}(x, y) &= \sum_{n=-\infty}^{\infty} \sum_{m=-\infty}^{\infty} e^{i\vec{k}\cdot\vec{r}} \phi(x - ma, y - na) \\
&= \sum_{n=-\infty}^{\infty} \sum_{m=-\infty}^{\infty} e^{i(k_x\hat{x} + k_y\hat{y}) \cdot (ma\hat{x} + na\hat{y})} \phi(x - ma, y - na) \\
&= \sum_{n=-\infty}^{\infty} \sum_{m=-\infty}^{\infty} e^{i(k_x ma + k_y na)} \phi(x - ma, y - na) \\
&= \sum_{n=-\infty}^{\infty} \sum_{m=-\infty}^{\infty} e^{ik_x ma} e^{ik_y na} \phi(x - ma, y - na)
\end{aligned}$$

Before calculating energy, we normalize the wavefunction. Let the normalization constant be C. Then,

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} |C|^2 |\psi_{k_x, k_y}(x, y)|^2 dx dy = 1$$

The orbital wavefunction of electron is normalised. So,

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} |\phi(x - ma, y - na)|^2 dx dy = 1$$

Suppose there are N_x atoms in \hat{x} direction and N_y atoms in \hat{y} direction. So we have a total of $N_x N_y$ atoms. Therefore:

$$\begin{aligned}
|C|^2 N_x N_y &= 1 \\
|C| &= \frac{1}{\sqrt{N_x N_y}}
\end{aligned}$$

So, the normalized wavefunction for electron in k space is:

$$\psi_{k_x, k_y}(x, y) = \frac{1}{\sqrt{N_x N_y}} \sum_n \sum_m e^{ik_x ma} e^{ik_y na} \phi(x - ma, y - na)$$

We use Hamiltonian to calculate energy:

$$\begin{aligned}
&\langle \psi_{k_x, k_y} | \hat{H} | \psi_{k_x, k_y} \rangle \\
&= \frac{1}{N_x N_y} \langle \sum_{n'} \sum_{m'} e^{ik_x m' a} e^{ik_y n' a} \phi(x - m' a, y - n' a) | \hat{H} | \sum_n \sum_m e^{ik_x m a} e^{ik_y n a} \phi(x - m a, y - n a) \rangle \\
&= \frac{1}{N_x N_y} e^{ik_x(m-m')a} e^{ik_y(n-n')a} \langle \sum_{n'} \sum_{m'} \phi(x - m' a, y - n' a) | \hat{H} | \sum_n \sum_m \phi(x - m a, y - n a) \rangle
\end{aligned}$$

We separate terms with $m'=m$ and $n'=n$ and other terms. For $m'=m$ and $n'=n$:

$$\frac{1}{N_x N_y} \sum_n \sum_m \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \phi^*(x - m' a, y - n' a) \hat{H} \phi(x - m a, y - n a) dx dy = E_{atomic} \quad (39)$$

For the remaining terms, we use nearest neighbour approximation. In case of 2D lattice, we get 4 nearest neighbours, given by $m' = m, n' = n \pm 1$ and $m' = m \pm 1, n' = n$. Let the energy obtained by applying the nearest neighbour approximation be E_o . We now use the nearest neighbour approximation:

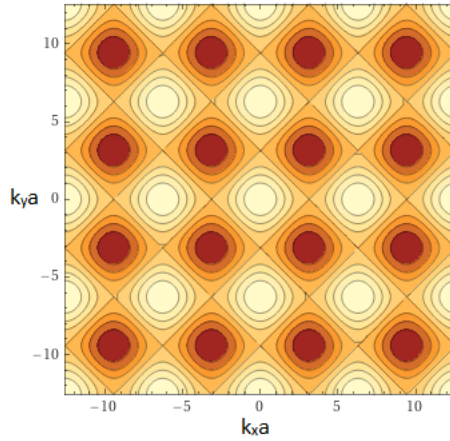
$$\begin{aligned} \frac{1}{N_x N_y} \sum_n \sum_m \left[\left(e^{ik_x(m-(m-1))a} + e^{ik_x(m-(m+1))a} \right) \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \phi^*(x - m'a, y - na) \hat{H} \phi(x - ma, y - na) dx dy + \right. \\ \left. \left(e^{ik_y(n-(n-1))a} + e^{ik_y(n-(n+1))a} \right) \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \phi^*(x - ma, y - n'a) \hat{H} \phi(x - ma, y - na) dx dy \right] \\ = 2\gamma(\cos(k_x a) + \cos(k_y a)) \end{aligned}$$

