

Chapter II



Electronic structure of carbon nanotubes

This chapter aims at setting the stage with a brief review of the essential concepts which we shall encounter in later chapters of this research. This makes us gradually understand the limitation of the theory to understand the behavior of carbon nanotube field emission and assumptions used.

2.1 Electronic band structure of graphite

Graphite band structure takes an essential role to define the band structure of carbon nanotubes. Insight understanding on the electronic structure of graphite will merit in detailed understanding the physical behavior of carbon nanotube electronic wave functions which directs us to the understanding of field emission from carbon nanotubes. Electrons in graphite can be separated into three groups: a) the core electrons $1s$ which cannot go further than atomic neighborhood that it belongs to, b) the hybridization electrons $2s2p^2$, so-called σ bond electrons, and c) The π bonding electrons e.g. atomic electronic orbital hybridization of $2p_z$ electron of each carbon atom in graphene plane which have quite most mobility of electron in our carbon material (valence electrons) and anti- π bonding electrons which are the most mobility of electron in our carbon material (conduction electrons). In our problem, we assume no σ electron emitted from our carbon nanotubes. If

this group of electrons emit, the deterioration will occur at the tip of our carbon nanotube. We assume that the emitted electrons come only from anti- π bonding electrons which have much larger mobility and more sensitivity to get response from external electric field and have much larger tunneling probability at the end of nanotip. To concern with the behavior of electrons in carbon nanotube we start from the electronic structure of graphite.

Unit cell and Brillouin zone of graphite

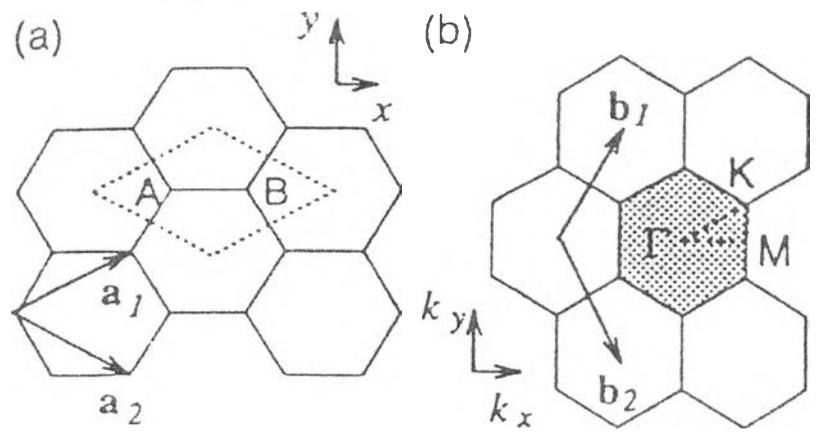


Figure 2.1: (a) The unit cell and (b) Brillouin zone of two dimensional graphite are shown as the dotted rhombus and the shaded hexagon, respectively. \vec{a}_i , and \vec{b}_i , ($i=1,2$) are unit vectors and reciprocal lattice vectors, respectively.

In Fig. 2.1, the real space unit vectors \vec{a}_1 and \vec{a}_2 can be defined as

$$\vec{a}_1 = \left(\frac{\sqrt{3}}{2}a, \frac{a}{2} \right), \quad \vec{a}_2 = \left(\frac{\sqrt{3}}{2}a, -\frac{a}{2} \right) \quad ; \quad a = |\vec{a}_1| = |\vec{a}_2| = 0.142\sqrt{3} = 0.246 \text{ nm} \tag{2.1}$$

From the real and reciprocal lattice basis vectors, \vec{b}_1 and \vec{b}_2 , relationship

$$\begin{aligned} \vec{a}_1 \cdot \vec{b}_1 &= 2\pi, & \vec{a}_1 \cdot \vec{b}_2 &= 0 \\ \vec{a}_2 \cdot \vec{b}_1 &= 0, & \vec{a}_2 \cdot \vec{b}_2 &= 2\pi \end{aligned} \tag{2.2}$$

We get corresponding unit vectors in reciprocal space of this 2D graphite as given by

$$\vec{b}_1 = \left(\frac{2\pi}{a\sqrt{3}}, \frac{2\pi}{a} \right), \quad \vec{b}_2 = \left(\frac{2\pi}{a\sqrt{3}}, -\frac{2\pi}{a} \right) \quad ; b = |\vec{b}_1| = |\vec{b}_2| = \frac{4\pi}{a\sqrt{3}} \quad (2.3)$$

H	value(eV)	S	value
H_{ss}	-6.769	S_{ss}	0.212
H_{sp}	-5.580	S_{sp}	0.102
H_σ	-5.037	S_σ	0.146
$H_\pi \equiv t$	-3.033	$S_\pi \equiv s$	0.129
$\varepsilon_{2s}^{(a)}$	-8.868		

^{a)} The value for ε_{2s} is given relative to setting $\varepsilon_{2p} = 0$.

