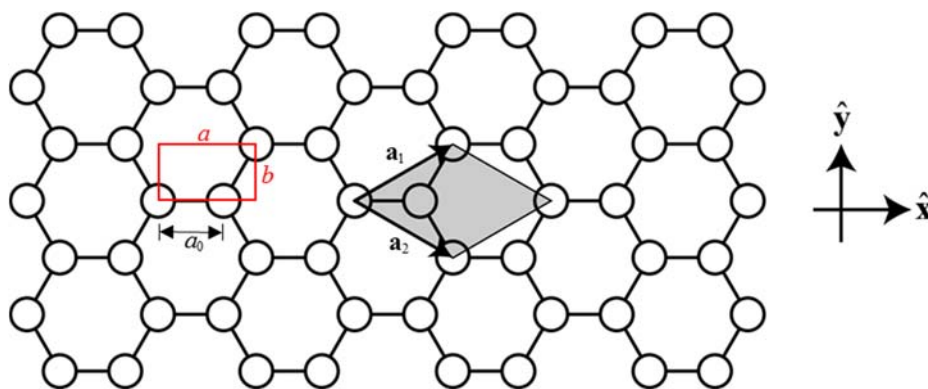


Graphene

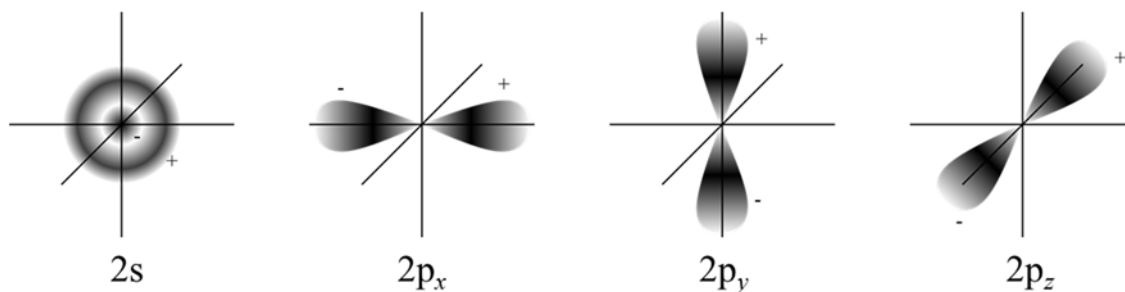
Graphene consists of two-dimensional sheets of carbon (C) atoms in an hexagonal lattice. The 2-D unit cell contains two C atoms, which are usually selected to be nearest neighbors, separated by a distance of $a_0 = 0.142 \text{ nm}$. Though possibly not the best choice, one could define lattice vectors

$$\mathbf{a}_1 = a\hat{x} + b\hat{y} \quad \text{and} \quad \mathbf{a}_2 = a\hat{x} - b\hat{y}$$

where $a = 3a_0/2$ and $b = \sqrt{3}a_0/2$.



Consider the electronic structure of an isolated C atom. Just as for a He atom, its core electrons are in 1s orbitals, with four additional electrons in its valence shell. Its lowest-energy configuration has two electrons in the 2s orbital and two in 2p orbitals. The 2s orbital is spherically symmetric, with one radial node, whereas the 2p orbitals have a node at the origin.



Molecular orbitals can form by hybridization of any combination of these basis states. In this case, we can form $2sp^2$ bonding orbitals oriented parallel to the plane of the graphene sheet. For example, $2p_x$ and $2p_y$ can be combined with amplitudes specified by an angle θ , i.e.

$$\psi_{2p^2, \theta} = \cos \theta \cdot \psi_{2p_x} + \sin \theta \cdot \psi_{2p_y}$$

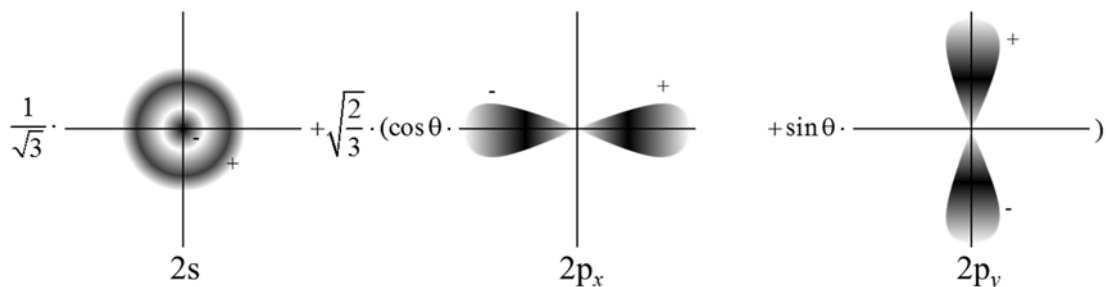
These can be mixed with the 2s orbital as

$$\psi_{2p^2, \theta} = \frac{1}{\sqrt{3}} \cdot \psi_{2s} + \sqrt{\frac{2}{3}} \cdot \psi_{2p^2, \theta}$$

We could write the hybridized state as

$$|\theta\rangle = \frac{1}{\sqrt{3}} \cdot |2s\rangle + \sqrt{\frac{2}{3}} \cdot (\cos\theta \cdot |2p_x\rangle + \sin\theta \cdot |2p_y\rangle)$$

We can interpret this linear combination as shown below:



