

Notes on basic nanotube concepts

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These notes have been written in the hope that they will provide a useful preliminary understanding of how the band structure of carbon nanotubes arises from that of the two-dimensional “parent material” graphene. This treatment is based on the tight-binding description of non-interacting electrons in graphene, and on the “zone-folding” scheme for carbon nanotubes. The purpose of the Monte Carlo calculations of Ref. [1] is to study how such band structure is modified in the presence of strong electron-electron interactions.

1 Graphene

The electronic structure of graphene serves as a starting point to forming an understanding of the electronic band structure of carbon nanotubes. As the nearest-neighbor distance of two carbon atoms, $a_{C-C} \simeq 1.42\text{\AA}$ is significantly larger than the $\sim 3.35\text{\AA}$ distance between adjacent layers of graphite, the electronic structure of graphene also provides a useful first approximation to that of graphite.

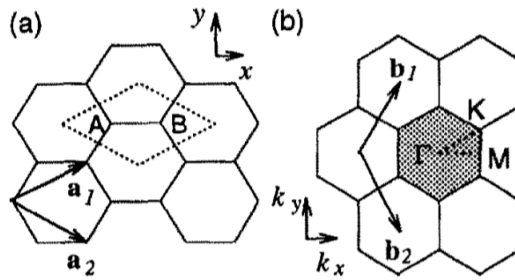


Figure 1: (from Ref. [2]) Unit cell (dotted rhombus) and Brillouin zone (shaded hexagon) of graphene. The unit vectors are denoted by \vec{a}_i , and the reciprocal lattice vectors by \vec{b}_i . The two triangular sub-lattices of carbon atoms are denoted A and B, and the high-symmetry points in the Brillouin zone by Γ , M and K , respectively.

In terms of the x, y coordinates of Fig. 1, the real-space unit vectors of the hexagonal lattice are given by

$$\vec{a}_1 \equiv \left(\frac{\sqrt{3}}{2}\tilde{a}, \frac{\tilde{a}}{2} \right), \quad \vec{a}_2 \equiv \left(\frac{\sqrt{3}}{2}\tilde{a}, -\frac{\tilde{a}}{2} \right), \quad (1)$$

with

$$\tilde{a} = |\vec{a}_1| = |\vec{a}_2| = \sqrt{3}a \simeq \sqrt{3} \times 1.42\text{\AA} = 2.46\text{\AA}, \quad (2)$$

where $a \simeq 1.42\text{\AA}$ is the lattice constant of graphene. Similarly, the unit vectors of the reciprocal lattice are

$$\vec{b}_1 \equiv \left(\frac{2\pi}{\sqrt{3}\tilde{a}}, \frac{2\pi}{\tilde{a}} \right), \quad \vec{b}_2 \equiv \left(\frac{2\pi}{\sqrt{3}\tilde{a}}, -\frac{2\pi}{\tilde{a}} \right), \quad (3)$$

with a reciprocal lattice constant of $4\pi/\sqrt{3}\tilde{a}$. Note that the reciprocal lattice vectors are rotated by 90° with respect to the lattice vectors in real space. The conventional choice of the first Brillouin zone is the shaded hexagon shown in Fig. 1, which gives the highest symmetry for the Brillouin zone of graphene. We define the three ‘‘high symmetry points’’ Γ , K and M as the center, corner, and center of the zone edge, respectively.

A simple and useful approximation for the dispersion of graphene can be obtained from the tight-binding description of an isolated sheet of graphite (see, for instance, Chapter 2 of Ref. [2]), giving

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

where $t \simeq 2.8$ eV is the nearest-neighbor hopping amplitude in graphene. The band energies in the Brillouin zone assume the values $\pm 3t$, $\pm t$ and 0 at the points Γ , M and K , respectively.

We note that the Brillouin zone contains two inequivalent ‘‘valleys’’ K and K' , where the conduction and valence bands meet. In this non-interacting picture, graphene is a zero-gap semiconductor. This situation may change when the atoms on the sub-lattices A and B are unequal, or in the presence of substantial electron-electron interactions.

