Carbon Nanotubes - McEuen

Reading, Additional Material

(1) "Nanostructures," Chap 18 in new edition of Kittel.
(2) Nanotube05 Website (Google NT05)
Reviews by J. Nygaard. ⇒ Transport
M. Dresselhaus ⇒ Optics.
(3) Tuning Band Structure ⇒ Ethan Minot, thesis
(McEuen group website).
(4) Numerous books....

Rough Outline of Lectures

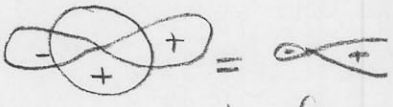
Lecture # 1: Band Structure I: Metals & Semic.
Lecture # 2: BS II: Breaking Symmetry (Bending, Twisting, B, etc.)
Lecture # 3: Vibrations, Phonons, & Tiny Guitars.
(plus unanswered questions)

Public Lecture: Small is All: Bio, Nano, & the Future of Technology: ⇒ Half-baked musings on nearly everything under the sun.

Lecture #1 Graphite & NT Band Structure

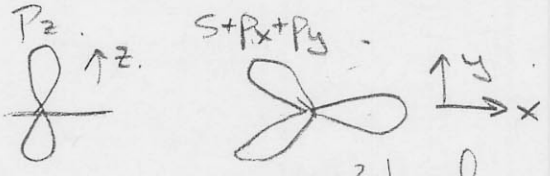
note
Don't trust details of notes!

Carbon: 6 electrons $1s^2 2s^2 2p^2$ atomic.
$1s^2 2s 2p^3$ bonding.
sp bonds.



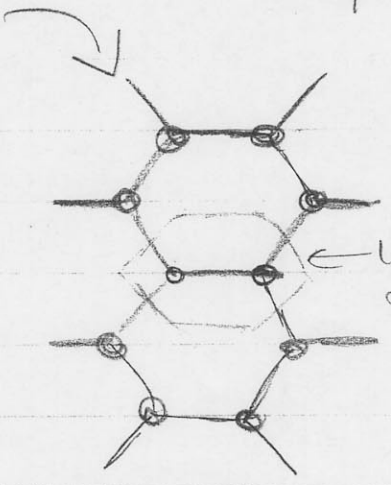
sp^2 bonds give honeycomb lattice. One p_z orbital left over per C-atom.

p_z responsible for conduction

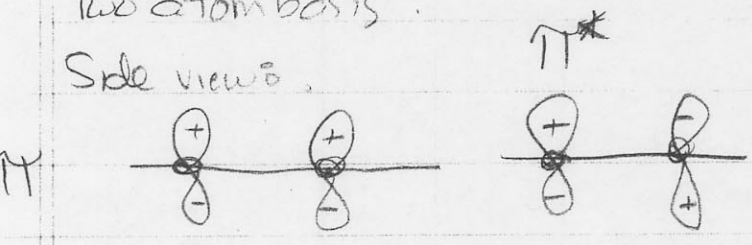


Unit cell: Two atom basis.

Lattice.

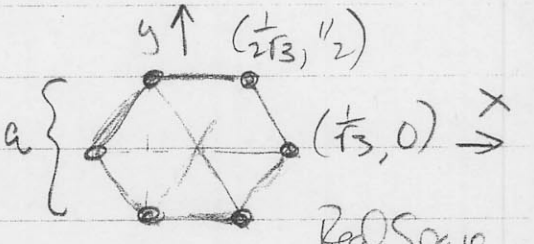


Side view:



bonding antibonding.
called "pi" orbitals.

Unit Cell. Real & Recip Space.
Set "a" = 1. $a = \sqrt{3} \cdot$ c-c bond length.

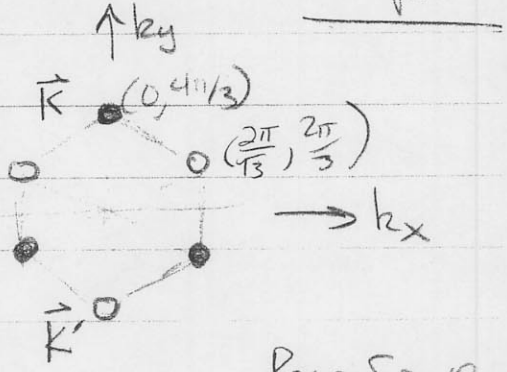


First Brillouin Zone ⇒ exactly filled by 2 atom lattice.

Two "special" points:

- $\vec{K} = (0, \frac{4\pi}{3})$
- $\vec{K}' = (0, -\frac{4\pi}{3})$

Note: other corners related by recip. lattice vectors.

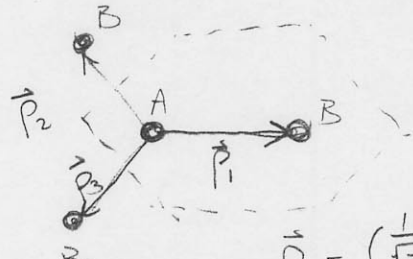


Tight Binding Model:

Assume N-N hopping with element t.

Need two #'s to describe basis

Write as column vector.



$\vec{\rho}_1 = (\frac{1}{\sqrt{3}}, 0)$

$\vec{\rho}_{2,3} = (-\frac{1}{2\sqrt{3}}, \pm\frac{1}{2})$

$\begin{pmatrix}1\\0\end{pmatrix} \Rightarrow$ electron on A $\qquad \begin{pmatrix}0\\1\end{pmatrix} \Rightarrow$ electron on B.

$\Rightarrow$ Hopping is off-diagonal (from A to B)

Assume $\psi(r) = \psi(0)\, e^{i\vec{k}\cdot\vec{r}}$ Bloch waves.

