Carbon Nanotubes[a]– Electronic Properties

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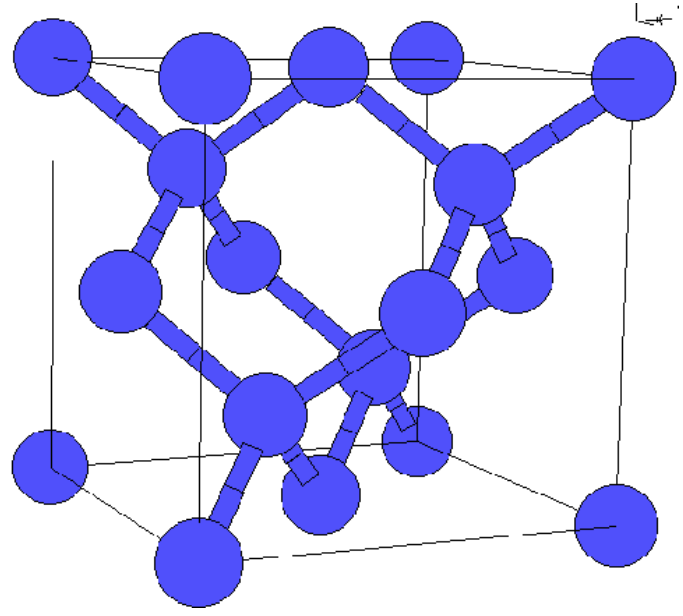
[a] An excuse to do one electron theory!

Overview

- CNTs - What are they?
  - Why should we care?
- CNTs - Electronic puzzles
  - Transport properties
- Puzzle "solved"!
  - Is it really?

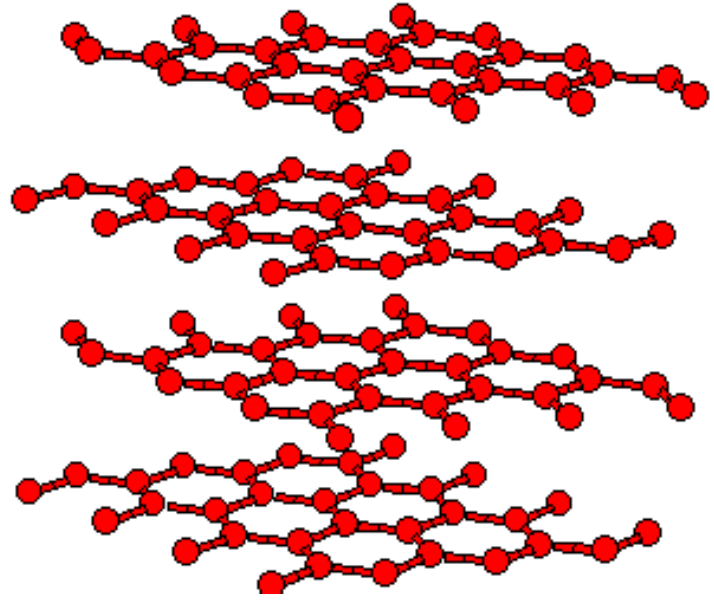
But first, carbon...amazing carbon!

Carbon: Diamond



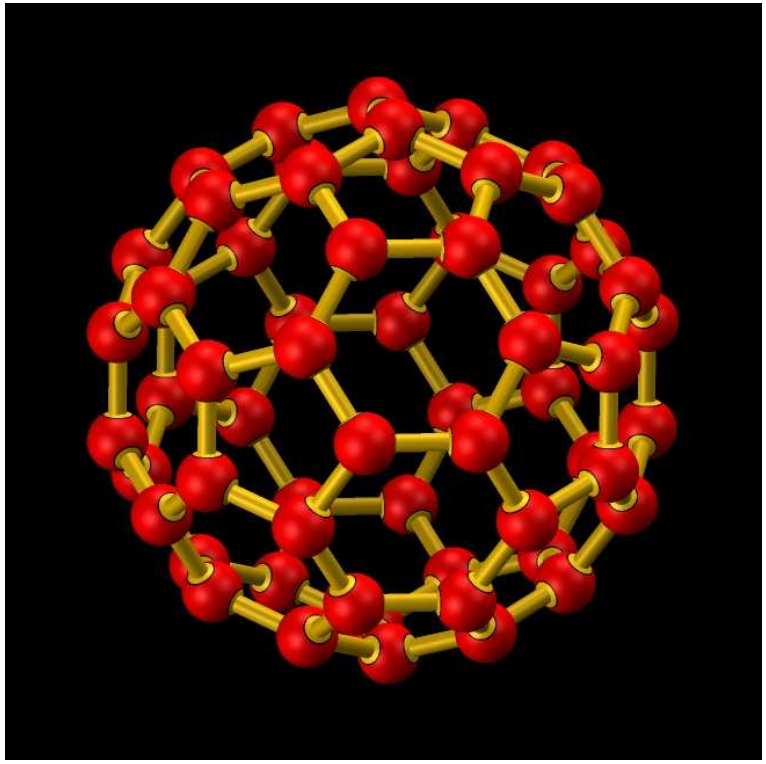
- **High Stiffness**
- **Poor Electrical Conductivity**
- **High Thermal Conductivity**