2 Chiral and translational vectors

The chiral vector \vec{C}_h can be expressed in terms of the real space unit vectors of Eq. (1) according to

$$\vec{C}_h \equiv n\vec{a}_1 + m\vec{a}_2 \equiv (n, m), \quad 0 \leq |m| \leq n, \quad (5)$$

where n, m are integers. We denote the special cases of $\vec{C}_h = (n, n)$ as ‘‘arm-chair’’ nanotubes and $\vec{C}_h = (n, 0)$ as ‘‘zigzag’’ nanotubes. The general case is

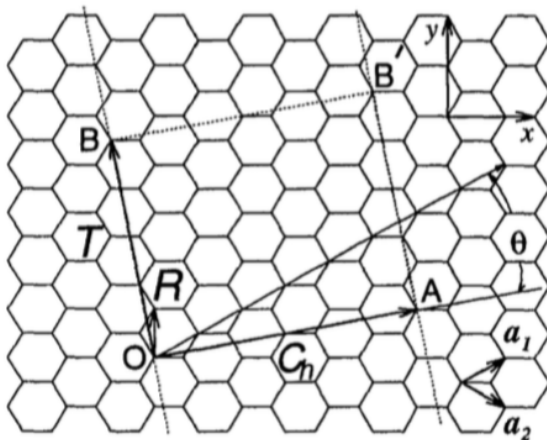


Figure 2: (from Ref. [2]) The unrolled honeycomb lattice of a carbon nanotube. The rectangle OAB'B defines the unit cell of the nanotube. The chiral vector \vec{C}_h and the translational vector \vec{T} are defined by OA and OB, respectively. The figure shows a “chiral nanotube” with $\vec{C}_h = (4, 2)$, $d = d_R = 2$, $\vec{T} = (4, -5)$, and $N = 28$.

referred to as a “chiral” nanotube. Because of the hexagonal symmetry, we only need to consider chiral nanotubes with $0 < |m| < n$.

If we denote by L the length of the nanotube circumference, the diameter d_t of the tube is given by

$$d_t = \frac{L}{\pi}, \quad L = |\vec{C}_h| = \tilde{a} \sqrt{n^2 + m^2 + nm}, \quad (6)$$

where it should be noted that the real space unit vectors of Eq. (1) satisfy

$$\vec{a}_1 \cdot \vec{a}_1 = \vec{a}_2 \cdot \vec{a}_2 = \tilde{a}^2, \quad \vec{a}_1 \cdot \vec{a}_2 = \frac{\tilde{a}^2}{2}, \quad (7)$$

and are hence not mutually orthogonal. Here, the lattice constant \tilde{a} of Eq. (2) is given by $\tilde{a} \simeq \sqrt{3} \times 1.44 \text{Å} = 2.49 \text{Å}$ in a carbon nanotube (compared with 2.46Å in graphene or graphite). We also define the “chiral angle” as the angle θ between the vectors \vec{C}_h and \vec{a}_1 ,

$$\cos(\theta) \equiv \frac{\vec{C}_h \cdot \vec{a}_1}{|\vec{C}_h| |\vec{a}_1|} = \frac{2n + m}{2\sqrt{n^2 + m^2 + mn}}, \quad 0 \leq |\theta| \leq 30^\circ, \quad (8)$$

where the restriction on θ is again due to the hexagonal symmetry. We note that $\theta = 0$ for zigzag nanotubes, and $\theta = 30^\circ$ for armchair nanotubes.

The translation vector \vec{T} is defined as the unit vector of a 1D carbon nanotube, such that \vec{T} is parallel to the nanotube axis and normal to the chiral

vector \vec{C}_h as shown in Fig. 2. In terms of the basis vectors (1), we have

$$\vec{T} \equiv t_1 \vec{a}_1 + t_2 \vec{a}_2 \equiv (t_1, t_2), \quad (9)$$

where t_1 and t_2 are integers. Clearly, the translation vector \vec{T} corresponds to the first lattice point of the 2D graphene sheet through which the line OB normal to the chiral vector \vec{C}_h passes. Thus, t_1 and t_2 do not have a common divisor except for unity. By means of the relationship $\vec{C}_h \cdot \vec{T} = 0$, the definitions (5) and (9), and the relations (7), we find