Table 2.1: Values for the coupling parameter for carbon atoms corresponding to the Hamiltonian for π and σ bonds in 2D graphite. ε_{2s} is the energy of electron at 2s orbital.

π bonds of two-dimensional graphite

Using the secular equation and carbon coupling parameter given in Table 2.1, we get the following dispersion relationship

$$E_{g2D}(\vec{k}) = \frac{\varepsilon_{2p} \pm tw(\vec{k})}{1 \pm sw(\vec{k})} \quad (2.4)$$

where ε_{2p} represents the orbital energy of the 2p level. The values of atomic energy for the crystal potential of carbon material is given in Table 2.1. The + signs in the numerator and denominator give the bonding π band, and likewise for the - signs, give the anti-bonding π^* band, and t is the transfer integral of π bond and is given by

$$t = \langle \varphi_A(\vec{r} - \vec{R}) | H | \varphi_B(\vec{r} - \vec{R}') \rangle = H_\pi = -3.033eV \quad (2.5)$$

where H is our π electronic orbital Hamiltonian derived from the geometry of real space unit cell structure of our crystal, φ_A and φ_B are the wave functions of π electrons at A site and B site in our crystal unit cell see Fig. 2.1 and s is the overlap integral between the nearest neighbor atoms of carbon material given by

$$s = \langle \varphi_A(\vec{r} - \vec{R}) | \varphi_B(\vec{r} - \vec{R}') \rangle = S_\pi = 0.129/eV \quad (2.6)$$

while the function $w(\vec{k})$ is given by:

$$w(\vec{k}) = \sqrt{1 + 4 \cos\left(\frac{\sqrt{3}k_x a}{2}\right) \cos\left(\frac{k_y a}{2}\right) + 4 \cos^2\left(\frac{k_y a}{2}\right)}. \quad (2.7)$$

The energy dispersion relation in the case of $s = 0$ (i.e., in the Slater-Koster scheme) are commonly used as a simple approximation for the electronic structure of a graphene layer:

$$E_{g2D}(k_x, k_y) = \pm t \sqrt{1 + 4 \cos\left(\frac{\sqrt{3}k_x a}{2}\right) \cos\left(\frac{k_y a}{2}\right) + 4 \cos^2\left(\frac{k_y a}{2}\right)} \quad (2.8)$$

Eq. 2.8 will be used for the energy dispersion relation of carbon nanotube in the next section.

2.2 Carbon nanotube physics

Carbon nanotube can be described as a graphene sheet rolled into a cylindrical shape. We can define any carbon nanotube spiral conformation from chirality which is given by a single vector in real space of two dimensional graphene sheet called the chiral vector. Many important parameters of carbon nanotubes can be derived from the chiral vector. The chiral vector \vec{C}_h can be expressed in terms of the real space unit vectors \vec{a}_1 and \vec{a}_2 of the hexagonal lattice as

$$\vec{C}_h = n\vec{a}_1 + m\vec{a}_2 \equiv (n, m) \quad (2.9)$$

where n and m are intergers. $0 \leq |m| \leq n$. The diameter of the carbon nanotube, d_t , is given by

$$d_t = L/\pi, \quad L = |\vec{C}_h| = \sqrt{\vec{C}_h \cdot \vec{C}_h} = a\sqrt{n^2 + m^2 + 2nm \cos \theta} = a\sqrt{n^2 + m^2 + nm} \quad (2.10)$$

Type	θ	C_h	Shape of cross section	Symmetry
armchair	30°	(n, n)	cis-type	$D_n \otimes C_i$
zigzag	0°	$(n, 0)$	trans-type	$D_n \otimes C_i$
chiral	$0^\circ < \theta < 30^\circ$	(n, m)	mixture of cis and trans	$C_d \otimes C_{N/d}$

Table 2.2: Classification of carbon nanotubes.

where L is the perimeter of CNT given by above expression.