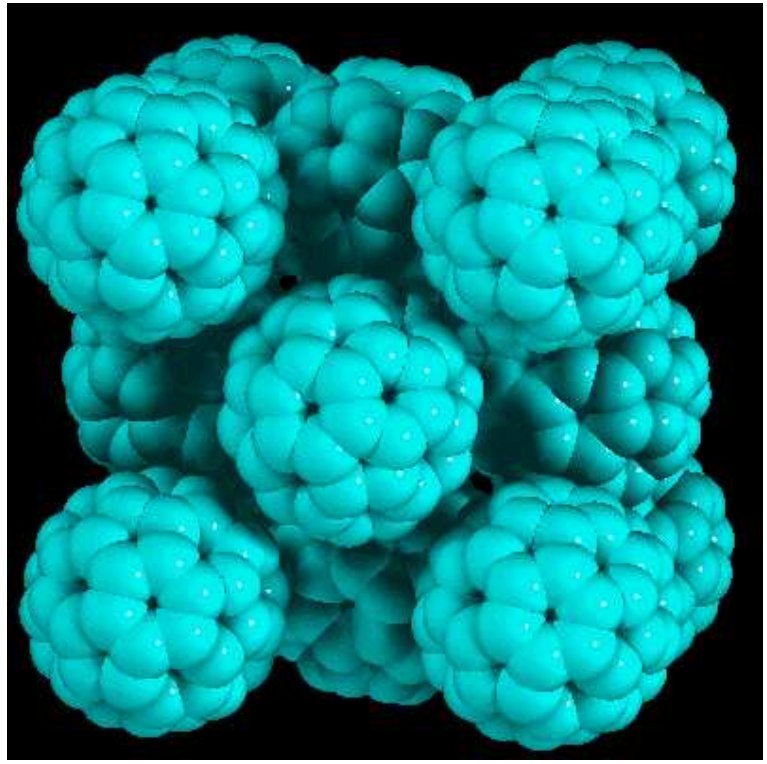
Carbon: Graphite



- **Electrical Conductor (Semi-Metal)**
- **Less Stiff (than Diamond)**

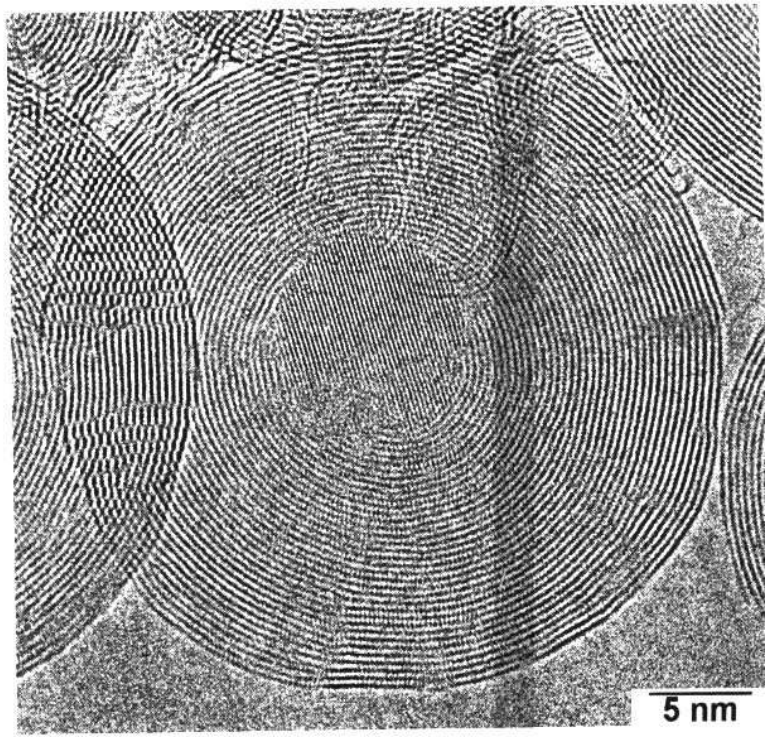
Carbon: Fullerenes





- **Superconductivity!**

Carbon: Onions!!

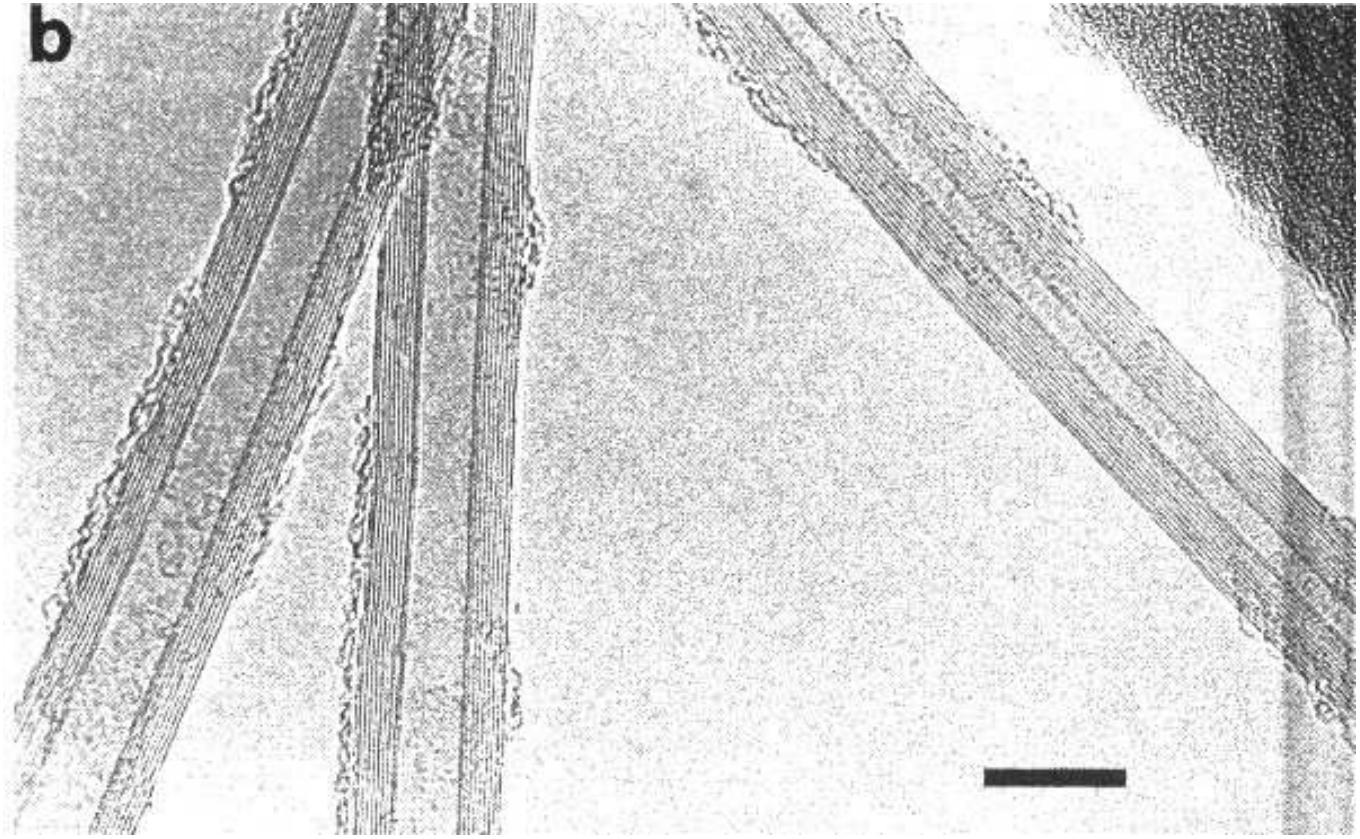


(Harris 2001)

- **Very Tasty!!**

Carbon: Nanotubes (CNTs)

