PH 673 Nano

Lecture # 9

Carbon nanotubes

Recall from graphene band structure calculation

$$E = \pm t \sqrt{1 + 4\cos^2 \frac{k_x a\sqrt{3}}{2} \pm 4\cos\frac{k_x a\sqrt{3}}{2}\cos\frac{k_y 3a}{2}}$$

Now let's roll up a tube $\Rightarrow$

$$\underbrace{\vec{C}_h}_{\text{chiral vector}} = \underbrace{n}_{\text{wrapping}}\vec{a}_1 + \underbrace{m}_{\text{indices}}\vec{a}_2 \quad ; \quad \vec{C}_h \cdot \vec{k} = 2\pi \underbrace{l}_{\text{integer}} \leftarrow \text{periodic boundary condition}$$

<u>Armchair</u> $\underset{n=m}{\Rightarrow} (n,n) \Rightarrow$ e.g. $(5,5), (10,10), \ldots$

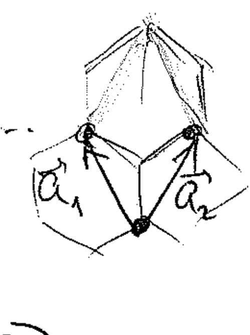
$\theta = 30°$ ← chiral angle

<u>Zigzag</u> $\underset{m=0}{\Rightarrow} (n,0) \Rightarrow$ e.g. $(9,0), (10,0), \ldots$

$\theta = 0°$

<u>Chiral</u> $\Rightarrow (n,m) \Rightarrow$ e.g. $(10,5), \ldots$

$0° < \theta < 30°$



So, for <u>armchair</u> $\Rightarrow \vec{C}_h = n\underbrace{(\vec{a}_1 + \vec{a}_2)}_{3a\hat{y}} \Rightarrow$

$$n \cdot 3a k_y = 2\pi l \Rightarrow \boxed{k_y = \frac{2\pi l}{3an}}$$

Do we still have $E=0$ at K-points?
(are $k_y = 0$ and $k_y = \pm\frac{2\pi}{3a}$ consistent with $k_y = \frac{2\pi l}{3an}$?)

$k_y = 0$ if $l = 0$;
$k_y = \pm\frac{2\pi}{3a}$ if $l = n \in \mathbb{Z}$ (integer) $\Big\}$ ✓

So, armchair tubes are metallic, regardless of n

Now zigzag $\Rightarrow C_h = n\vec{a}_1 = na\left(-\frac{\sqrt{3}}{2}\hat{x} + \frac{3}{2}\hat{y}\right)$

$$\frac{na}{2}\left(-\sqrt{3}k_x + 3k_y\right) = 2\pi l$$

K-point check: 1) $k_x = \pm\frac{4\pi}{3\sqrt{3}a}$, $k_y = 0 \Rightarrow$

$$\frac{na}{2}\left(-\sqrt{3}\cdot\frac{-4\pi}{3\sqrt{3}a} + 0\right) = \frac{2\pi n}{3} = 2\pi l$$

if $n = 3l \Rightarrow E = 0$

2) $k_x = \pm\frac{2\pi}{3\sqrt{3}a}$, $k_y = \pm\frac{2\pi}{3a}$

$$\frac{na}{2}\left(\mp\sqrt{3}\cdot\frac{2\pi}{3\sqrt{3}a} \,(\pm)\, 3\cdot\frac{2\pi}{3a}\right) = \begin{cases} \pm\frac{4\pi}{3a}\cdot\frac{na}{2} = \frac{2\pi n}{3} = 2\pi l \Rightarrow n = 3l \text{ (integer)} \\ \pm\frac{8\pi}{3a}\frac{na}{2} = \frac{4\pi n}{3} = 2\pi l \Rightarrow n = \frac{3}{2}l \text{ (not integer)} \end{cases}$$

So, if $n = 3l \Rightarrow$ metallic

if $n \neq 3l \Rightarrow$ semiconducting

$a/\sqrt{3}a = \sqrt{3}/2$

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Bandgap depends on by how much allowed k-values missed the K-points:

say, $n = 3l + 1 \Rightarrow$ mismatch $\frac{2\pi}{3}(3l+1) -$

$- 2\pi l = \frac{2\pi}{3} = |C_h| \Delta K \Rightarrow \Delta K = \frac{2\pi}{3\pi d} = \frac{2}{3d}$