Then:

$$\mathcal{H} = \begin{pmatrix} 0 & t^* \underbrace{\sum_i e^{-i\vec{k}\cdot\vec{\rho}_i}}_{h^*} \\ t\sum_i e^{i\vec{k}\cdot\vec{\rho}_i} & 0 \end{pmatrix} \Rightarrow E = \pm|t|^2 \left|\sum e^{i\vec{k}\cdot\vec{\rho}_i}\right|^2 = \pm|h|$$

↑ Two roots correspond to π & π^* bands.

$\Rightarrow$ see graph.

$$h = t\left[e^{ik_x/\sqrt{3}} + e^{-\frac{ik_x}{2\sqrt{3}}} 2\cos(k_y/2)\right]$$

Interesting case: $\vec{K} = \vec{K}' = (0, 4\pi/3)$.

$$h = t\left[1 + 2\cos(2\pi/3)\right] = t\left[1 + 2(-\tfrac{1}{2})\right] = 0.$$

$E(\vec{K}) = \pm 0 \leftarrow$ same energy

$\Rightarrow$ **Gap Vanishes at $\vec{K} \neq \vec{K}'$**

What about nearby $\vec{K}$ point?

$\vec{k} = \vec{K} + \delta\vec{k} \Rightarrow k_x = \delta k_x \quad k_y = \frac{4\pi}{3} + \delta k_y \quad (\delta k \ll 1)$

$$h = t\left[(1 + i\delta k_x/\sqrt{3}) + (1 - i\delta k_x/2\sqrt{3})\, 2\left[-\tfrac{1}{2} + (-\sin(\tfrac{2\pi}{3}))\,\delta k_y/2\right]\right]$$

$$= t\left[\tfrac{\sqrt{3}}{2} i\delta k_x - \tfrac{\sqrt{3}}{2}\delta k_y\right.$$

$$= \tfrac{\sqrt{3}}{2} t\,(i\delta k_x - \delta k_y). \quad \text{or:}$$

$$\mathcal{H} = -\tfrac{\sqrt{3}}{2} t \begin{pmatrix} 0 & i\delta k_x + \delta k_y \\ -i\delta k_x + \delta k_y & 0 \end{pmatrix} = A\,\vec{\sigma}\cdot\vec{p}$$

2D Massless Dirac Hamilt.!

Band Structure – low energies.

Massless Dirac Fermions.

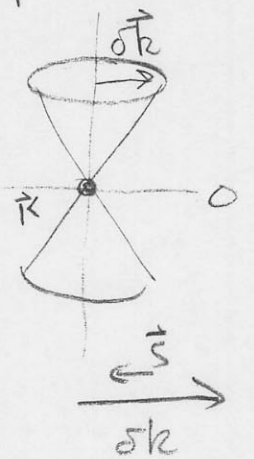
Sublattice structure $\Longleftrightarrow$ "spin" → $\frac{1}{\sqrt{2}}(1,1)$ → bonding → $+S_x$

$\frac{1}{\sqrt{2}}(1,-1)$ → antibonding → $-S_x$.

"spin" points along propagation direction (won't prove).

Putting in units, etc.:

$$E_\pm(\delta\vec{k}) = \pm \hbar v_F (\delta k_x^2 + \delta k_y^2)^{1/2}$$



At K', same except. "spin" is antiparallel to $\delta\vec{k}$.

$\Rightarrow$ left $\neq$ right handed fermions

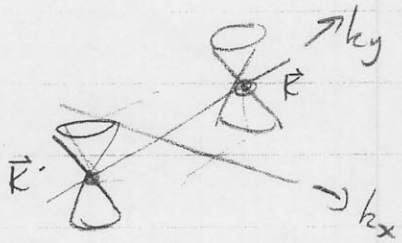
$\Rightarrow$ Very Unusual 2D system!

$\Rightarrow$ Zero Bandgap Semiconductor.

Unlike "massive" 2D system $\Rightarrow$ DOS not constant.

LL's not equally spaced, etc.

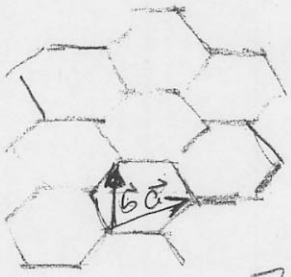
New experiments (Geim et al, Kim et al) on single sheets underway!



Summary $\Rightarrow$ Band structure set by 2 2D Dirac cones

$v_F = 8 \cdot 10^5$ m/s.

NT's ⇒ Rolled up graphene



Rollup vector: $\vec{R} = (n,m) = n\vec{a} + m\vec{b}$

Two special cases:

(n,0) "Zigzag" along $\vec{R}$: ← Perp. to tube axis!

(n,n) "Armchair" along $\vec{R}$: ← Perp. to tube axis!

I will stick to these for now.

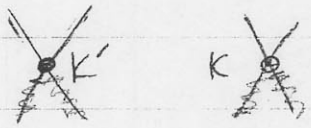
Quantization of k:

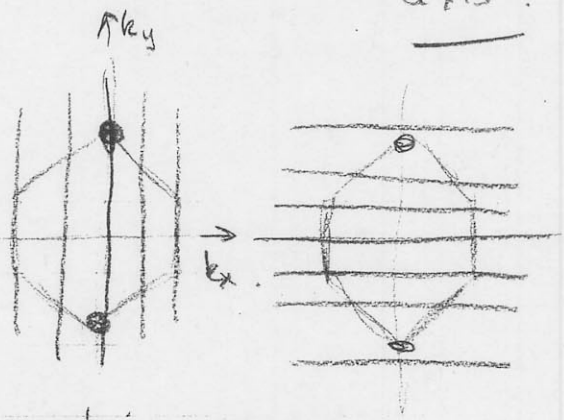
$\vec{k} \cdot \vec{R} = 2\pi j$. j = integer.