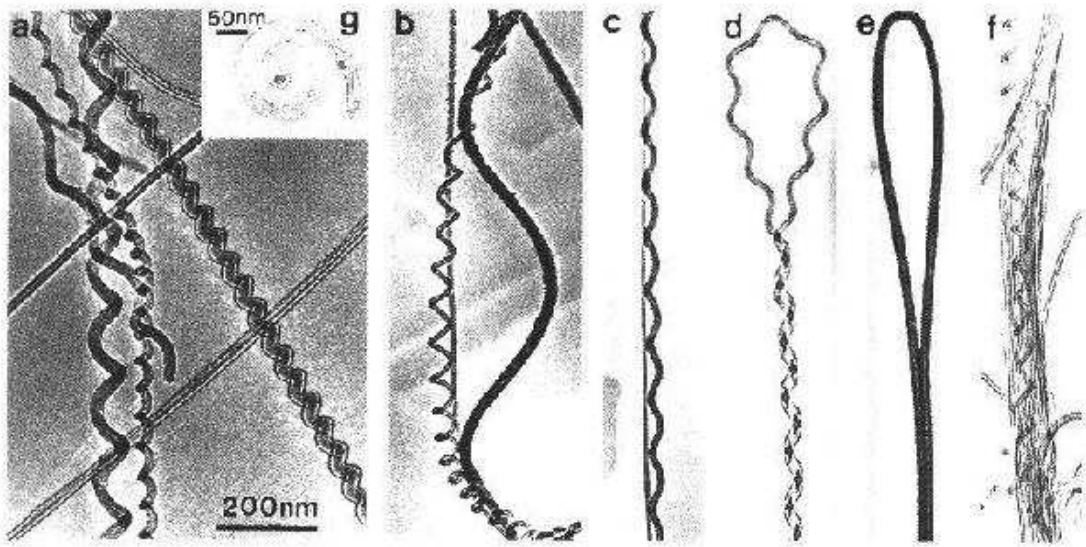
- **Made by "Physical" and "Chemical" Routes**



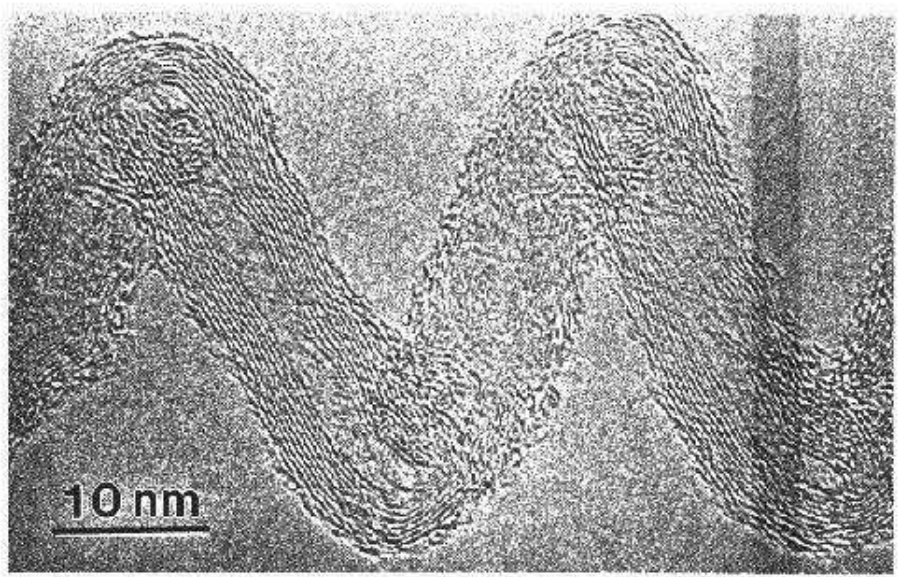
(Harris 2001)

- **May be Single-Walled and/or Multi-Walled**

Carbon: More Nanotubes



(Harris 2001)



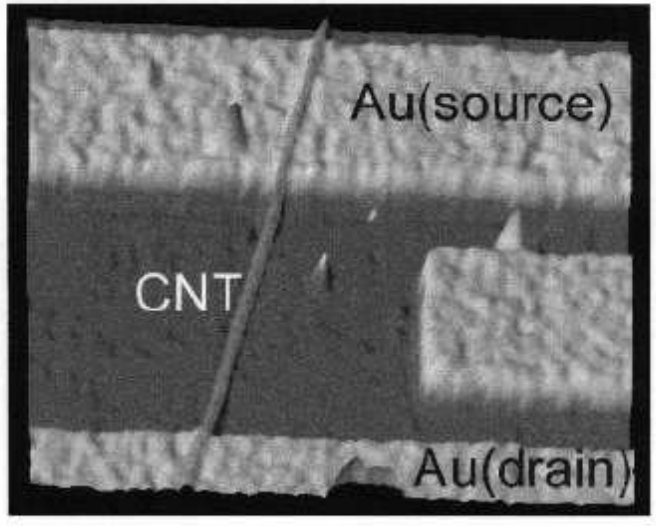
CNTs – Wonder Materials?

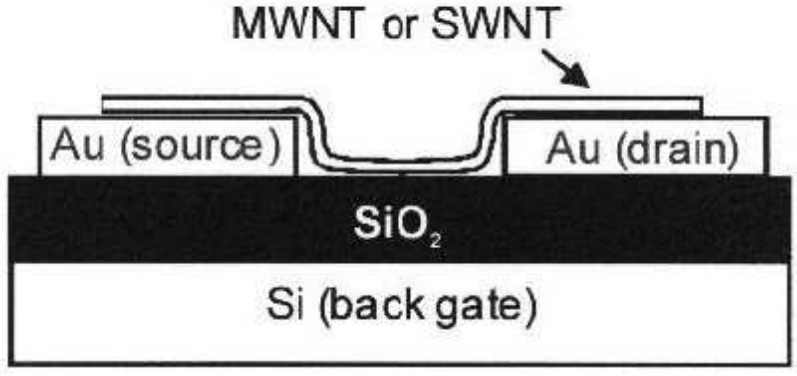
- "Amazing" Properties of CNTs
  - "Interesting" electronic properties
  - High elastic stiffness ($\sim$5–10 $\times$ steel)
  - High strength
  - High thermal conductivity
  - ...
- Nanotube electronics
- Nanotube sensors

Question: How do you measure transport properties of CNTs?