Notice that the state is normalized for any angle θ :

$$\langle\theta|\theta\rangle = \frac{1}{3} + \frac{2}{3} \cdot (\cos^2\theta + \sin^2\theta) = 1$$

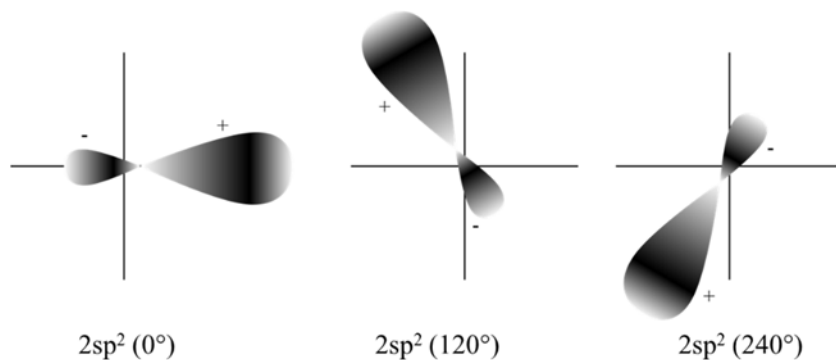
Let's pick $\theta = 0^\circ$. Then

$$|0^\circ\rangle = \frac{1}{\sqrt{3}} \cdot |2s\rangle + \sqrt{\frac{2}{3}} \cdot |2p_x\rangle$$

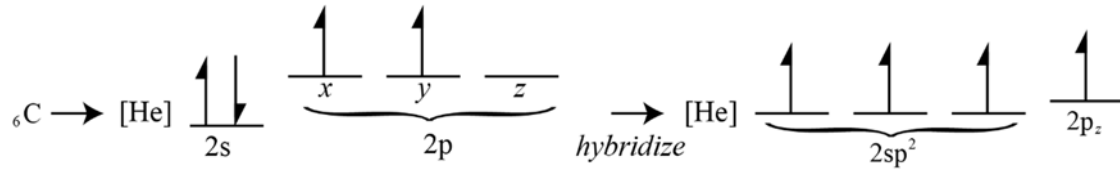
We will need two additional orbitals to form covalent bonds among nearest-neighbor C atoms: These states should be orthogonal, so

$$\langle\theta|0^\circ\rangle = \frac{1}{3} + \frac{2}{3} \cdot \cos\theta = 0$$

Then $\cos\theta = -\frac{1}{2}$ and $\theta = \pm 120^\circ$. The resulting $2sp^2$ orbitals allow each C atom to share one of its valence electrons with each of its three neighboring C atoms on the graphene hexagonal lattice.



Three of the four valence electrons for each C atom are involved in bonding within the graphene sheet. The fourth valence electron can remain in orbitals derived from $2p_z$ that contribute to conductivity.



Let's write the hamiltonian for a single-electron in graphene as

$$\hat{H} = \frac{\hat{P}^2}{2m} + U(\mathbf{r})$$

It is reasonable to assume that the potential energy involves a term for each C atom in the unit cell, whose positions are specified by the vectors $\mathbf{d}_A = \mathbf{0}$ and $\mathbf{d}_B = a_0 \hat{\mathbf{x}}$:

$$U(\mathbf{r}) = \sum_n \{U_C[\mathbf{r} - (\mathbf{r}_n + \mathbf{d}_A)] + U_C[\mathbf{r} - (\mathbf{r}_n + \mathbf{d}_B)]\}$$

where the sum is over all units cells in the graphene, located at $\mathbf{r}_n = u_n \mathbf{a}_1 + v_n \mathbf{a}_2$, with $(u_n, v_n) \in \mathbb{Z}^2$. We will choose as basis functions the $2p_z$ orbitals centered on each of the C atoms within the unit cell:

$\phi_C[\mathbf{r} - (\mathbf{r}_n + \mathbf{d}_A)]$ and $\phi_C[\mathbf{r} - (\mathbf{r}_n + \mathbf{d}_B)]$. The state associated with each unit cell is

$$\{\psi\} = \begin{pmatrix} \psi_{nA} \\ \psi_{nB} \end{pmatrix}$$

and the wave function for the whole crystal is

$$\{\psi\} = \begin{pmatrix} \{\psi_1\} \\ \{\psi_1\} \\ \vdots \end{pmatrix}$$

We want to solve the time-independent schrodinger equation:

$$[H]\{\psi\} = E \cdot \{\psi\}$$

We use the ansatz

$$\{\psi_n(\mathbf{k})\} = \{\psi_0\} \cdot e^{i\mathbf{k} \cdot \mathbf{r}_n}$$

We just need

$$\{\psi_0\} = \begin{pmatrix} \psi_A \\ \psi_B \end{pmatrix}$$

The ansatz turns this into

$$[h(\mathbf{k})] = \sum_n [H_{0n}] \cdot e^{i\mathbf{k} \cdot \mathbf{r}_n}$$

where $[H_{0n}]$ is the matrix coupling the basis states in unit cell 0 to those in unit cell n .

$$[H_{0n}] = \begin{pmatrix} \langle 0A | \hat{H} | nA \rangle & \langle 0A | \hat{H} | nB \rangle \\ \langle 0B | \hat{H} | nA \rangle & \langle 0B | \hat{H} | nB \rangle \end{pmatrix}$$