Therefore, the energy of 2D square lattice is given by:

$$E = E_{atomic} + E_o \quad (40)$$

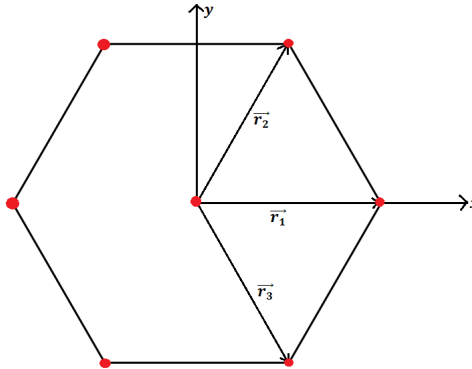
$$E = E_{atomic} + 2\gamma(\cos(k_x a) + \cos(k_y a)) \quad (41)$$

The contour plot showing $\frac{E_o}{\gamma}$ is plotted below:



Contour plot of $\frac{E_o}{\gamma}$ with $k_x a$ on x axis and $k_y a$ on y axis

7 Tight binding model for 2D triangular lattice



Triangular lattice with nearest neighbours denoted by $\vec{r}_1, \vec{r}_2, \vec{r}_3$

We consider an equilateral triangular lattice. Therefore, all angles are $\frac{\pi}{3}$. Let each side of triangular lattice be of length a . The primitive translational vectors are $\vec{a}_1 = a\hat{x}$ and $\vec{a}_2 = \frac{1}{2}a\hat{x} + \frac{\sqrt{3}}{2}a\hat{y}$. We could easily conclude that there will be 6 nearest neighbours each at a distance of a . They lie on corners of hexagon of side a and their positions are given by $\vec{r}_1 = \vec{a}_1$, $\vec{r}_2 = \vec{a}_2$, $\vec{r}_3 = \vec{a}_1 - \vec{a}_2$ and $-\vec{r}_1, -\vec{r}_2, -\vec{r}_3$. Before proceeding, we can also calculate reciprocal translational vectors just for completeness purpose. We know that lattice vectors (represented by \vec{a}_i) and reciprocal translational vectors (represented by \vec{b}_j) satisfy the relation:

$$\vec{a}_i \cdot \vec{b}_j = 2\pi\delta_{ij}, \delta_{ij} = \begin{cases} 1, & \text{if } i = j \\ 0, & \text{if } i \neq j \end{cases}$$

Let $\vec{b}_1 = b_{11}\hat{x} + b_{12}\hat{y}$ and $\vec{b}_2 = b_{21}\hat{x} + b_{22}\hat{y}$. Using above relation:

$$\begin{aligned} ab_{11} &= 2\pi, \text{ and} \\ \frac{ab_{11}}{2} + \frac{\sqrt{3}ab_{12}}{2} &= 0 \end{aligned}$$

Which on solving gives $b_{11} = \frac{2\pi}{a}$ and $b_{12} = -\frac{2\pi}{\sqrt{3}a}$. So, $\vec{b}_1 = \frac{2\pi}{a}\hat{x} - \frac{2\pi}{\sqrt{3}a}\hat{y}$. Similarly, on solving for \vec{b}_2 , we get $\vec{b}_2 = \frac{4\pi}{\sqrt{3}a}\hat{y}$. So, the reciprocal translational vectors are:

$$\vec{b}_1 = \frac{2\pi}{a}\hat{x} - \frac{2\pi}{\sqrt{3}a}\hat{y}, \vec{b}_2 = \frac{4\pi}{\sqrt{3}a}\hat{y}$$

We now apply the tight binding model. We follow the same procedure as discussed in 2D square lattice. We will get an E_{atomic} term. Since we have 6 nearest neighbours, we get 6 terms while using nearest neighbour approximation. Let the value of hopping integral be γ and let E_o denote the energy term we get using nearest neighbour approximation. We have:

$$\begin{aligned} E_o &= \gamma \left(\sum_{i=1}^3 (e^{-i\vec{k} \cdot \vec{r}_i} + e^{i\vec{k} \cdot \vec{r}_i}) \right) \\ &= 2\gamma \left(\sum_{i=1}^3 \cos(\vec{k} \cdot \vec{r}_i) \right) \\ &= 2\gamma \left[\cos(k_x a) + \cos\left(\frac{k_x a}{2} + \frac{\sqrt{3}k_y a}{2}\right) + \cos\left(\frac{k_x a}{2} - \frac{\sqrt{3}k_y a}{2}\right) \right] \end{aligned}$$