The chiral angle θ is defined by taking the inner product of \vec{C}_h and \vec{a}_1 , to reach $\cos\theta$ as:

$$\cos\theta = \frac{\vec{C}_h \cdot \vec{a}_1}{|\vec{C}_h||\vec{a}_1|} = \frac{2n + m}{2\sqrt{n^2 + m^2 + nm}} \quad (2.11)$$

Translational vector: \vec{T}

The translational vector \vec{T} is defined to be the unit vector of carbon nanotube which is parallel to the nanotube axis and normal to the chiral vector. Thus, we can express \vec{T} in terms of the basis vectors in real space of two dimensional graphite as:

$$\vec{T} = t_1\vec{a}_1 + t_2\vec{a}_2 \equiv (t_1, t_2) \quad (2.12)$$

where t_1 and t_2 are integers which we can define them as following

$$t_1 = \frac{2m + n}{d_R}, \quad t_2 = -\frac{2n + m}{d_R} \quad (2.13)$$

where d_R is the greatest common divisor of $(2m+n)$ and $(2n+m)$. The area of the nanotube unit cell $|\vec{C}_h \times \vec{T}|$. Then we can get the number of hexagons per unit cell N as a function of n and m as:

$$N = \frac{|\vec{C}_h \times \vec{T}|}{|\vec{a}_1 \times \vec{a}_2|} = \frac{2(m^2 + n^2 + nm)}{d_R} = \frac{2L^2}{a^2 d_R} \quad (2.14)$$

It should be noted that each hexagon contains two carbon atoms. Thus, there are $2N$ carbon atoms in each unit cell of the carbon nanotube.

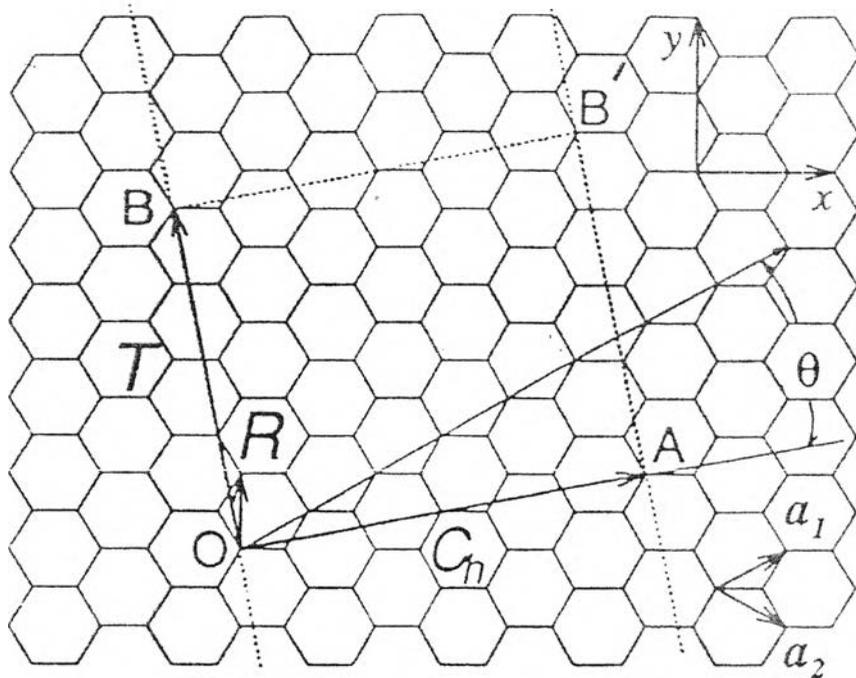


Figure 2.2: The unrolled honeycomb lattice of a nanotube is shown. OA and OB define the chiral vector \vec{C}_h and the translational vector \vec{T} of a nanotube, respectively. The rectangle $OAB'B$ defines a unit cell for the nanotube. The vector \vec{R} denotes a symmetry vector. This figure corresponds to $\vec{C}_h = (4, 2)$, $d = d_R = 2$, $\vec{T} = (4, -5)$, $N = 28$, $\vec{R} = (1, -1)$.