We might as well simplify by relabeling $|nA\rangle \rightarrow |(u_n, v_n)A\rangle$ and $|nB\rangle \rightarrow |(u_n, v_n)B\rangle$. Also $[H_{0n}] \rightarrow [H_{(u_n, v_n)}]$. We will need to know the self-energy term

$$E_0 = \langle (0,0)A | \hat{H} | (0,0)A \rangle = \langle (0,0)B | \hat{H} | (0,0)B \rangle$$

The next important term involves coupling among nearest neighbors.

$$\begin{aligned} -t &= \langle (0,0)A | \hat{H} | (0,0)B \rangle \\ &= \langle (0,0)A | \hat{H} | (\bar{1},0)B \rangle \\ &= \langle (0,0)A | \hat{H} | (0,\bar{1})B \rangle \\ &= \langle (0,0)B | \hat{H} | (1,0)A \rangle \\ &= \langle (0,0)B | \hat{H} | (0,1)A \rangle \end{aligned}$$

Various studies have found a value of approximately $t = 2.8$ eV. We can get a good sense of the electronic structure of graphene if we assume all higher-order terms (second nearest neighbors, and beyond) are negligible. We have

$$[H_{(0,0)}] = \begin{pmatrix} E_0 & -t \\ -t & E_0 \end{pmatrix}$$

and

$$[H_{(\bar{1},0)}] = [H_{(0,\bar{1})}] = \begin{pmatrix} 0 & -t \\ 0 & 0 \end{pmatrix}, [H_{(1,0)}] = [H_{(0,1)}] = \begin{pmatrix} 0 & 0 \\ -t & 0 \end{pmatrix}$$

Combining

$$\begin{aligned} [h(\mathbf{k})] &= [H_{(0,0)}] + [H_{(1,0)}] \cdot e^{ik \cdot \mathbf{a}_1} + [H_{(0,1)}] \cdot e^{ik \cdot \mathbf{a}_2} \\ &\quad + [H_{(\bar{1},0)}] \cdot e^{-ik \cdot \mathbf{a}_1} + [H_{(0,\bar{1})}] \cdot e^{-ik \cdot \mathbf{a}_2} \end{aligned}$$

Defining $h_0(\mathbf{k}) = -t \cdot (1 + e^{-ik \cdot \mathbf{a}_1} + e^{-ik \cdot \mathbf{a}_2})$, this gives

$$[h(\mathbf{k})] = \begin{pmatrix} E_0 & h_0(\mathbf{k}) \\ h_0^*(\mathbf{k}) & E_0 \end{pmatrix}$$

Now we solve the eigenvalue problem

$$[h(\mathbf{k})] \cdot \{\psi_0\} = E(\mathbf{k}) \cdot \{\psi_0\}$$

Use $\det([h(\mathbf{k})] - E(\mathbf{k}) \cdot [I]) = 0$, or

$$\det \begin{pmatrix} E_0 - E(\mathbf{k}) & h_0(\mathbf{k}) \\ h_0^*(\mathbf{k}) & E_0 - E(\mathbf{k}) \end{pmatrix} = 0$$

NANO 705-Notes

The two eigenvalues for each wavevector \mathbf{k} describe the two electronic bands

$$E_{\pm}(\mathbf{k}) = E_0 \pm |h_0(\mathbf{k})| = E_0 \pm t \cdot |1 + e^{-i\mathbf{k}\cdot\mathbf{a}_1} + e^{-i\mathbf{k}\cdot\mathbf{a}_2}|$$

One might be inclined to write $\mathbf{k} = k_x\hat{\mathbf{x}} + k_y\hat{\mathbf{y}}$. Then

$$h_0(k_x, k_y) = -t \cdot [1 + e^{-i(ak_x + bk_y)} + e^{-i(ak_x - bk_y)}] = -t \cdot [1 + 2e^{-iak} \cdot \cos(bk_y)]$$

The magnitude is

$$|h_0(k_x, k_y)| = t \cdot \sqrt{1 + 4\cos(k_x a)\cos(k_y b) + 4\cos^2(k_y b)}$$

It is often more useful to write $\mathbf{k} = u\mathbf{b}_1 + v\mathbf{b}_2$, where $\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi\delta_{i,j}$. We can find these vectors by inverting the 2-D direct lattice vectors. In matrix form:

$$[\mathbf{A}] = (\mathbf{a}_1 \quad \mathbf{a}_2) = \begin{pmatrix} a & a \\ b & -b \end{pmatrix}$$

The inverse is

$$[\mathbf{A}]^{-1} = \frac{1}{2} \begin{pmatrix} 1/a & 1/b \\ 1/a & -1/b \end{pmatrix}$$

The reciprocal lattice basis vectors are given by

$$[\mathbf{B}] = 2\pi([\mathbf{A}]^{-1})^T = \begin{pmatrix} \pi/a & \pi/a \\ \pi/b & -\pi/b \end{pmatrix} = (\mathbf{b}_1 \quad \mathbf{b}_2)$$