Using $\cos(2\theta) = 2\cos^2\theta - 1$, $\cos(A+B) = \cos A \cos B - \sin A \sin B$ and $\cos(A-B) = \cos A \cos B + \sin A \sin B$

$$\begin{aligned}
E_o &= 2\gamma \left[\cos(k_x a) + \cos\left(\frac{k_x a}{2}\right) \cos\left(\frac{\sqrt{3}k_y a}{2}\right) - \sin\left(\frac{k_x a}{2}\right) \sin\left(\frac{\sqrt{3}k_y a}{2}\right) + \right. \\
&\quad \left. \cos\left(\frac{k_x a}{2}\right) \cos\left(\frac{\sqrt{3}k_y a}{2}\right) + \sin\left(\frac{k_x a}{2}\right) \sin\left(\frac{\sqrt{3}k_y a}{2}\right) \right] \\
&= 2\gamma \left[2\cos^2\left(\frac{k_x a}{2}\right) - 1 + 2\cos\left(\frac{k_x a}{2}\right) \cos\left(\frac{\sqrt{3}k_y a}{2}\right) \right] \\
&= 4\gamma \cos\left(\frac{k_x a}{2}\right) \left[\cos\left(\frac{k_x a}{2}\right) + \cos\left(\frac{\sqrt{3}k_y a}{2}\right) \right] - 2\gamma
\end{aligned}$$

We make $E_o(0) = 0$ by introducing a constant c . So,

$$\begin{aligned}
E_o &= 4\gamma \cos\left(\frac{k_x a}{2}\right) \left[\cos\left(\frac{k_x a}{2}\right) + \cos\left(\frac{\sqrt{3}k_y a}{2}\right) \right] - 2\gamma + c \\
E_o(0) &= 0 \\
6\gamma + c &= 0 \\
c &= -6\gamma
\end{aligned}$$

So, $c = -6\gamma$. Therefore,

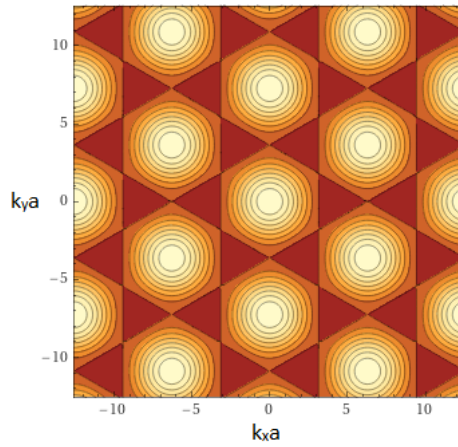
$$E_o = 4\gamma \cos\left(\frac{k_x a}{2}\right) \left[\cos\left(\frac{k_x a}{2}\right) + \cos\left(\frac{\sqrt{3}k_y a}{2}\right) \right] - 8\gamma \quad (42)$$

The total energy for 2D triangular lattice is then given by:

$$E = E_{atomic} + E_o \quad (43)$$

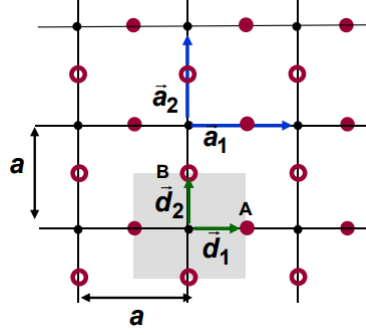
$$E = E_{atomic} + 4\gamma \cos\left(\frac{k_x a}{2}\right) \left[\cos\left(\frac{k_x a}{2}\right) + \cos\left(\frac{\sqrt{3}k_y a}{2}\right) \right] - 8\gamma \quad (44)$$

The contour plot showing $\frac{E_o}{\gamma}$ is plotted below:



Contour plot of $\frac{E_o}{\gamma}$ with $k_x a$ on x axis and $k_y a$ on y axis