Armchair:

$j = 0$ always goes through K, K' point.

⇒ 1D Metal!





Zigzag:

$k_y n = 2\pi j \Rightarrow k_y = 2\pi \cdot \frac{j}{n}$. $K = \frac{4\pi}{3}$

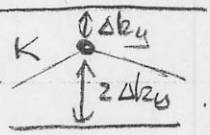
Case #1: n multiple of 3. $k_y = K$ for $\frac{j}{n} = \frac{2}{3}$. Metal.

#2 n ≠ mult. of 3: $\frac{j}{n} \neq 2/3$ ⇒ Semiconductor

"Closest Approach": $\Delta k_{y_n} = 2\pi(\frac{j}{n}) - \frac{4\pi}{3} = 2\pi \cdot (\frac{3j-2n}{3n})$

The result is: (won't prove)

$\boxed{\Delta k_{y_{min}} = \pm \frac{2}{3d}}$ where d = diameter $= \frac{12}{\pi} = \frac{na}{\pi}$.



↳ + sign if $n = 3q+1$. (4, 7, 10, 13, etc)

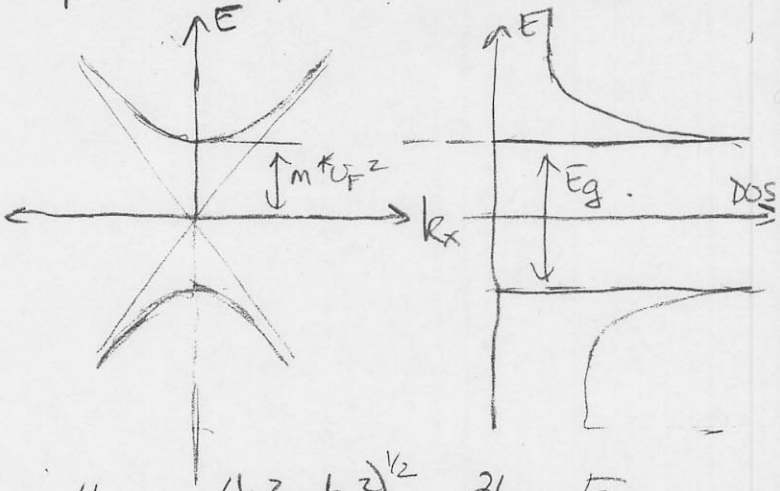
− sign if $n = 3q-1$. (5, 8, 11, 14, etc).

General result: $n_1 - n_2 = 3q + p$, where $p = 0, \pm 1$ ↑ same answer

Dispersion & DOS of 1D Subbands

$$E_k = \pm \hbar v_F \left(k_x^2 + \Delta k_y^2\right)^{1/2}$$
$$= \pm \left[p_x^2 v_F^2 + (m^* v_F^2)^2\right]^{1/2} \quad \text{where } m^* = \frac{\hbar \Delta k_y}{v_F}$$

"Relativistic" Dispersion w/ $v_F \Leftrightarrow c$ & $m^* \Leftrightarrow$ rest mass.



$E_g = 2m^* v_F^2$

For Semic tubes:

$$E_g = 2\hbar v_F \left(\frac{2}{3d}\right) = \frac{4\hbar v_F}{3d}.$$

$$\simeq 0.7\,\text{eV}/d\,[\text{nm}]$$

Density of States:

$$dN/dE = dN/dk \cdot dk/dE = \frac{4}{(2\pi/L)} \cdot \frac{(k_x^2 + \Delta k_y^2)^{1/2}}{\hbar v_F k_x} = \frac{2L}{\hbar v_F \pi} \cdot \frac{E}{(E^2 - E_g^2)^{1/2}}.$$

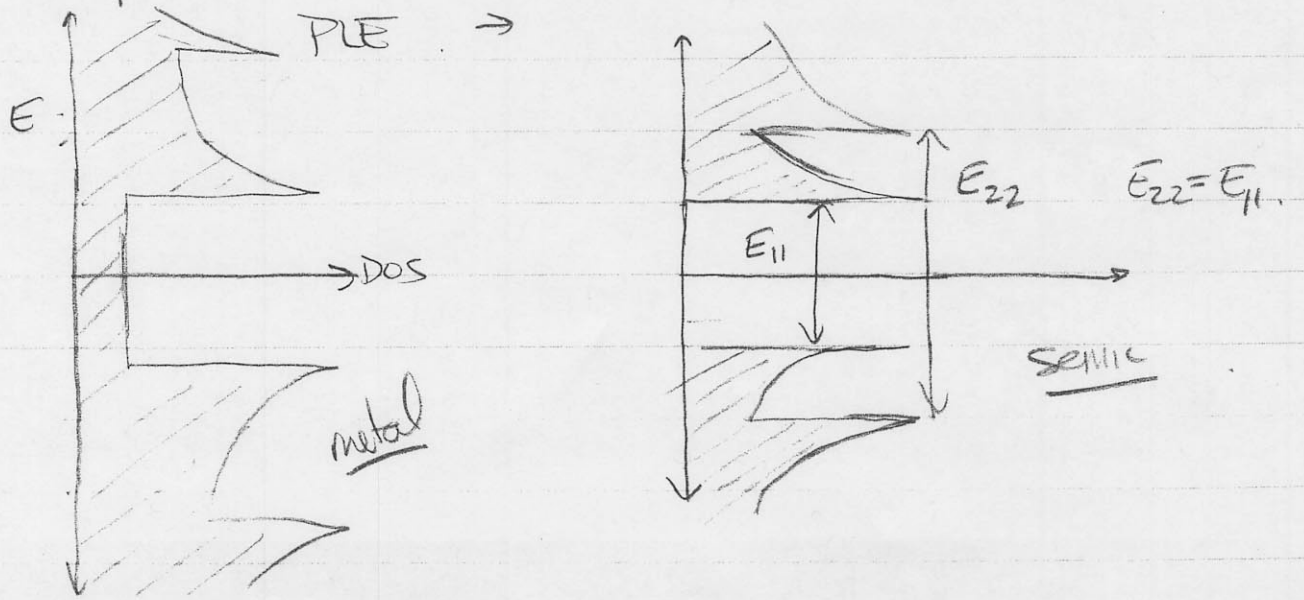
DOS diverges at subband Bottom.