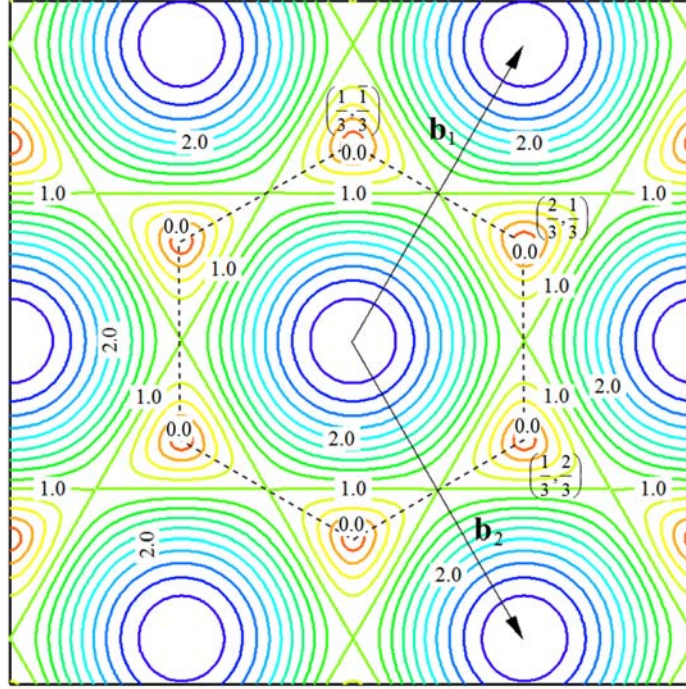
So $\mathbf{b}_1 = (\pi/a)\hat{\mathbf{x}} + (\pi/b)\hat{\mathbf{y}}$ and $\mathbf{b}_2 = (\pi/a)\hat{\mathbf{x}} - (\pi/b)\hat{\mathbf{y}}$. Now $\mathbf{k} \cdot \mathbf{a}_1 = 2\pi u$ and $\mathbf{k} \cdot \mathbf{a}_2 = 2\pi v$, which gives

$$h_0(u, v) = -t \cdot (1 + e^{-2\pi i u} + e^{-2\pi i v})$$

and the magnitude is

$$|h_0(u, v)| = t \cdot \sqrt{3 + 2\cos(2\pi u) + 2\cos(2\pi v) + 2\cos[2\pi(u - v)]}$$

The separation between the two bands at some point in reciprocal space is $2|h_0(u, v)|$. The maximum band separation of $6t$ occurs at reciprocal-lattice points, where both u and v are integers. The band separation is zero at the Fermi points, with coordinates (u_0, v_0) . These often have a dominant effect on the conducting properties of graphene. We must have $e^{-2\pi i u_0} + e^{-2\pi i v_0} = -1$, so $\cos(2\pi u_0) + \cos(2\pi v_0) = -1$ and $\sin(2\pi u_0) + \sin(2\pi v_0) = 0$. Then $u_0 = p \pm 1/3$ ($p \in \mathbb{Z}$) and $v_0 = -u_0 + p'$ ($p' \in \mathbb{Z}$), so $v_0 = -(p \pm 1/3) + p' = q \mp 1/3$ ($q \in \mathbb{Z}$). The Fermi points coordinates are then $(p \pm 1/3, q \mp 1/3)$. The first Brillouin-zone boundary is a regular hexagon with Fermi points at each of the six corners. It is useful at this point to form a contour plot of $|h_0(u, v)|/t$.



Consider the region near any Fermi point, with coordinates $(u_0 + \delta u, v_0 + \delta v)$. We have

$$\begin{aligned}
 h_0(\delta u, \delta v) &= -t \cdot (1 + e^{-2\pi i(u_0 + \delta u)} + e^{-2\pi i(v_0 + \delta v)}) \\
 &= -t \cdot (1 + e^{-2\pi i(p \pm 1/3)} \cdot e^{-2\pi i \delta u} + e^{-2\pi i(q \mp 1/3)} \cdot e^{-2\pi i \delta v}) \\
 h_0(\delta u, \delta v) &= -t \cdot \left[1 - \frac{1}{2} \cdot (e^{-2\pi i \delta u} + e^{-2\pi i \delta v}) \mp i \frac{\sqrt{3}}{2} \cdot (e^{-2\pi i \delta u} - e^{-2\pi i \delta v}) \right]
 \end{aligned}$$

Now let's assume $(\delta u, \delta v)$ is small. To first order

$$h_0(\delta u, \delta v) \approx -\pi t \cdot (\pm\sqrt{3}(\delta v - \delta u) + i(\delta u + \delta v))$$

Notice that $\delta k_x = \pi(\delta u + \delta v)/a$ and $\delta k_y = \pi(\delta u - \delta v)/b$. So

$$h_0(\delta k_x, \delta k_y) = -t \cdot (\mp\sqrt{3} \cdot \delta k_y \cdot b + i \cdot \delta k_x \cdot a) = -\frac{3ta_0}{2} \cdot (\mp\delta k_y + i \cdot \delta k_x)$$

The magnitude is

$$|h_0(\delta k_x, \delta k_y)| = \frac{3ta_0}{2} \cdot \sqrt{\delta k_y^2 + \delta k_x^2}$$