8 Tight binding model with two atom basis



2D square lattice with a basis

Reference: <https://courses.cit.cornell.edu/ece407/Lectures/handout10.pdf>

Suppose there are two atoms in a basis. Let the wavefunction satisfying Bloch's theorem for the electron in this basis be:

$$\Phi_k(\vec{r}) = c_1 e^{i\vec{k} \cdot \vec{d}_1} \phi_1(\vec{r} - \vec{R}_m - \vec{d}_1) + c_2 e^{i\vec{k} \cdot \vec{d}_2} \phi_2(\vec{r} - \vec{R}_m - \vec{d}_2) \quad (45)$$

Where ϕ_1 is the wavefunction of the electron in atom A and ϕ_2 is the wavefunction of the electron in atom B. \vec{R}_m is the translational vector representing the location of the basis in the crystal lattice and \vec{d}_1 and \vec{d}_2 are the location of the atoms within the basis. The wavefunction for the crystal will be:

$$\Psi_k(\vec{r}) = \sum_{\vec{R}_m} e^{i\vec{k} \cdot \vec{R}_m} \Phi_{i\vec{k}} \quad (46)$$

$$= \sum_{\vec{R}_m} e^{i\vec{k} \cdot \vec{R}_m} \left[c_1 e^{i\vec{k} \cdot \vec{d}_1} \phi_1(\vec{r} - \vec{R}_m - \vec{d}_1) + c_2 e^{i\vec{k} \cdot \vec{d}_2} \phi_2(\vec{r} - \vec{R}_m - \vec{d}_2) \right] \quad (47)$$

We know that:

$$\hat{H} |\Psi\rangle = E |\Psi\rangle \quad (48)$$

Multiplying by $\langle e^{i\vec{k} \cdot \vec{d}_1} \phi_1(\vec{r} - \vec{R}_m - \vec{d}_1) |$ on both sides give:

$$H_{11}c_1 + H_{12}c_2 = Ec_1 \quad (49)$$

where:

$$H_{11} = \sum_{\vec{R}_m} \sum_{\vec{R}'_m} e^{i\vec{k} \cdot (\vec{R}_m - \vec{R}'_m)} \int \phi_1^*(\vec{r} - \vec{R}_m - \vec{d}_1) H \phi_1(\vec{r} - \vec{R}'_m - \vec{d}_1) d\vec{r}$$

and

$$H_{12} = \sum_{\vec{R}_m} \sum_{\vec{R}'_m} e^{i\vec{k} \cdot (\vec{R}_m - \vec{R}'_m - \vec{d}_1 - \vec{d}_2)} \int \phi_1^*(\vec{r} - \vec{R}_m - \vec{d}_1) H \phi_2(\vec{r} - \vec{R}'_m - \vec{d}_2) d\vec{r}$$

Similarly, multiplying by $\langle e^{\vec{k} \cdot \vec{d}_2} \phi_2(\vec{r} - \vec{R}_m - \vec{d}_2) |$ gives H_{22} which is similar to H_{11} and H_{21} equal to H_{12}^* . So, we get,

$$H_{22}c_2 + H_{21}c_1 = Ec_2 \quad (50)$$

So we have,

$$\begin{aligned} (H_{11} - E)c_1 + H_{12}c_2 &= 0 \\ H_{21}c_1 + (H_{22} - E)c_2 &= 0 \end{aligned}$$

To have a non-trivial solution,

$$\begin{vmatrix} H_{11} - E & H_{12} \\ H_{21} & H_{22} - E \end{vmatrix} = 0$$

which on solving gives

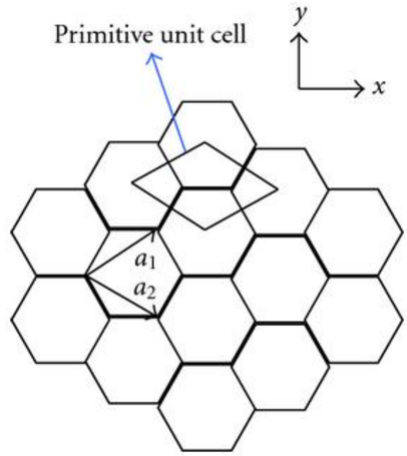
$$E^2 - (H_{11} + H_{22})E + H_{11}H_{22} - |H_{12}|^2 = 0$$

which has solutions:

$$\frac{(H_{11} + H_{22})}{2} \pm \sqrt{\left(\frac{H_{11} - H_{22}}{2}\right)^2 + |H_{12}|^2} \quad (51)$$