CNT Electronic Transport Properties

- **Field Effect Transistor Measurements**

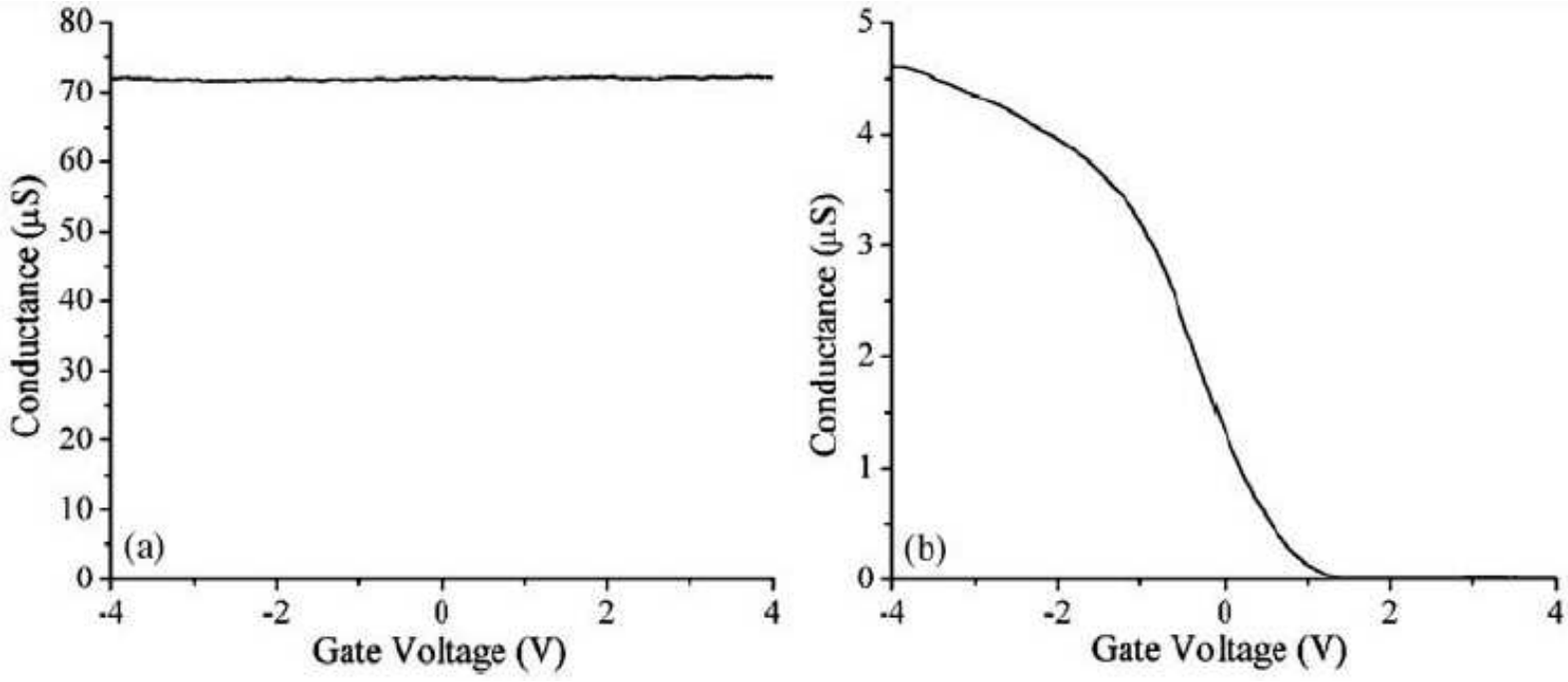




(Avouris et al. 2003)

Electronic Transport Properties

- **FET Characteristics**



(Dürkup et al. 2004)

- **May be Metallic or Semiconducting! Huh..how?**
- **Our task: explain this!**

Quantum Review

- **Key concept : the state** $|\psi\rangle$
- **Expected value of observable** $\langle\psi|O|\psi\rangle$
- **Something called the Hamiltonian** H
- **Time evolution** $H|\psi\rangle = i\hbar\frac{\partial|\psi\rangle}{\partial t}$
- **Stationery states** $H|\psi\rangle = E|\psi\rangle$
- **...**
- **One electron theory: No interactions between electrons...many particle state constructed from one particle states...hence,** $one\ electron$ **theory**

"Solid State" Review

- In the elementary (free electron) theory of metals this leads to the idea of the "filling of states" and Fermi energy
- Semiconductors – the idea of a gap
- Transport properties – Temperature dependence
- ...
- How about a "free electron" CNT?

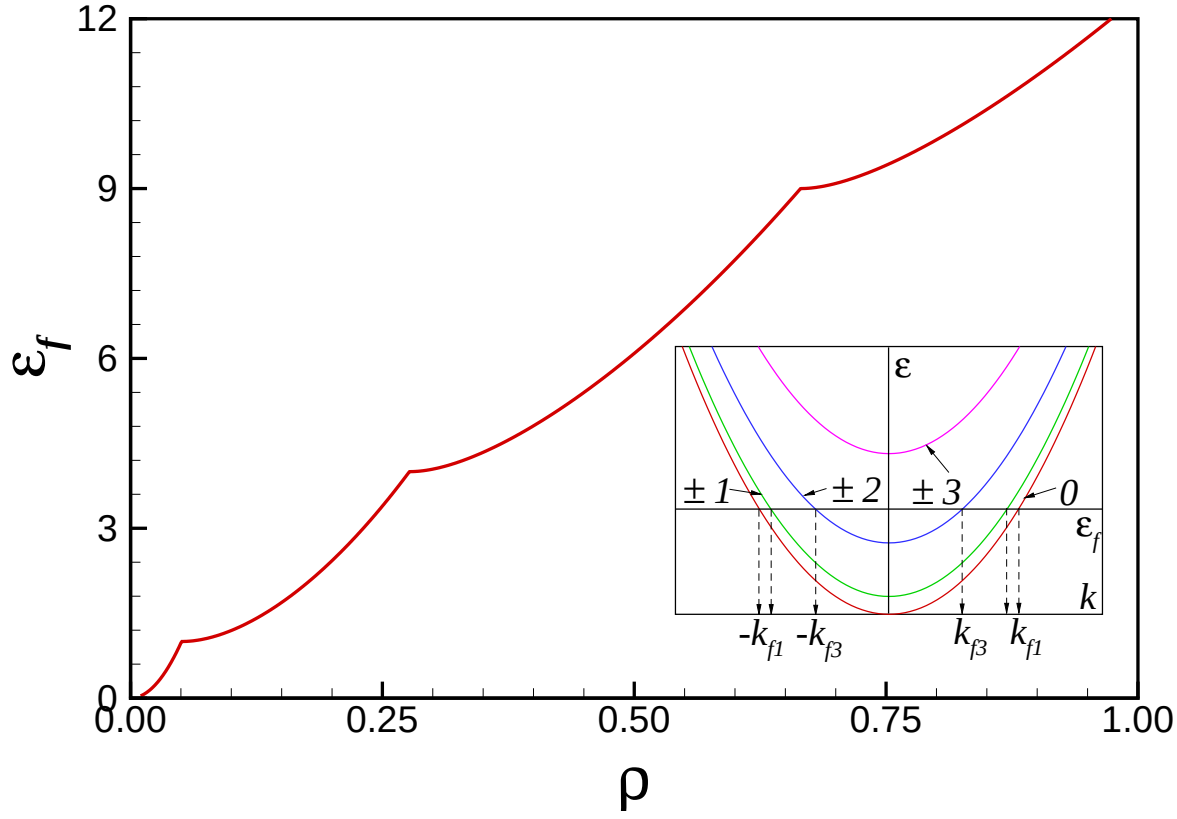
A "Free Electron" Theory of CNTs

- **Imagine a single walled CNT to be a "very long" cylinder of radius R, electron density Σ**
- **Energy states decide by two quantum number k and n...k is due to motion $along$ the tube axis and n is due to revolution around the tube**
- **Energy states and levels (quantum number k and n)**