$n|\vec{a}_1| = na\sqrt{3} = \pi d$

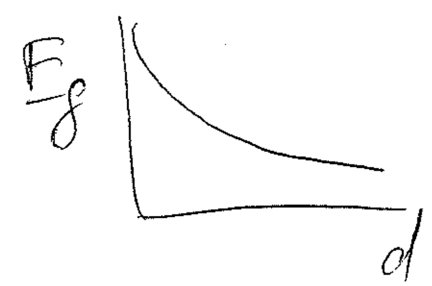
nanotube diameter

$$E_g = 2 \underbrace{\frac{dE}{dK}}_{=\hbar v_F} \underbrace{\Delta K}_{=\frac{2}{3d}} = \frac{4\hbar v_F}{3d} \approx \frac{0.7\,eV}{d\,(nm)}$$

bandgap

for SWNT $d = 0.8-3$ nm $\Rightarrow$ $E_g \sim 0.2 - 0.9\,eV$

So, $E_g \sim \frac{1}{d} \Rightarrow$



<u>In reality</u>: Curvature mixes π & σ orbitals (they are not $\perp$ anymore) $\Rightarrow$ $\pi - \sigma$ hybridization

"quasi-metallic" $\Leftarrow$
- bandgap opens in metallic zigzag nanotubes
- $E_g \sim \frac{1}{d^2}$ for $d \leq 3$ nm in metallic zigzag tubes

few to 10 meV $\Leftarrow$

Generalization to any $(n, m) \Rightarrow$ 4

$n - m = 3l + p \Rightarrow$ if $p = 0 \leftarrow$ metallic

$p = 1, 2 \Rightarrow$ semiconducting

Density of states

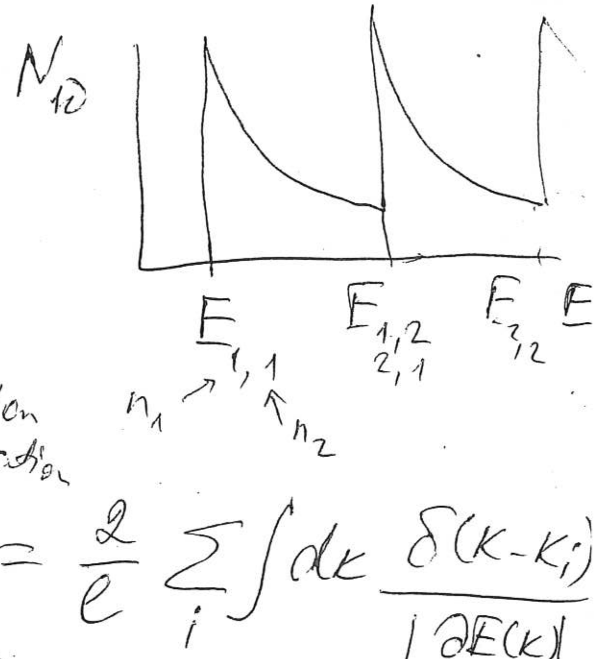
PRL 81(12), 2506 (1998)

<u>recall</u> for 1D wire: $N_{1D}(E)\,dE = \frac{1}{L} \cdot \underset{\uparrow \text{spin}}{2} \cdot \underset{\uparrow k \text{ + or - degeneracy}}{2} \cdot \frac{dk}{\frac{2\pi}{L}}$

$$N_{1D}(E) = \frac{2}{\pi}\frac{dk}{dE} \underset{\uparrow}{=} \frac{\sqrt{2m^*}}{\pi\hbar}\frac{1}{\sqrt{E}}$$

if $E = \frac{\hbar^2 k^2}{2m^*}$ ← within a sub-band

$$E = \frac{\hbar^2 k_x^2}{2m} + \underbrace{E_{n_1} + E_{n_2}}_{\text{2D box}} \Rightarrow$$