Unit cells and Brillouin zones of carbon nanotube

Since we have $2N$ carbon atoms in each CNT unit cell, we will have $2N$ π bonds and $2N$ anti- π bonds. The reciprocal lattice vectors of carbon nanotubes are defined by \vec{K}_1 and \vec{K}_2 . \vec{K}_1 is the unit vector in the circumferential direction. Therefore \vec{K}_2 is the unit vector along the nanotube axis. Both \vec{K}_1 and \vec{K}_2 are obtained from the relation

$$\begin{aligned} \vec{C}_h \cdot \vec{K}_1 &= 2\pi & \vec{T} \cdot \vec{K}_1 &= 0, \\ \vec{C}_h \cdot \vec{K}_2 &= 0 & \vec{T} \cdot \vec{K}_2 &= 2\pi. \end{aligned}$$

(2.15)

We get expressions for \vec{K}_1 and \vec{K}_2 as

$$\vec{K}_1 = \frac{1}{N} \left(-t_2 \vec{b}_1 + t_1 \vec{b}_2 \right), \quad \vec{K}_2 = \frac{1}{N} \left(m \vec{b}_1 - n \vec{b}_2 \right) \quad (2.16)$$

where \vec{b}_1 and \vec{b}_2 are the reciprocal lattice vectors of two dimensional graphite.

Electronic band structure of single wall carbon nanotubes

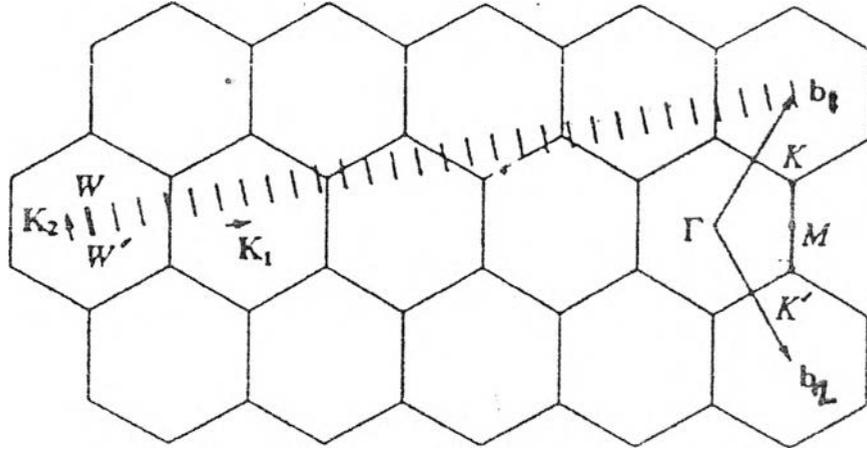


Figure 2.3: The Brillouin zone of a carbon nanotube is represented by the line segment $W\vec{W}'$ which is parallel to \vec{K}_2 . The vectors \vec{K}_1 and \vec{K}_2 are reciprocal lattice vectors corresponding to \vec{C}_h and \vec{T} , respectively. The figure corresponds to $\vec{C}_h = (4, 2)$, $\vec{T} = (4, -5)$, $N = 28$, $\vec{K}_1 = (5\vec{b}_1 + 4\vec{b}_2)/28$, $\vec{K}_2 = (2\vec{b}_1 - 4\vec{b}_2)/28$.

By using periodic boundary conditions in the circumferential direction, the wave vector associated with the \vec{C}_h direction becomes quantized, while the wave vector associated with the direction of the translational vector \vec{T} remains continuous for a nanotube of infinite length. Thus the energy bands consist of a set of one-dimensional energy dispersion relations which are cross sections of those for two-dimensional graphite. This 1D energy dispersion relation is given by

$$E_\mu(k) = E_{g2D} \left(k \frac{\vec{K}_2}{|\vec{K}_2|} + \mu \vec{K}_1 \right) \quad ; \mu = 0, \dots, N-1 \quad \text{and} \quad -\frac{\pi}{T} < k < \frac{\pi}{T} \quad (2.17)$$

The periodic boundary condition for (n,n) armchair carbon nanotubes is given by

$$n\sqrt{3}k_{x,q}a = 2\pi q, \quad (q = 1, \dots, 2n) \quad (2.18)$$

Substitution of these discrete allowed wave vectors in the circumferential direction, we will get the energy dispersion relation for the armchair nanotube (n,n) as

$$E_q^a(k) = \pm t \sqrt{1 \pm 4 \cos\left(\frac{q\pi}{n}\right) \cos\left(\frac{ka}{2}\right) + 4 \cos^2\left(\frac{ka}{2}\right)} \quad (-\pi < ka < \pi), \quad (q = 1, \dots, 2n) \quad (2.19)$$

where k is the magnitude of wave vector in the direction of \vec{K}_2 which corresponds to the direction from Γ point to K point in 2D Brillouin zone of graphite.

In the next chapter, we will review the basic of electron emission that we have to apply to our carbon nanotube model to find the characteristics of emission current which depend on the external applied electric field.