$$E(k,n) = E_\circ \epsilon_{k,n} = \frac{\hbar^2}{2m_e R^2}(k^2 + n^2)$$

A "Free Electron" Theory of CNTs

- **Chemical Potential (Fermi Energy)** ϵ_f



- **"Size Parameter"** $\rho = \Sigma R^2$**:** ϵ_f **Specified by** $N_f, \{k_{fn}\}$
- **How is this related to the 2D sheet?...The FECNT dispersion are "slices" of the 2D dispersion!**

A "Free Electron" Theory of CNTs

- **"But, there is just one more thing my dear Watson...all your FECNTs are metallic!" Not really surprising (for Holmes, of course)!**
- **Holmes back in business!**
- **...**
- **Puzzle...how do we get a semiconductor?**
- **Even more fundamental puzzle...** *Why are there semiconductors at all*?
- **And why are some CNTs metallic and some semi conducting? (Now you begin to fear hair-loss!)**

Free Electron needs Repair

- **Electrons are not really free!**
- **They move in a** *periodic potential*

$$V(\boldsymbol{r}) = \sum_{\boldsymbol{R}} V_a(\boldsymbol{r} - \boldsymbol{R})$$

- **Schrödinger equation**

$$\left(-\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2 + V(\boldsymbol{r})\right)\psi = E\psi$$

- **What are allowed Es and associated ψs?**
- **Bloch theorem $\psi_k(x) = e^{ikx}u(x)$, u lattice periodic**
- **What can we say without solving anything? (Stick to 1D)**

1D Solid – Simple Arguments

- **Solid with $V(r)$, $V(r+na) = V(r)$, a is lattice parameter**
- **Imagine that $V(r)$ is a perturbation on free electrons**
- **What effect does $V(r)$ have on the "free" electron?**
- **Well, it is like Bragg reflection!**
- **If the wavelength of the electron is related to the lattice parameter a, then the electron cannot "travel" through the crystal...Bragg reflection will make it a standing wave!**
- **This happens when the electron wavelength satisfies $n\lambda = 2a$ or when electron wavevector satisfies $k = \frac{n\pi}{a}$!**
- **Clearly, the electron energies are also changed!**

1D Solid – Simple Arguments

- **Since the state of the electron for $k = \frac{n\pi}{a}$ is not a propagating one, we can imagine it as a superposition of a forward moving wave and backward moving wave of amplitude to get two types of standing waves**

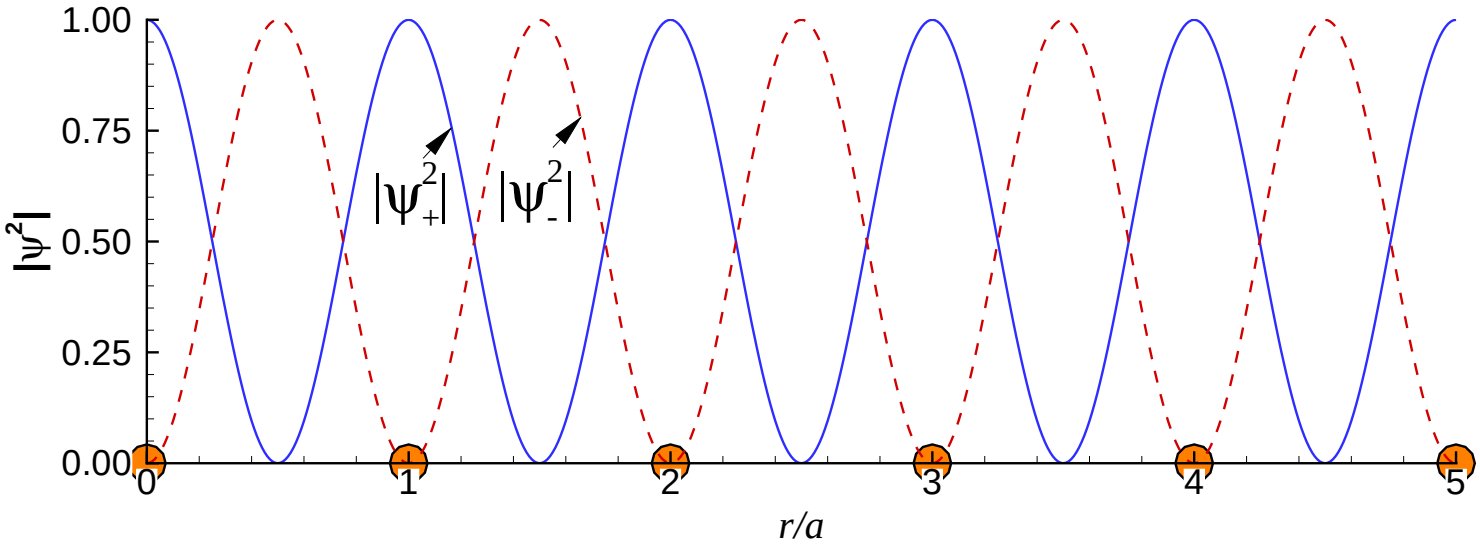
$$\begin{aligned} \psi_+ &= e^{ikx} + e^{-ikx} = 2\cos(kx), \\ \psi_- &= e^{ikx} - e^{-ikx} = 2i\sin(kx) \end{aligned}$$

Note that these are *standing waves*!