There is rotational symmetry in the vicinity of the Fermi point. Writing the radius in reciprocal space as

$$\delta k_r = \sqrt{\delta k_y^2 + \delta k_x^2}, \text{ we have}$$

$$|h_0(\delta k_r)| = \frac{3ta_0}{2} \cdot \delta k_r$$

So the bands near these points vary as

$$E_{\pm}(\delta k_r) = E_0 \pm \frac{3ta_0}{2} \cdot \delta k_r$$

Graphene: DOS

We saw that the number of states in a sheet of area S having wavevector shorter than k_r increases with wave vector as

$$\frac{1}{S} \frac{dN}{dk} = \frac{k_r}{2\pi}$$

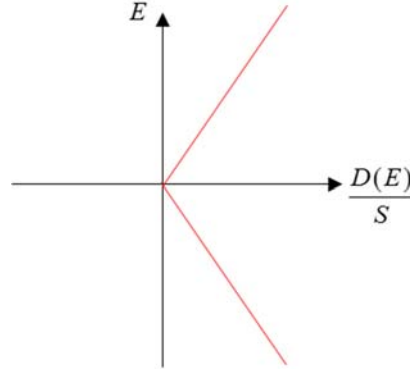
For graphene, at a short distance δk_r from a Fermi point (setting $E_0 = 0$)

$$E_{\pm}(\delta k_r) = \pm ta \cdot \delta k_r$$

The DOS is $D(E) = |dN/dE|$, so

$$\frac{D(E)}{S} = \frac{|E|}{2\pi t^2 a^2}$$

as sketched below.



Carbon nanotubes

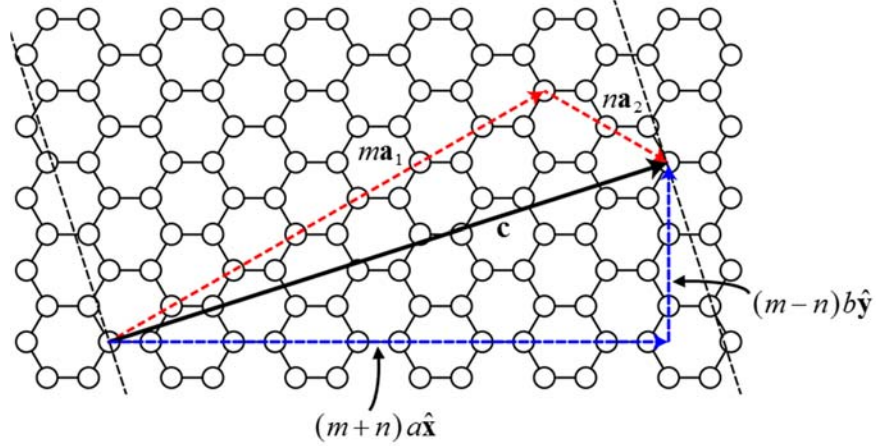
A graphene sheet can be rolled into a carbon nanotube (CNT) along some roll-up vector $\mathbf{c} = m\mathbf{a}_1 + n\mathbf{a}_2$, where $(m, n) \in \mathbb{Z}^2$. We can write

$$\mathbf{c} = (m+n)a\hat{\mathbf{x}} + (m-n)b\hat{\mathbf{y}}$$

The circumference of the nanotube is then

$$c = \sqrt{(m+n)^2 a^2 + (m-n)^2 b^2} = \sqrt{3}a_0 \sqrt{m^2 + n^2 + mn}$$

Assuming a uniform, cylindrical shape, the diameter is $d = c/\pi$.



Consider the wavefunction we used for an infinite graphene sheet. It must be single-valued, so its value in the unit cell located at $\mathbf{r}_n = \mathbf{c}$ must equal that at $\mathbf{0}$ (since they are the same unit cell.) This gives

$$\{\Psi_{m,n}(\mathbf{k})\} = \{\Psi_0\} \cdot e^{i\mathbf{k} \cdot \mathbf{c}} = \{\Psi_0\}$$

We then have $\mathbf{k} \cdot \mathbf{c} = 2\pi\ell$, where the index $\ell \in \mathbb{Z}$ specifies a subband. Recalling that $\mathbf{k} = u\mathbf{b}_1 + v\mathbf{b}_2$, we can see that all wavevectors on this subband must satisfy $mu + nv = \ell$, which specifies a line through the reciprocal lattice. The possible subbands, and thus the electrical properties, will depend on (m, n) . It is useful to establish a coordinate system aligned with the CNT axis: $\mathbf{k} = k_{\perp}\hat{\mathbf{e}}_{\perp} + k_{\parallel}\hat{\mathbf{e}}_{\parallel}$. Then unit vector along the roll-up vector is

$$\hat{\mathbf{e}}_{\perp} = \mathbf{c}/c = \frac{(m+n)a\hat{\mathbf{x}} + (m-n)b\hat{\mathbf{y}}}{\pi d}$$

We can specify a Fermi point as $\mathbf{k}_0 = k_{\perp 0}\hat{\mathbf{e}}_{\perp} + k_{\parallel 0}\hat{\mathbf{e}}_{\parallel}$.

$$k_{\perp 0} = \mathbf{k}_0 \cdot \hat{\mathbf{e}}_{\perp} = \frac{(m+n)k_{x0}a + (m-n)k_{y0}b}{\pi d}$$

Noting that $k_x = \pi(u+v)/a$ and $k_y = \pi(u-v)/b$

$$k_{\perp 0} = \frac{1}{d} \left[(m+n) \cdot (p+q) + (m-n) \cdot \left(p - q \pm \frac{2}{3} \right) \right]$$

In the vicinity of a Fermi point at, we can write $k_{\perp} = k_{\perp 0} + \delta k_{\perp}$. From the local rotational symmetry, we have

$$|h_0(\delta k_{\perp}, \delta k_{\parallel})| = \frac{3ta_0}{2} \cdot \sqrt{\delta k_{\perp}^2 + \delta k_{\parallel}^2}$$