$$t_1 = \frac{2m+n}{d_R}, \quad t_2 = -\frac{2n+m}{d_R}, \quad (10)$$

where we introduce the notation

$$d_R \equiv \text{gcd}(2m+n, 2n+m), \quad d \equiv \text{gcd}(n, m), \quad (11)$$

with “gcd” denoting the greatest common divisor. This can be shown to equal the statement that $d_R = d$ if $n-m$ is not a multiple of $3d$, and $d_R = 3d$ if $n-m$ is a multiple of $3d$.

The length T of the translation vector \vec{T} is

$$T \equiv |\vec{T}| = \frac{\sqrt{3}L}{d_R}, \quad (12)$$

in terms of the circumferential length given in Eq. (6). It should be noted that T is greatly reduced when (n, m) have a common divisor or when $n-m$ is a multiple of $3d$. For instance, for the chiral (4, 2) nanotube, we have $\vec{T} = (4, -5)$. In contrast, for the armchair (5, 5) nanotube, we have $\vec{T} = (1, -1)$, and for the zigzag (9, 0) nanotube, $\vec{T} = (1, -2)$.

The number of hexagons N per (nanotube) unit cell is obtained by dividing the area of the nanotube unit cell by the area of the hexagonal unit cell of graphene,

$$N \equiv \frac{|\vec{C}_h \times \vec{T}|}{|\vec{a}_1 \times \vec{a}_2|} = \frac{2(m^2 + n^2 + nm)}{d_R} = \frac{2L^2}{\tilde{a}^2 d_R}, \quad (13)$$

with L given by Eq. (6) and d_R by Eq. (11). Note that the area of the rhombus spanned by the unit vectors \vec{a}_1 and \vec{a}_2 is

$$|\vec{a}_1 \times \vec{a}_2| = \frac{\sqrt{3}\tilde{a}^2}{2}, \quad (14)$$

and equals that of the hexagon. Since each hexagon contains two carbon atoms, there are $2N$ carbon atoms in each unit cell of the nanotube.

3 Nanotube unit cells and Brillouin zones

The unit cell of a carbon nanotube in real space is given by the rectangle spanned by the chiral vector \vec{C}_h and the translational vector \vec{T} , as shown in Fig. 2. The

expressions for the nanotube reciprocal lattice vectors \vec{K}_2 along the nanotube axis and \vec{K}_1 in the circumferential direction are obtained from the relation

$$\vec{R}_i \cdot \vec{K}_i = 2\pi\delta_{ij}, \quad (15)$$

where the \vec{R}_i and \vec{K}_i are, respectively, lattice vectors in real and reciprocal space. Using the relations

$$\vec{C}_h \cdot \vec{K}_1 = 2\pi, \quad \vec{C}_h \cdot \vec{K}_2 = 0, \quad (16)$$

and

$$\vec{T} \cdot \vec{K}_1 = 0, \quad \vec{T} \cdot \vec{K}_2 = 2\pi, \quad (17)$$

and Eqs. (10) and (13), one finds

$$\vec{K}_1 \equiv \vec{k}_\perp = \frac{1}{N}(-t_2\vec{b}_1 + t_1\vec{b}_2), \quad \vec{K}_2 \equiv \vec{k}_\parallel = \frac{1}{N}(m\vec{b}_1 - n\vec{b}_2), \quad (18)$$

in terms of the reciprocal lattice vectors of graphene, given in Eq. (3). We have also shown the equivalent notation used in Ref. [1]. In Fig. 3, the reciprocal lattice vectors \vec{K}_1 and \vec{K}_2 are shown for a $\vec{C}_h = (4, 2)$ chiral nanotube. The line segment WW' is the first Brillouin zone of this one-dimensional material.