- **What are (estimates of) $E_\pm$?**
- **To get an idea, think of $|\psi_+|^2$...it is the probability density...if the atomic potential V_a is attractive, then E_+ will be** *lower* **than E_-, since the electron in ψ_+ state is "located closer to the atom"!**

1D Solid – Simple Arguments

- **Clearly, ψ_+ has lower energy (for the attractive atomic potential)**



- **This implies for the same value of free electron wavevector k, there are two possible energy levels...in other words, energy values between these levels are not allowed...a band gap opens up!**

1D Solid – A Simple Model

- 1-D solid with lattice parameter a
- Smallest reciprocal vector $G = \frac{2\pi}{a}$
- Simple model "ionic potential" $V(x) = 2V_G \cos Gx$ (Note that $V(x)$ is lattice periodic, V_G is the "strength" of the potential)
- What are eigenvalues and eigenstates of $H = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)$?
- We know from previous arguments that when $k \approx \frac{G}{2}$ we expect strong Bragg reflection of a plane wave state...based on this it is reasonable to take the energy eigenstate as a linear combination of the forward going wave and the reverse going wave $|\psi\rangle = C_k|k\rangle + C_{k-G}|k-G\rangle$, where C_k, C_{k-G} are numbers that we need to determine...

1D Solid – A Simple Model

- **Determine C_k, C_{k-G} using $H|\psi\rangle = E|\psi\rangle$; a bit of algebra gives ($\epsilon(k) = \frac{\hbar^2 k^2}{2m}$)**

$$\begin{pmatrix} \epsilon(k) & V_G \\ V_G & \epsilon(k-G) \end{pmatrix} \begin{pmatrix} C_k \\ C_{k-G} \end{pmatrix} = E \begin{pmatrix} C_k \\ C_{k-G} \end{pmatrix}$$

- **Energy eigenvalues are**

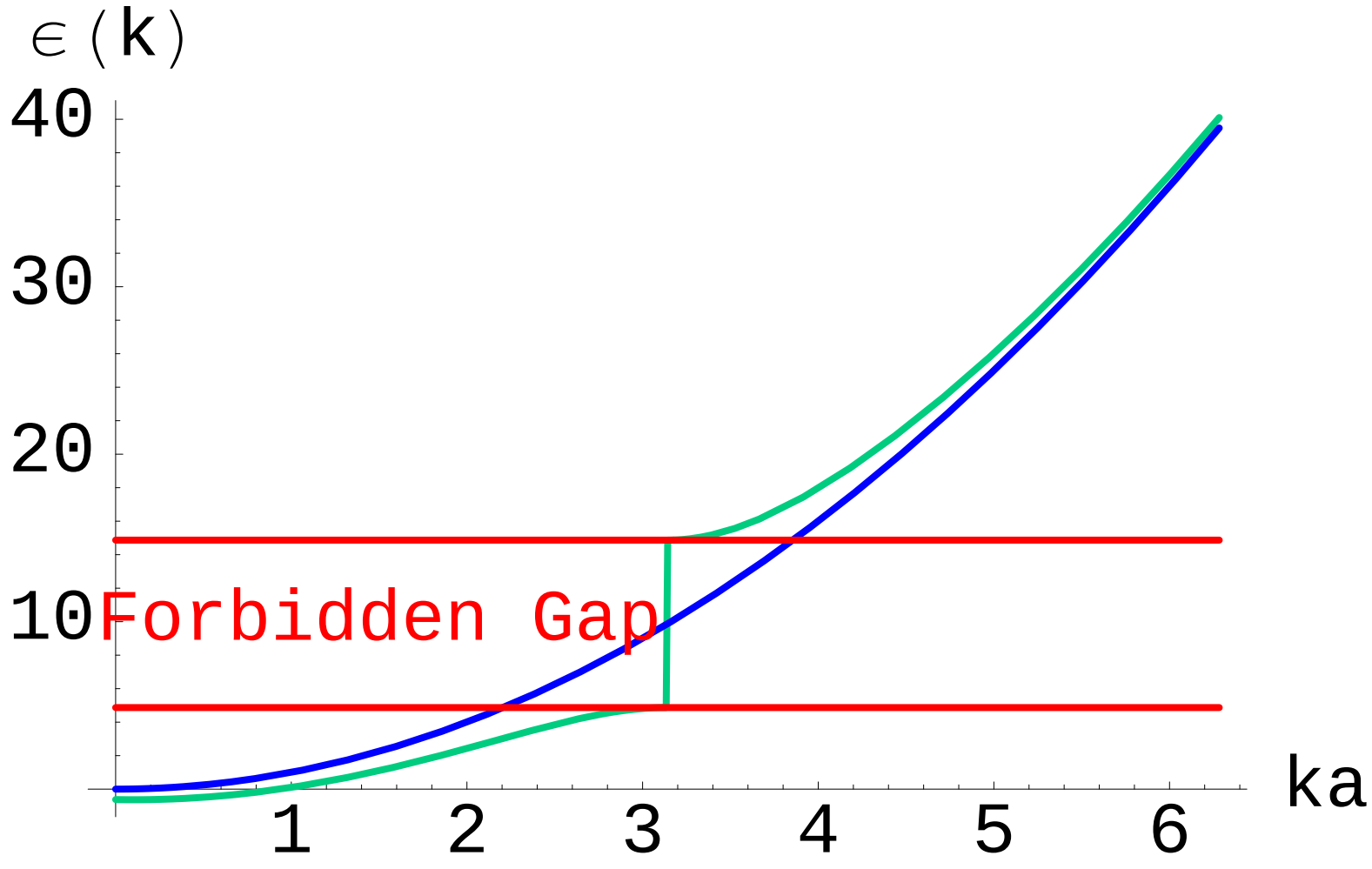
$$E_{\pm}(k) = \frac{\epsilon(k) + \epsilon(k-G) \pm \sqrt{(\epsilon(k) + \epsilon(k-G))^2 - 4(\epsilon(k)\epsilon(k-G) - V_G^2)}}{2}$$

with associated eigenstates

$$\psi_{\pm}(x) = \underbrace{\left(C_k^{\pm} + C_{k-G}^{\pm} e^{-iGx}\right)}_{u_{\pm}(x)\ldots lattice\ periodic} e^{ikx}$$

1D Simple Model – What is learned?

- **An energy gap opens up at** $k = \frac{G}{2}$, $E_+ - E_- = 2V_G$



A 1D chain

- **Electrons can hop to neighbouring atom with amplitude t (Tight binding model...What does this mean?)**

$$H = \sum_l e_0 |l\rangle\langle l| - t \sum_{<lm>} |l\rangle\langle m| + |m\rangle\langle l|$$