For the CNT, $\mathbf{k} \cdot \mathbf{c} = \pi k_{\perp} d$, so for a particular subband $k_{\perp} = 2\ell/d$, whereas k_{\parallel} is unrestricted. Now

$$\delta k_{\perp} = \frac{2\ell - (m+n) \cdot (p+q) + (m-n) \cdot \left(p - q \pm \frac{2}{3} \right)}{d}$$

The minimum band separation for a particular subband will always occur where $\delta k_{\parallel} = 0$. Then

$$|h_0| = \frac{3ta_0}{2d} \cdot \left| 2\ell - (m+n) \cdot (p+q) + (m-n) \cdot \left(p - q \pm \frac{2}{3} \right) \right|$$

Rearranging

$$|h_0| = \frac{ta_0}{d} \cdot |3(\ell - mq - np) \pm (m-n)|$$

We can thus compute the bandgap for a particular CNT with roll-up indices (m, n) as $E_g = 2|h_0|$, evaluated using the combination of integers (ℓ, p, q) that minimize $|h_0|$. Note that ℓ can be any integer, so $s = \ell - mq - np$ can, likewise, be any integer. Therefore, we are looking for the minimum of $|3s \pm (m-n)|$. Clearly $|3(-s) + (m-n)| = |3s - (m-n)|$, so subbands arising from $\pm s$ give the same E_g , (though they may correspond to different subbands ℓ .) Note that, for any (m, n) , of the three numbers $m-n-1$, $m-n$, and $m-n+1$, exactly one will be divisible by 3, so either $m-n$ is equal to 3 times some integer s , or it is one different from $3s$. Combining the factors $t = 2.8$ eV and $a_0 = 0.142$ nm, we conclude that, for any CNT

$$E_g = \begin{cases} \frac{0.80 \text{ eV} \cdot \text{nm}}{d}, & m-n \neq 3s \\ 0, & m-n = 3s \end{cases}$$

The first type, which has a non-zero bandgap, can be considered semiconducting. The second type, with no bandgap, is metallic.

Whereas, the graphene sheet has sixfold rotational symmetry about a point in the center of each open hexagon, each atom is at a site of threefold symmetry. This leaves the structure unchanged under a 120° rotation. We can write a pair of roll-up indices (m, n) as a vector $\{X\}$. Given the basis matrix $[A]$, the roll-up vector is $\mathbf{c} = [A] \cdot \{X\}$. A rotation about the origin is affected by a matrix $[R]$, such that $\mathbf{c}' = [R] \cdot \mathbf{c} = [A] \cdot \{X'\}$. Then

$$\{X'\} = [A^{-1}] \cdot [R] \cdot [A] \cdot \{X\}$$

To rotate by $\pm 120^\circ$, we use

$$[R \pm] = \begin{pmatrix} -\frac{1}{2} & \mp \frac{\sqrt{3}}{2} \\ \pm \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$$

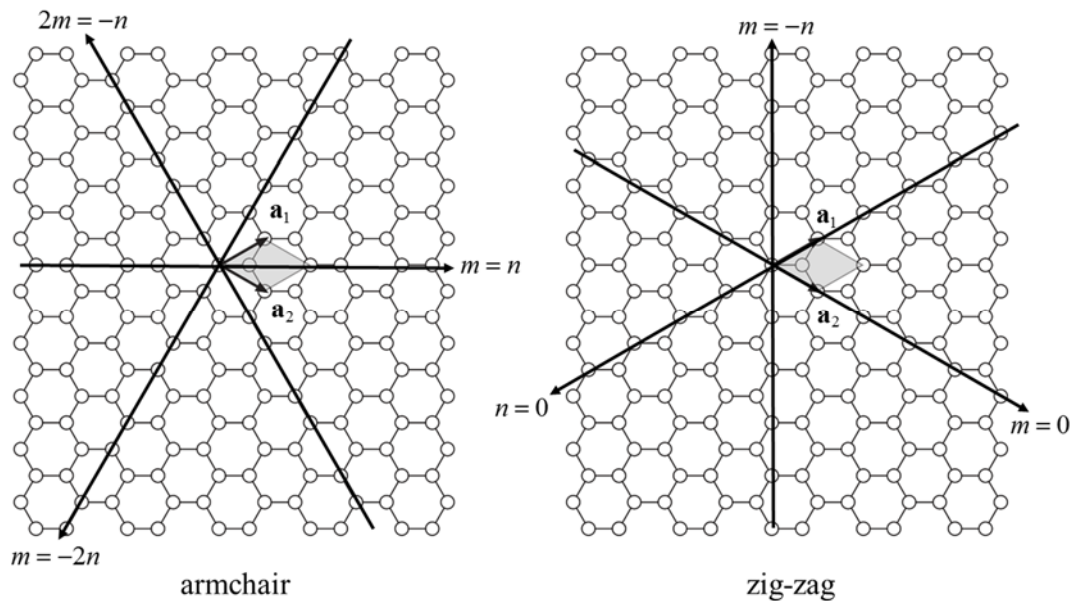
For clarity, write $(m, n) = (i, j)$. Then the the following three sets of roll-up vectors are equivalent:

$$\begin{pmatrix} m \\ n \end{pmatrix} = \begin{pmatrix} i \\ j \end{pmatrix}, \begin{pmatrix} m \\ n \end{pmatrix} = \begin{pmatrix} 0 & 1 \\ -1 & -1 \end{pmatrix} \cdot \begin{pmatrix} i \\ j \end{pmatrix} = \begin{pmatrix} j \\ -i-j \end{pmatrix}, \text{ and } \begin{pmatrix} m \\ n \end{pmatrix} = \begin{pmatrix} -1 & -1 \\ 1 & 0 \end{pmatrix} \cdot \begin{pmatrix} i \\ j \end{pmatrix} = \begin{pmatrix} -i-j \\ i \end{pmatrix}$$