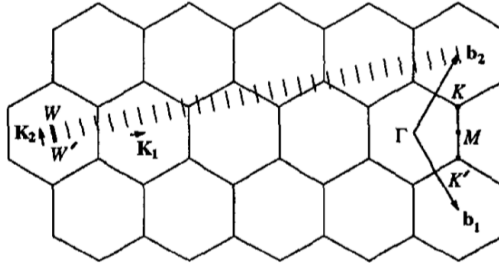


Figure 3: (from Ref. [2]) The Brillouin zone of a carbon nanotube is given by the line segment WW' parallel to \vec{K}_2 . Note that the vectors \vec{K}_1 and \vec{K}_2 are reciprocal lattice vectors corresponding to \vec{C}_h and \vec{T} , respectively. The figure shows the case of the chiral $\vec{C}_h = (4, 2)$ nanotube with $\vec{T} = (4, -5)$ and $N = 28$, giving $\vec{K}_1 = (5\vec{b}_1 + 4\vec{b}_2)/28$ and $\vec{K}_2 = (4\vec{b}_1 - 2\vec{b}_2)/28$.

Since $N\vec{K}_1 = -t_2\vec{b}_1 + t_1\vec{b}_2$ corresponds to a reciprocal lattice vector of graphene, it follows that two wave vectors which differ by $N\vec{K}_1$ are equivalent. Also, since t_1 and t_2 lack a common divisor other than unity, none of the $N - 1$ vectors $\mu\vec{K}_1$ (with $\mu = 1, \dots, N - 1$) are reciprocal lattice vectors of graphene. Thus, the N wave vectors $\mu\vec{K}_1$ (with $\mu = 0, \dots, N - 1$) give rise to N discrete k vectors, as shown by the $N = 28$ parallel line segments in Fig. 3. These

arise from the quantized wave vectors associated with the periodic boundary conditions on \vec{C}_h .

The length of the parallel lines in Fig. 3 equals $2\pi/T$, which is the length of the (one-dimensional) first Brillouin zone. Because of the translational symmetry of \vec{T} , we have continuous wave vectors in the direction of \vec{K}_2 for a carbon nanotube of infinite length. For a nanotube of finite length L_t , the spacing between wave vectors is $2\pi/L_t$.

If the energy dispersion relations of graphene $E_{2D}(k_x, k_y)$, for instance that of Eq. (4), at line segments shifted from WW' by $\mu\vec{K}_1$ are “folded” such that wave vectors parallel to \vec{K}_2 coincide with WW' (see Fig. 3), N pairs of one-dimensional dispersion relations $E_\mu(k)$ are obtained, given by

$$E_\mu(k) = E_{2D} \left(k \frac{\vec{K}_2}{|\vec{K}_2|} + \mu\vec{K}_1 \right), \quad (19)$$

where

$$\mu = 0, \dots, N-1, \quad -\frac{\pi}{T} < k < \frac{\pi}{T}. \quad (20)$$

The N pairs of energy dispersion curves given by Eq. (19) correspond to cross-sections of the two-dimensional energy dispersion surface of Eq. (4), where cuts are made along the lines $k\vec{K}_2/|\vec{K}_2| + \mu\vec{K}_1$. If, for a particular (n, m) nanotube, such a cutting line passes through a K point of the two-dimensional Brillouin zone, the one-dimensional energy bands will show a vanishing energy gap, and hence the nanotube is metallic. On the other hand, if the cutting line does not pass through a K point, the nanotube is semiconducting with a finite energy gap between the valence and conduction bands.

In practice, roughly one third of the possible carbon nanotubes are metallic and the rest semiconducting. Notably, the (n, n) armchair nanotubes are always metallic, and the zigzag $(n, 0)$ nanotubes are metallic when n is a multiple of 3. Empirically, the metallic nanotubes are prime candidates for interaction-induced gaps (such as a Mott insulating state) due to the lack of gap in the non-interacting picture. For this reason, the preliminary Monte Carlo calculations of Ref. [1] have focused on the $(3, 3)$ nanotube.

References

- [1] T. Luu and T. A. Lähde, Phys. Rev. B **93**, 155106 (2016).
- [2] R. Saito, G. Dresselhaus, and M. S. Dresselhaus, “Physical Properties of Carbon Nanotubes”