- **Energy eigenstates**

$$|k\rangle = \frac{1}{\sqrt{N}} \sum_l e^{ikl} |l\rangle$$

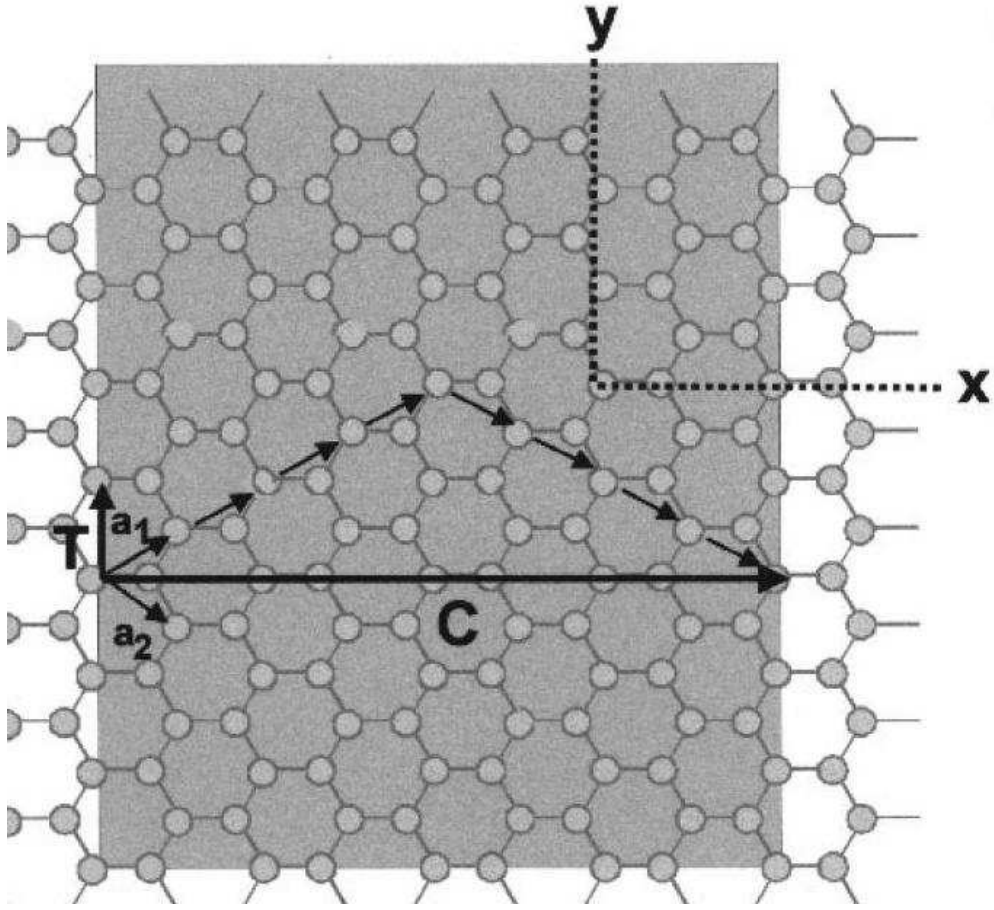
with eigenvalues

$$\epsilon(k) = -2t \cos k \qquad (1)$$

- **Exercise: Do this for a square lattice**

How about doing this for Graphene?

- First, how to describe graphene "crystal"?
- A triangular lattice with a two atom basis



Avouris et al. 2003

Graphene Band Structure

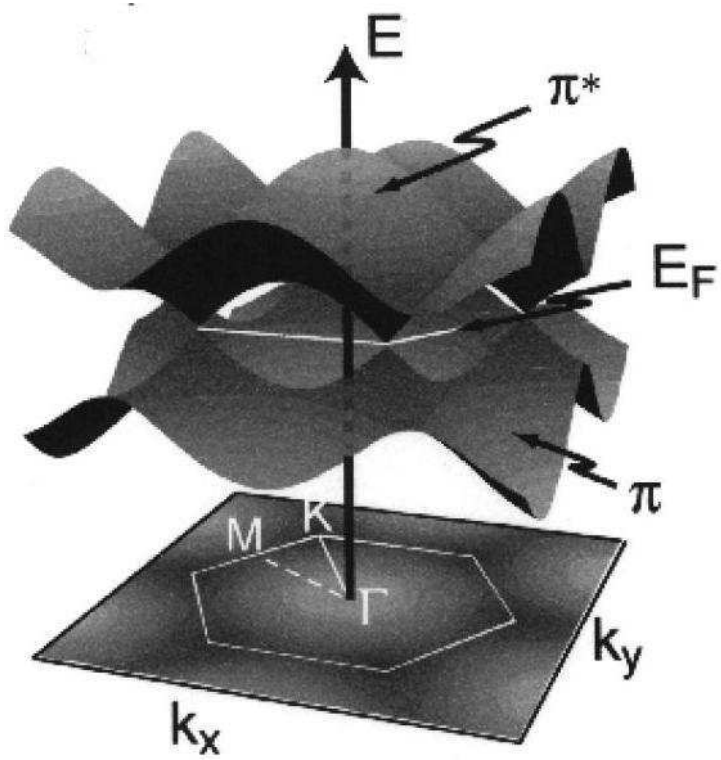
- **Tight binding model to understand electronic structure**
- **What are the relevant orbitals to be included?**
- **There are three sp^2 orbitals, and one p_z orbital on each carbon... the electronic physics is governed only by p_z-p_z "bonding" or π-bonding!**
- **Tight binding Hamiltonian**

$$H = -t \sum_{lm,\alpha\beta} |l\alpha\rangle\langle m\beta|$$

l, m, Bravais lattice index, α, β basis index, t is the p_z-p_z π overlap integral

Graphene Band Structure

- **There are** $two\ bands$**...the** π **band and** π^* **band**
- **One band is fully filled...but is there a gap?**
- **There are** six $points$ **in the corners of BZ where the gap is exactly zero**