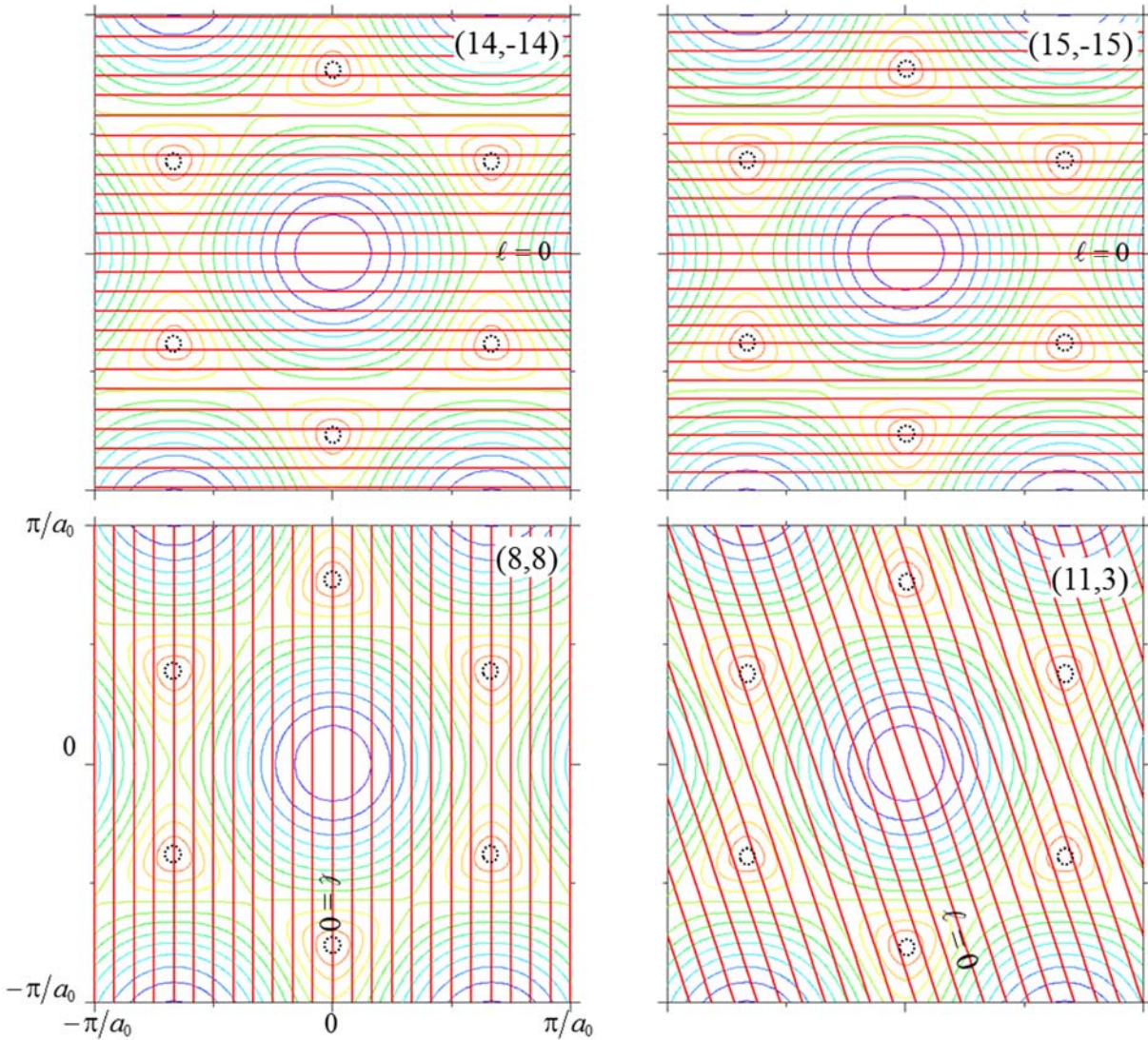
Since the CNT is not physically changed by reversing the direction of \mathbf{c} , flipping the overall sign on (m, n) also has no tangible effect.

Consider a CNTs with $m = n$. We can write the roll-up indices as (i, i) . The subband $\ell = 0$ will contain the Fermi points at $\pm(1/3, -1/3)$, so the CNT will always be metallic. (To check this, notice that $m - n = i - i = 0 = 3 \times 0$.) This is known as an *armchair* CNT. From the discussion above, this CNT is equivalent to those with indices $(i, -2i)$ and $(-2i, i)$, which are also armchair CNTs, satisfying the conditions $m = -2n$ and $2m = -n$, respectively. In summary, armchair CNTs have indices with $m = n$, $m = -2n$, or $2m = -n$.