9 Graphene

9.1 Crystal structure of Graphene

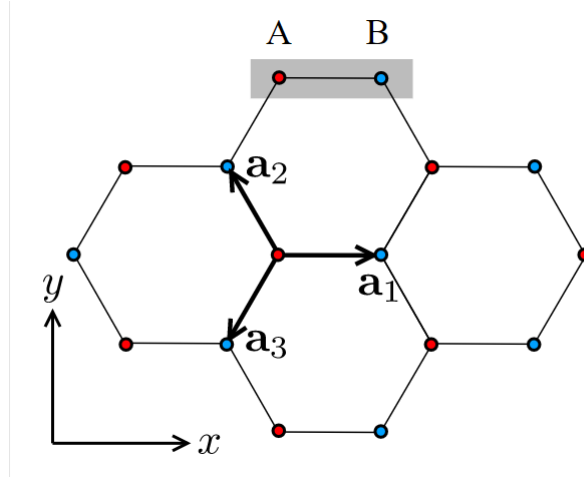


Primitive cell of graphene

Reference: <https://physics.stackexchange.com/questions/381777/primitive-cell-of-graphene>

Graphene is a single layer of graphite. It consists of hexagonal rings which forms a honeycomb lattice. To apply tight binding model to graphene, we need to first decide the primitive cell of graphene. The primitive cell of graphene consists of rhombus enclosing two atoms of carbon named A and B. Note that the surrounding environment of atoms A and B are different and hence we have labelled them differently. These two atoms form a basis and rhombus forms a primitive cell of graphene. Each A atom has three B atoms as its nearest neighbours at a distance of a . These three atoms are present at an angle of $\frac{2\pi}{3}$. Same applies for B atoms. We can now apply the tight binding model with two atoms in basis to graphene.

9.2 Tight binding model for graphene



Here, in figure, \vec{a}_1 , \vec{a}_2 , \vec{a}_3 represent \vec{r}_1 , \vec{r}_2 , \vec{r}_3 respectively

Reference: https://topocondmat.org/w4_haldane/haldane_model.html

Instead of ϕ_1 and ϕ_2 , we will use ϕ_A and ϕ_B for notations. For graphene, $H_{AA} = H_{BB}$. This can also be shown mathematically. So, the energy expression reduces to:

$$E(k) = H_{AA} \pm |H_{AB}| \quad (52)$$

We now calculate H_{AA} . We can split H_{AA} into two terms: $R_m = R'_m$ and $R_m \neq R'_m$. $R_m = R'_m$ approximately gives energy of orbital which we denote by ϵ . When $R_m \neq R'_m$, the contribution is nearly zero and hence it can be neglected. So,

$$H_{AA} = \epsilon \quad (53)$$

Also, $H_{BB} = H_{AA} = \epsilon$. We now calculate H_{AB} . As discussed above, each A atom (resp. B atom) has three B atoms (resp. A atoms) as its nearest neighbours. So, using the tight binding approximation, we get:

$$H_{AB} = (e^{i\vec{k} \cdot \vec{r}_1} + e^{i\vec{k} \cdot \vec{r}_2} + e^{i\vec{k} \cdot \vec{r}_3})\gamma$$

where $r_1 = a\hat{x}$, $r_2 = -\frac{1}{2}a\hat{x} + \frac{\sqrt{3}}{2}a\hat{y}$, $r_3 = -\frac{1}{2}a\hat{x} - \frac{\sqrt{3}}{2}a\hat{y}$, $\vec{k} = k_x\hat{x} + k_y\hat{y}$ and $\gamma = \langle \phi_1 | \hat{H} | \phi_2 \rangle$. So,