Similar for CNTs:

$$N_{1D}(E) = \frac{\overset{\text{spin}}{2}}{\underbrace{\int dk}_{l \,\leftarrow\, \text{length of Brillouin zone}}} \int dk\, \delta(\overbrace{E - E(k)}^{\text{dispersion relation}}) = \frac{2}{l}\sum_i \int dk \frac{\delta(k - k_i)}{\left|\frac{\partial E(k)}{\partial k}\right|_{k_i}}$$

k_i ← roots of $E - E(k_i) = 0$

$$\underset{\uparrow \text{PRL}}{=} \frac{4\sqrt{3}\,a}{\pi^2 \underset{\uparrow \text{transfer}}{t} \underset{\uparrow \text{diameter of nanotube}}{d}} \sum_{l'=-\infty}^{+\infty} g(E, E_{l'})$$

C-C bond

$$|E_{l'}| = \frac{|3l' - n + m|}{\cancel{2}}\, t\, \frac{a}{d/\cancel{2}}$$

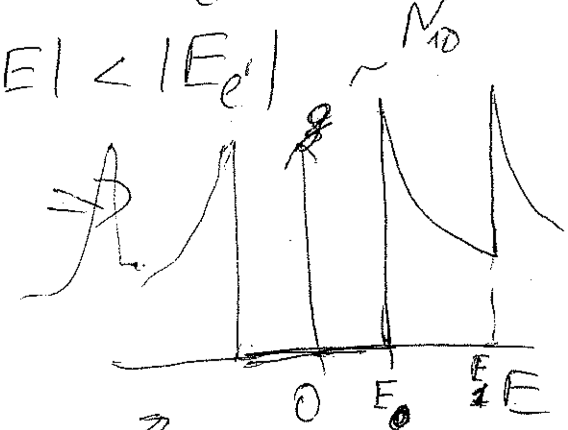
for (n, m) nanotube

diameter of nanotube

$$g(E, E_{l'}) = \begin{cases} \frac{|E|}{\sqrt{E^2 - E_{l'}^2}}, & |E| > |E_{l'}| \\ 0, & |E| < |E_{l'}| \end{cases}$$

if $E = E_{l'} \rightarrow$ blows up

if $E_{l'} = 0 \rightarrow g(E, 0) = 1$

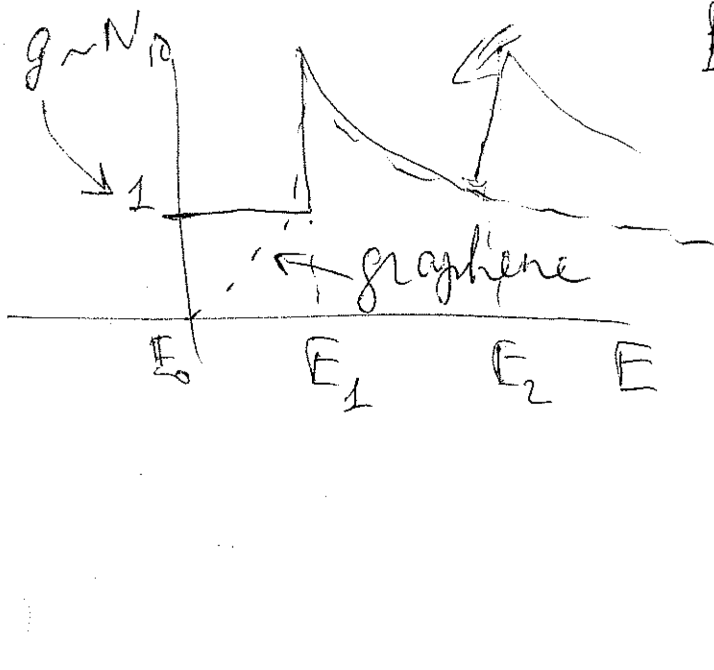


for $|n - m| \neq |3l'|$

if $n - m = 3l' \Rightarrow$

armchair : $n = m \Rightarrow n - m = 0 \leftarrow$ at $l' = 0 \Rightarrow$

$E_0 = 0$; $E_1 = 3\frac{ta}{d}$, ...



if zigzag metallic $\Rightarrow$

say, $n - m = 3 \Rightarrow \overset{3\frac{at}{d}}{E_0} \neq 0$

e.g. (22, 19)

but $E_1 = 0$