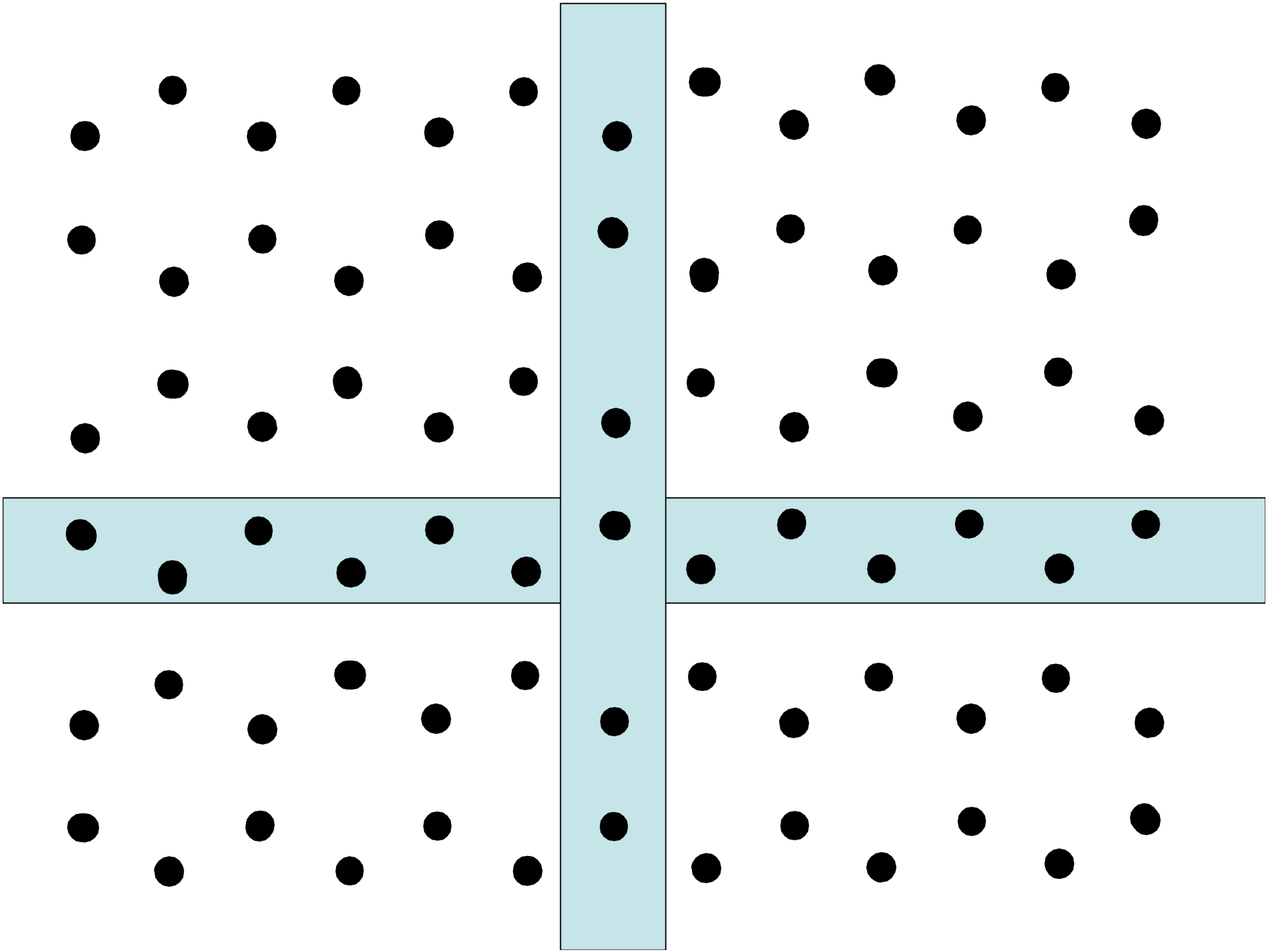
$\Rightarrow$ Van Hove Singularities.

DOES THIS WORK?

Expts: STM. → See UG's.