$$\begin{aligned}
H_{AB} &= (e^{i\vec{k}\cdot\vec{r}_1} + e^{i\vec{k}\cdot\vec{r}_2} + e^{i\vec{k}\cdot\vec{r}_3})\gamma \\
&= \left(e^{ik_x a} + e^{i(-\frac{k_x a}{2} + \frac{\sqrt{3}k_y a}{2})} + e^{i(-\frac{k_x a}{2} - \frac{\sqrt{3}k_y a}{2})} \right) \gamma \\
&= \left[e^{ik_x a} + e^{-i\frac{k_x a}{2}} \left(e^{i\frac{\sqrt{3}k_y a}{2}} + e^{-i\frac{\sqrt{3}k_y a}{2}} \right) \right] \gamma \\
&= \left[e^{ik_x a} + 2e^{-i\frac{k_x a}{2}} \cos\left(\frac{\sqrt{3}k_y a}{2}\right) \right] \gamma \\
&= \left[\cos(k_x a) + i\sin(k_x a) + 2\cos\left(\frac{\sqrt{3}k_y a}{2}\right) \cos\left(\frac{k_x a}{2}\right) - 2i\cos\left(\frac{\sqrt{3}k_y a}{2}\right) \sin\left(\frac{k_x a}{2}\right) \right] \gamma \\
&= \left[\cos(k_x a) + 2\cos\left(\frac{\sqrt{3}k_y a}{2}\right) \cos\left(\frac{k_x a}{2}\right) + i\sin(k_x a) - 2i\cos\left(\frac{\sqrt{3}k_y a}{2}\right) \sin\left(\frac{k_x a}{2}\right) \right] \gamma
\end{aligned}$$