CNTs with indices $(i, 0)$, $(0, -i)$, and $(i, -i)$ are equivalent, and are called *zig-zag* CNTs. We can say that zig-zag CNTs have either $m = 0$, $n = 0$, or $m = -n$. In the last case, the rule becomes $2m = 3s$. Regardless of the orientation, one out of three possible zig-zag CNTs is metallic, whereas the other two are semiconducting. This may not correspond to the actual abundances of each during synthesis, however.



If we focus on the Fermi point at $(1/3, -1/3)$ (i.e., $p = q = 0$), the quantity determining bandgap becomes $|3\ell \pm (m - n)|$. This leaves the bandgap formula unchanged, with 3ℓ substituted for $3s$. We can always find some index ℓ for a subband that determines bandgap by passing closest to this Fermi point. If $m - n = 3\ell$, then the CNT is metallic and $\ell = (m - n)/3$. Otherwise, we need to determine which of the two possibilities $\ell = (m - n \pm 1)/3$ returns an integer index.



CNT: DOS

Consider a rectangular sheet of graphene, with dimensions $c \times L$, that could be rolled into a large CNT. The area is $S = L \cdot c = \pi L d$. Then the DOS per unit length (of this carbon macrotube) is

$$\frac{D(E)}{L} = \frac{d}{2\pi t^2 a^2} \cdot |E|$$

In the vicinity of $(1/3, -1/3)$, we have $\delta k_{\perp} = 2[\ell - (m-n)/3]/d$, so

$$\delta k_r = \sqrt{\delta k_{\parallel}^2 + \left(\frac{2}{d}\right)^2 \left(\ell - \frac{m-n}{3}\right)^2}$$

For a particular subband ℓ , this gives

$$E_{\pm}(\delta k_{\parallel}) = \pm t a \cdot \sqrt{\delta k_{\parallel}^2 + \left(\frac{2}{d}\right)^2 \left(\ell - \frac{m-n}{3}\right)^2}$$

The incremental difference in parallel wavevector is

$$\delta k_{\parallel} = \frac{1}{ta} \cdot \sqrt{E^2 - E_{\ell}^2}$$

where

$$E_{\ell} = \frac{2ta}{d} \cdot \left| \ell - \frac{m-n}{3} \right|$$

The DOS for a single subband ℓ can be found using

$$\frac{1}{L} \frac{dN_{\ell}}{dE} = \frac{1}{L} \cdot \frac{dN_{\ell}}{d(\delta k_{\parallel})} \cdot \frac{d(\delta k_{\parallel})}{dE}$$

Applying periodic boundary conditions along the CNT axis

$$\frac{1}{L} \frac{dN_{\ell}}{d(\delta k_{\parallel})} = \frac{1}{\pi}$$

From the dispersion relation

$$\frac{d(\delta k_{\parallel})}{dE} = \frac{1}{ta} \cdot \frac{E}{\sqrt{E^2 - E_{\ell}^2}}$$

We get

$$\frac{D_{\ell}(E)}{L} = \frac{1}{\pi ta} \cdot \frac{|E|}{\sqrt{E^2 - E_{\ell}^2}} \theta(E - E_{\ell})$$

We can include contributions from all subbands, giving

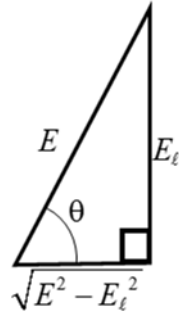
$$\frac{D(E)}{L} = \frac{1}{\pi ta} \cdot \sum_{\ell} \frac{|E|}{\sqrt{E^2 - E_{\ell}^2}} \theta(E - E_{\ell})$$

The resulting DOS is a very discontinuous DOS, with a spike each time E exceeds an addition subband edge E_{ℓ} .

Consider the limit as the CNT becomes macroscopic. The subbands become very close together as d becomes larger. Notice that $dE_{\ell}/d\ell = 2ta/d$, so $d\ell = (d/2ta) \cdot dE_{\ell}$. Changing the sum to an integral gives

$$\begin{aligned} \frac{D(E)}{L} &\rightarrow \frac{1}{\pi ta} \cdot \int_{\ell=-\infty}^{\infty} d\ell \cdot \frac{|E|}{\sqrt{E^2 - E_{\ell}^2}} \theta(E - E_{\ell}) \\ &= \frac{d \cdot |E|}{2t^2 a^2} \cdot \frac{1}{\pi} \cdot \left[\int_{E_{\ell}=-E}^E d\ell \cdot \frac{dE_{\ell}}{\sqrt{E^2 - E_{\ell}^2}} \right] \end{aligned}$$

Define a right triangle, such that $\cos \theta = \sqrt{E^2 - E_{\ell}^2}/E$ and $\sin \theta = E_{\ell}/E$.



Then $E_l = E \cdot \sin \theta$ and $dE_l = E \cdot \cos \theta \cdot d\theta$, giving

$$\frac{1}{\sqrt{E^2 - E_l^2}} = \frac{1}{E \cdot \cos \theta}$$

Our integral is simply

$$\int_{E_l=-E}^E d\ell \cdot \frac{dE_l}{\sqrt{E^2 - E_l^2}} = \int_{\theta=-\pi/2}^{\pi/2} d\theta = \pi$$

Finally we have

$$\frac{D(E)}{L} = \frac{d \cdot |E|}{2t^2 a^2}$$

which matches the result for the graphene sheet, as expected. The graphene DOS gives the overall slope for the CNT DOS, which shows spikes at each subband-edge energy.