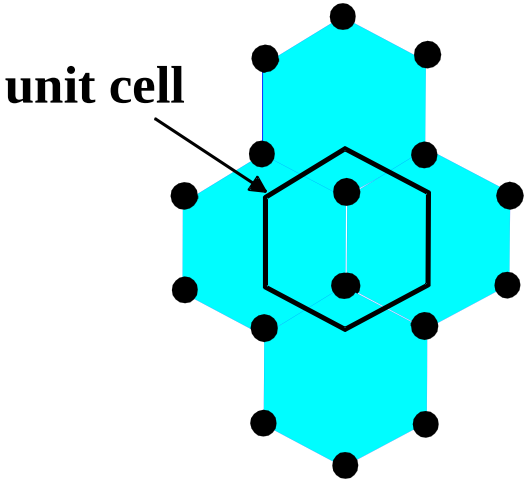
PLE →

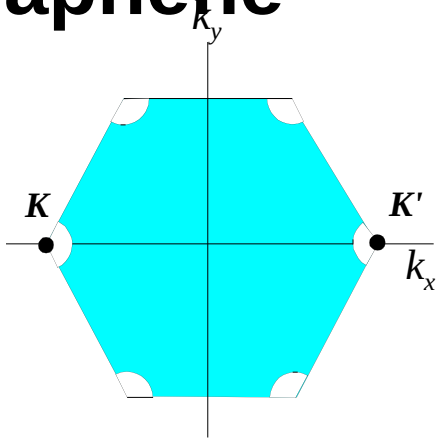




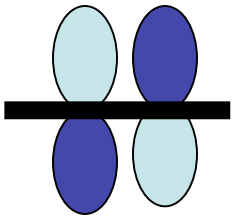
Electronic Properties of Graphene

Graphene

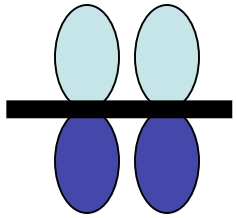




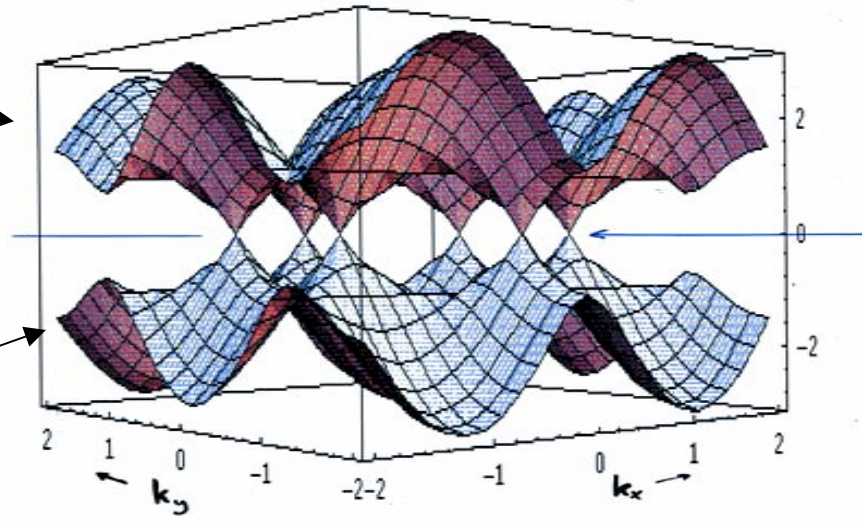
First Brillouin Zone



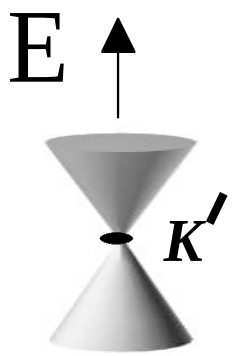
Anti-Bonding Orbitals



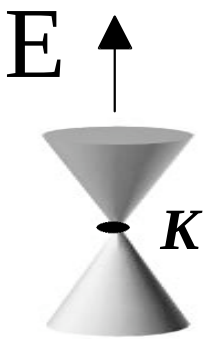
Bonding Orbitals



Low energy theory: 2D massless Dirac Fermions



left -handed



right-handed

Dirac (*k*•*p*) Hamiltonian

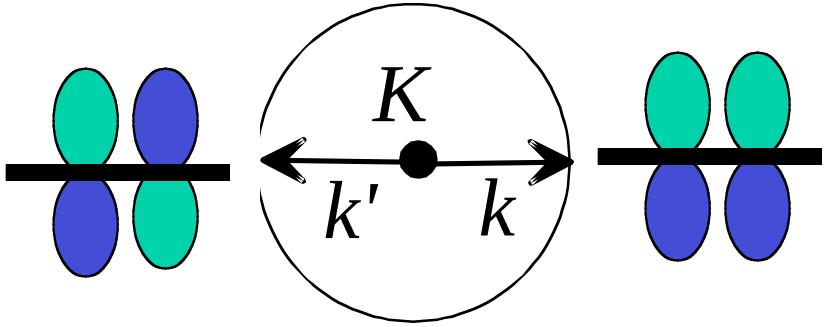
$$H = \hbar v_F \sigma \cdot k$$

$$E = b\hbar v_F |k|$$

$$|k\rangle = \frac{1}{\sqrt{2}} e^{ik\cdot r} \begin{pmatrix} -ibe^{-i\theta_k/2} \\ e^{i\theta_k/2} \end{pmatrix}$$