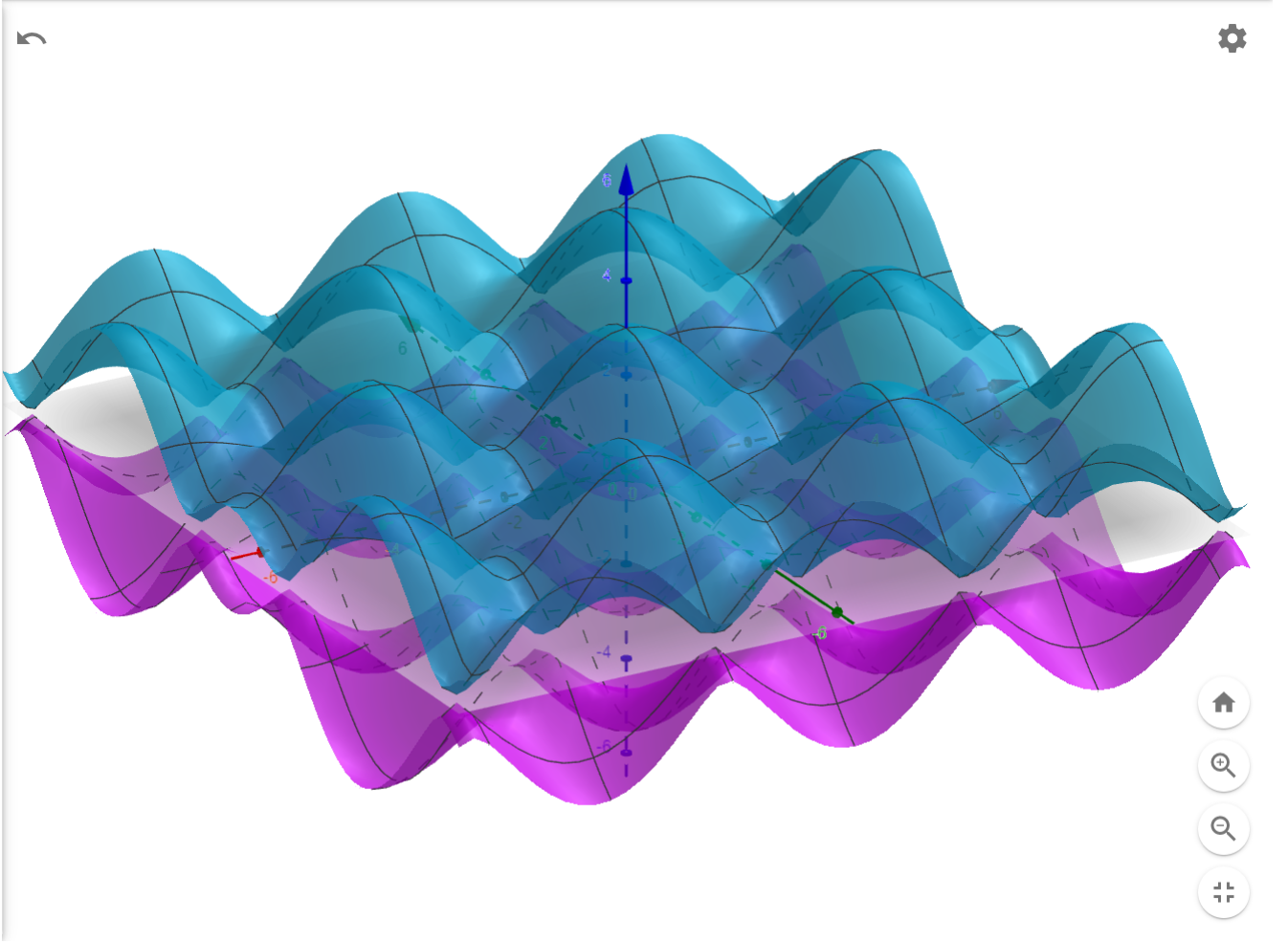
Now,

$$\begin{aligned}
|H_{AB}|^2 &= \left[\left(\cos(k_x a) + 2\cos\left(\frac{\sqrt{3}k_y a}{2}\right) \cos\left(\frac{k_x a}{2}\right) \right)^2 + \left(\sin(k_x a) - 2\cos\left(\frac{\sqrt{3}k_y a}{2}\right) \sin\left(\frac{k_x a}{2}\right) \right)^2 \right] \gamma^2 \\
&= \left(\cos^2(k_x a) + \sin^2(k_x a) + 4\cos^2\left(\frac{\sqrt{3}k_y a}{2}\right) \left[\cos^2\left(\frac{k_x a}{2}\right) + \sin^2\left(\frac{k_x a}{2}\right) \right] + \right. \\
&\quad \left. 4\cos\left(\frac{\sqrt{3}k_y a}{2}\right) \left[\cos(k_x a) \cos\left(\frac{k_x a}{2}\right) - \sin(k_x a) \sin\left(\frac{k_x a}{2}\right) \right] \right) \gamma^2 \\
&= \left[1 + 4\cos^2\left(\frac{\sqrt{3}k_y a}{2}\right) + 4\cos\left(\frac{3k_x a}{2}\right) \cos\left(\frac{\sqrt{3}k_y a}{2}\right) \right] \gamma^2
\end{aligned}$$

So, the energy of the bands of graphene is given by:

$$E(k) = \epsilon \pm \sqrt{1 + 4\cos^2\left(\frac{\sqrt{3}k_y a}{2}\right) + 4\cos\left(\frac{3k_x a}{2}\right) \cos\left(\frac{\sqrt{3}k_y a}{2}\right)} \gamma \quad (54)$$

The 3D plot of $E(k)$ is plotted below:



$k_x a$ is on x axis and $k_y a$ is on y axis

Plotted using GeoGebra 3D plotter

9.3 Analysis of tight binding model of graphene

The above plot shows the band structure of graphene obtained using tight binding model. In graphene, a carbon atom is bonded to three other carbon atoms and hence one electron of each carbon atom is free. This free electron delocalises in the entire lattice and resides in the bands obtained above using tight binding model. Dispersion relation has cos term in it and hence it is periodic.

In 3D plot, we could see that there are points where the two bands meet. Those points are known as Dirac points. When we join Dirac points, we get a hexagon. One peculiar thing about graphene is that the dispersion relation is linear in low energy region. Generally, metals or semiconductors have parabolic dispersion relation. The mass-energy equivalence relation states that:

$$E = \sqrt{(m_o c^2)^2 + (pc)^2} \quad (55)$$

where m_o is the rest mass. For a photon, the rest mass is zero and hence $E = pc$. Which means that in low energy region, the electrons in valence band of graphene behave massless like photons since

the dispersion relation is linear like photons. The energy of these electrons is directly proportional to momentum. All these electrons, just like photons, travel at the same speed which is about 0.3% the speed of light.

Linear dispersion relation near Dirac points forms Dirac cones. Dirac cones means that near Fermi level, the conduction and valence band have shapes resembling conical surfaces and they meet at Dirac point.

In metals, the valence band and conduction band have very small energy gap or sometimes they even overlap. As a result, electrons in metals freely flow from valence band to conduction band and metals are good conductors. Semiconductors have band gaps. Due to band gaps, the electron needs energy to jump from one band to other band. However, since the two bands in graphene touch each other, the electron doesn't need energy to jump to higher energy(conduction) band. Even a slight potential difference applied across graphene can cause electrons to flow which gives graphene its electrical conducting properties.

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