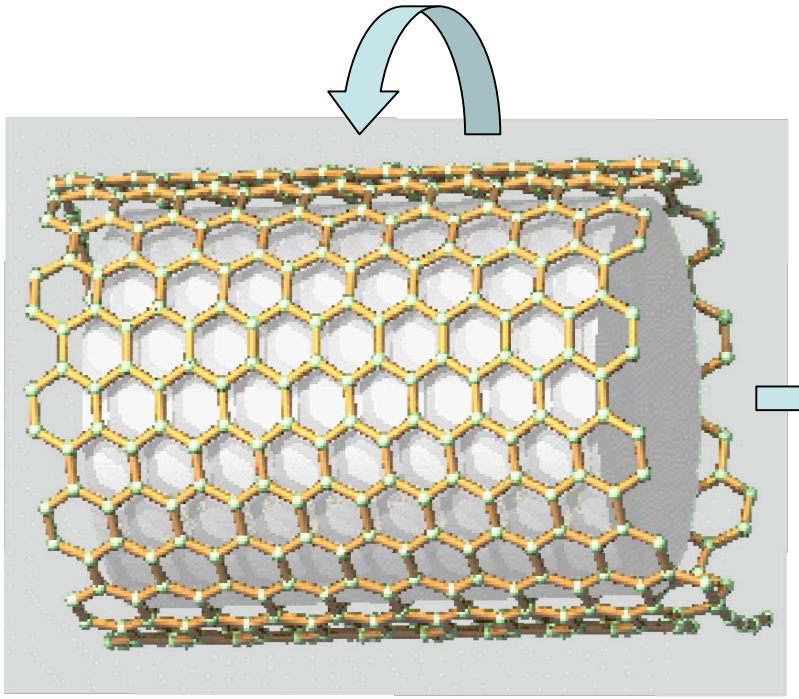
Kane and Mele, Ando...

"spin" = molec. orbital state

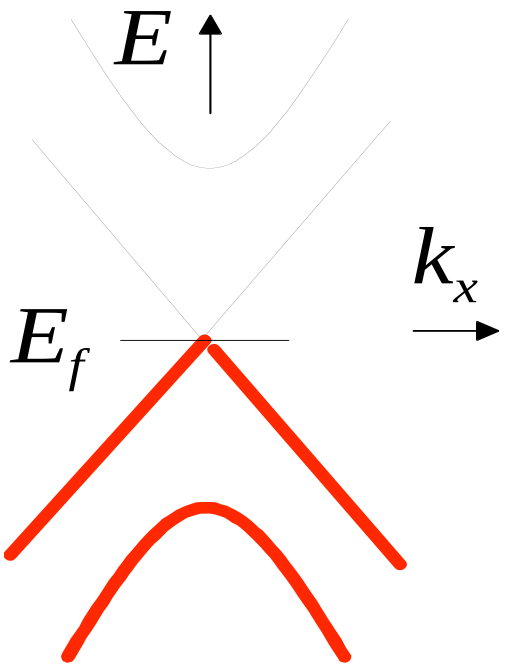


Curling up the Extra Dimension

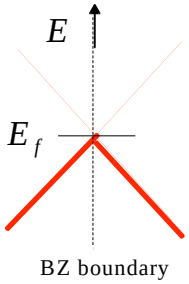
$k_y\,(2\pi R) = 2\pi j$



k_x

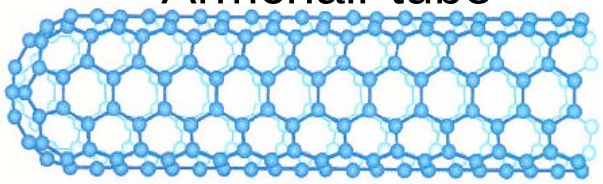


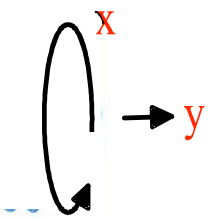
Nanotube Band Structure



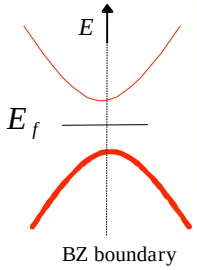
k_x

Armchair tube

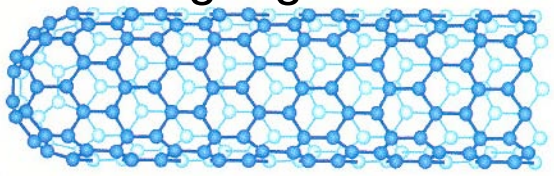


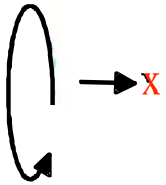


metallic



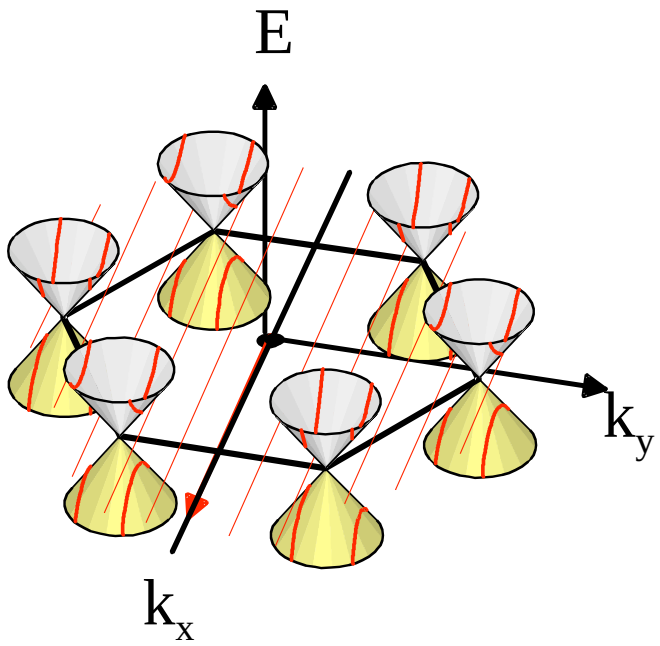
zigzag tube

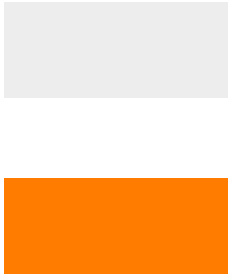




semiconducting

See, for example:
Kane and Mele
*PRL **78**, 1932 (97)*





$E_g \sim 1\ \text{eV} / d[\text{nm}]$

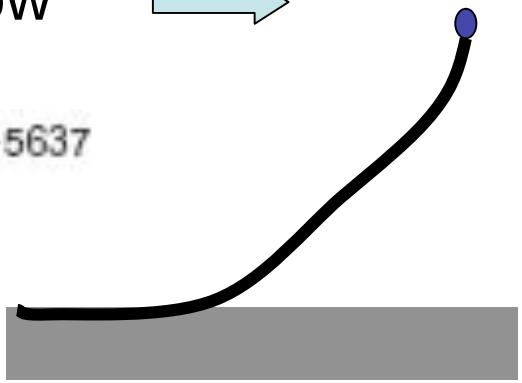
Verified by STM and transport expts.

Tans et al., Bockrath et al. (97)

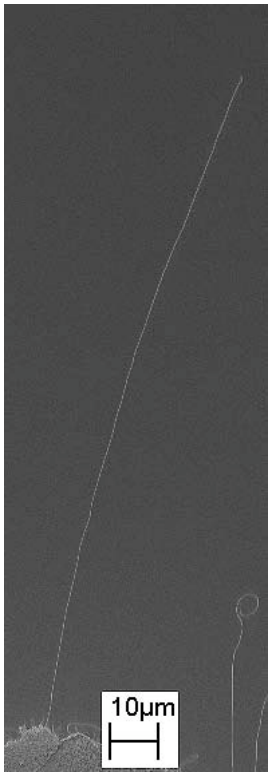
Parallel Device Fabrication - CVD

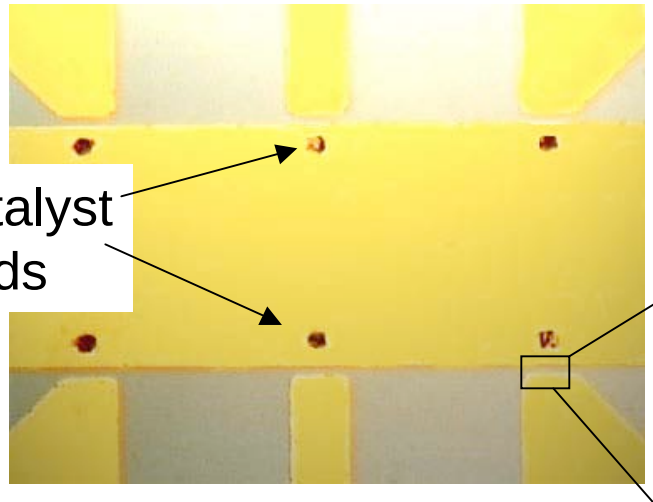
Flying catalyst growth (Liu group)

Gas flow

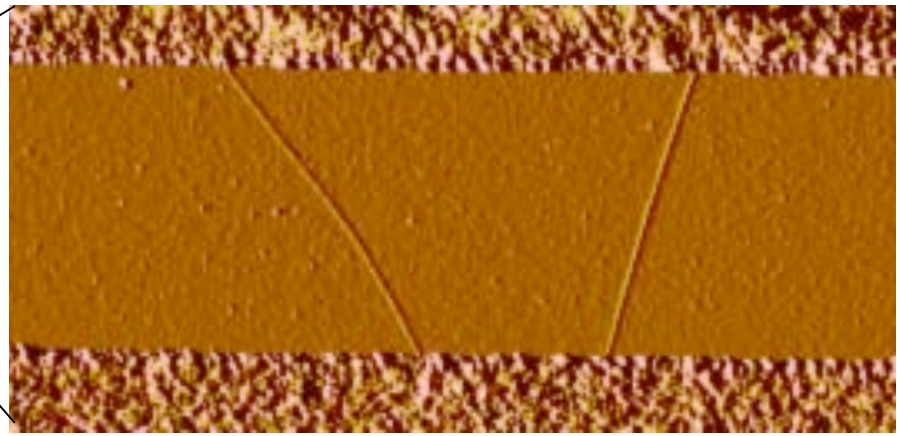


J. AM. CHEM. SOC. 2003, *125*, 5636−5637



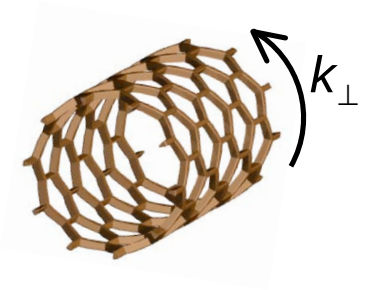


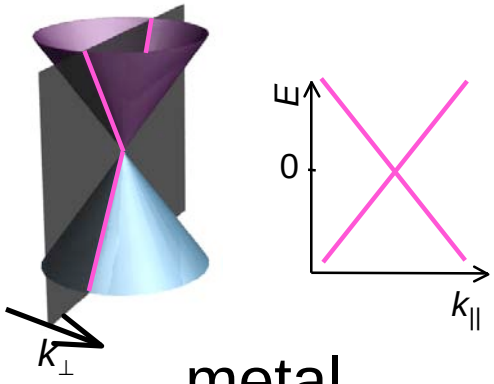
catalyst pads



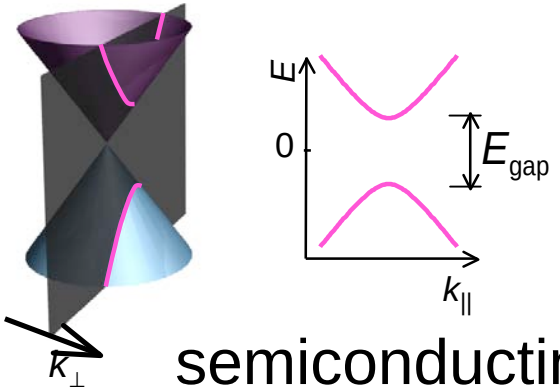
CORNELL CNF Cornell Nanofabrication Facility NSF

Nanotube band structure





metal

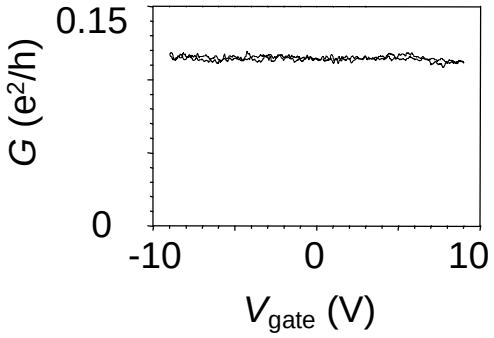


semiconducting

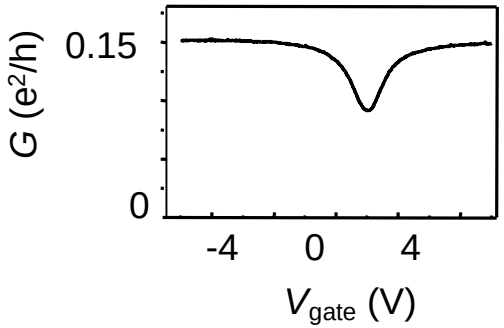
Quantized $k_\perp$

$\pi D k_\perp = 2\pi n$

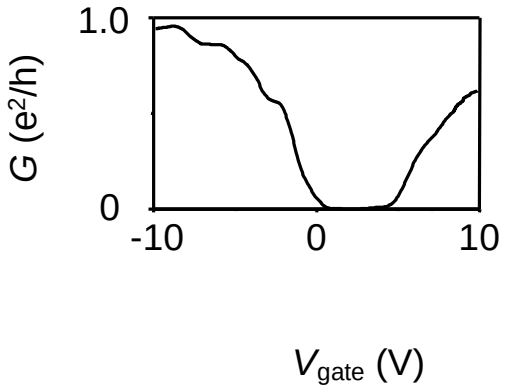
metal



small bandgap semiconducting

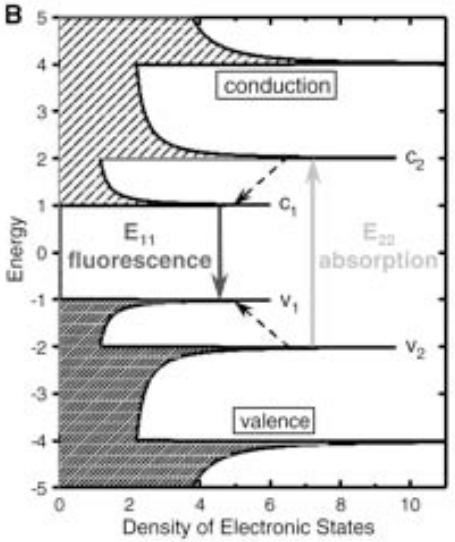


large bandgap semiconducting

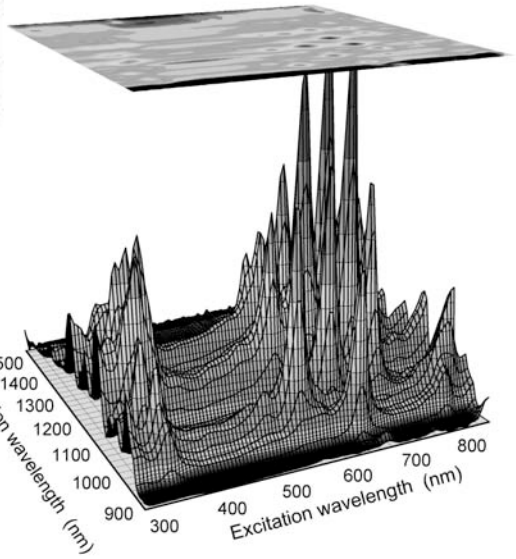


Due to curvature, strain, etc.

Nanotubes: Optical Properties

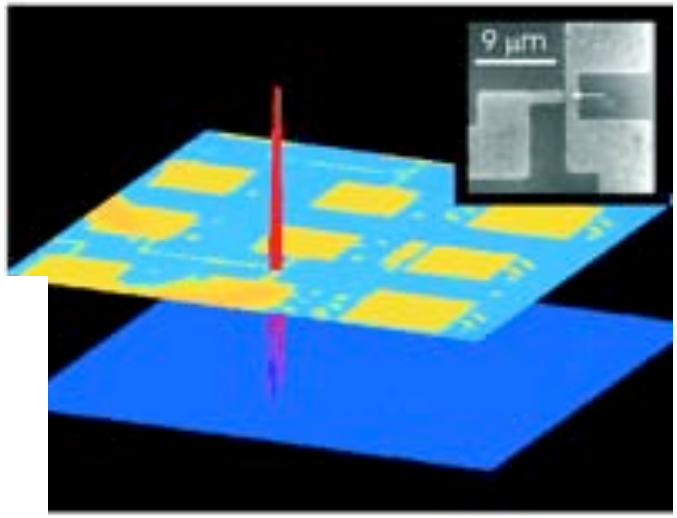


$$E_{\text{gap}} = \frac{0.7eV}{d[nm]}$$



Fluorescence Spectroscopy

Rice group
Science (02)



Electroluminescence

IBM group
Science (03)

Explosion of Interest in Optoelectronic Properties !