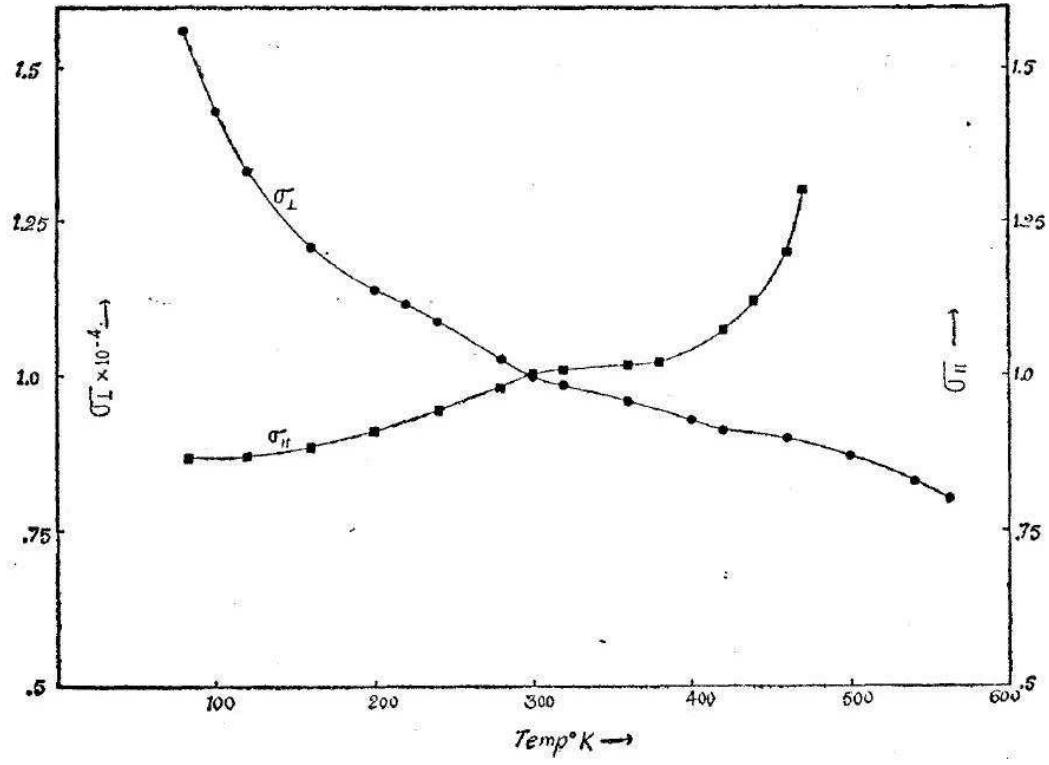


Avouris et al. 2003

- **Graphite is a "semi-metal in plane"!** c**-axis**

Graphite: Transport Experiments

- **Graphite is a "semi-metal in plane"! c-axis "semi-conductor"!**
- **Indeed seen in experiments**

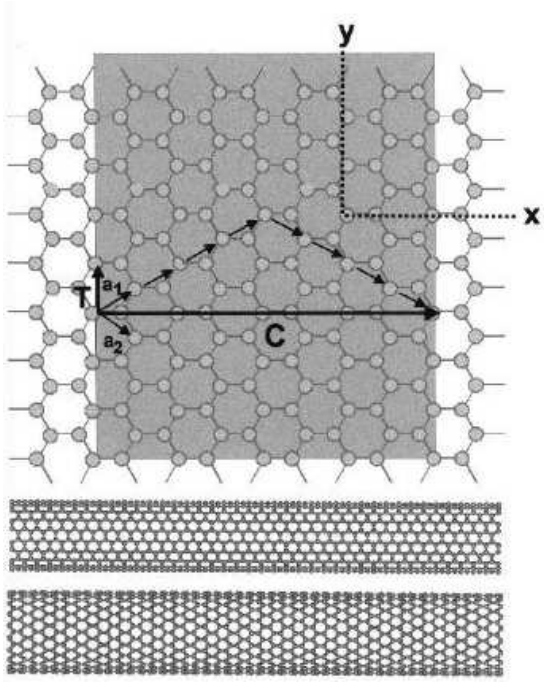


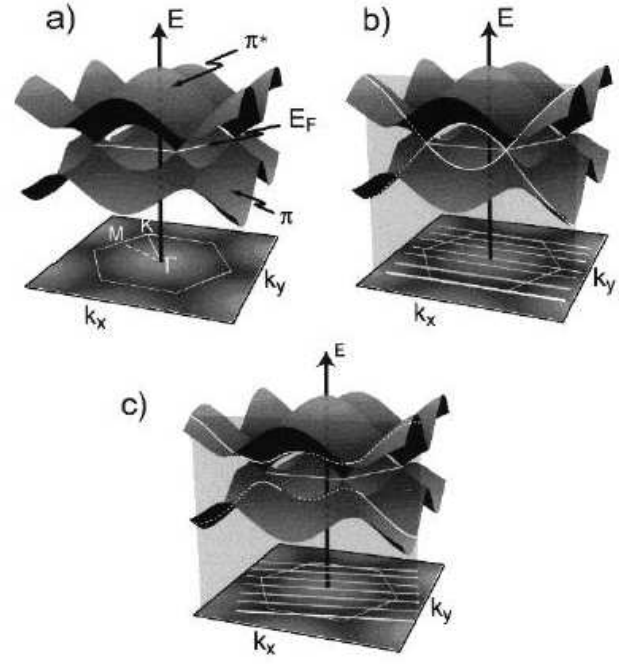
Dutta 1953

- **Ready to tackle CNTs**

Structure of CNTs

- **CNT = Rolled Up Graphene Sheet**



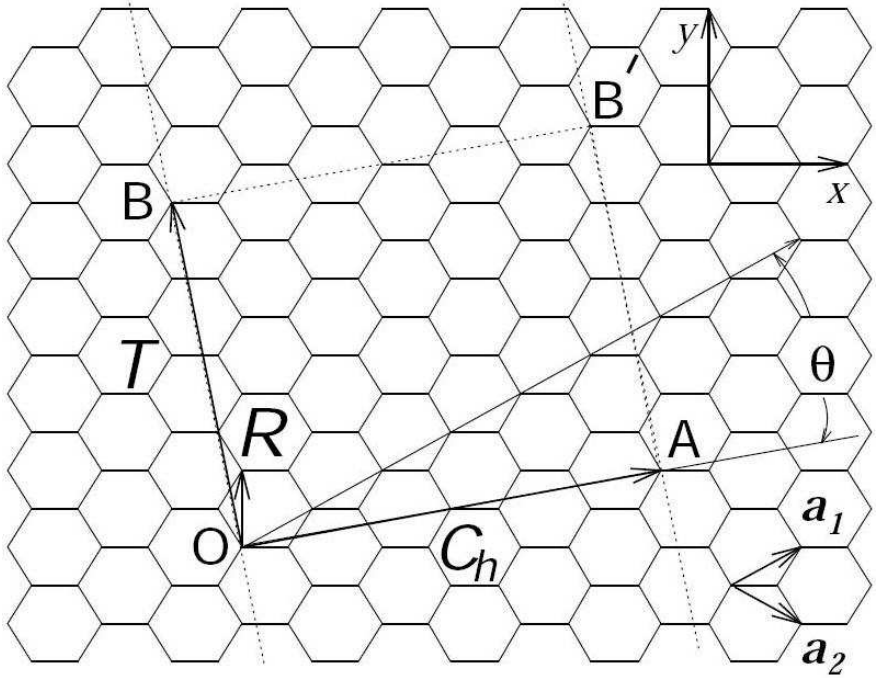


(Avouris et al. 2003)

- **CNT : Defined chiral vector (Bravais lattice vector)**
  $C = m\boldsymbol{a}_1 + n\boldsymbol{a}_2$

Structure of CNTs

- **To construct an (m, n) CNT cut the graphene sheet along two parallel lines which are both perpendicular to C to get at "graphene strip"...roll up and stick the long edges of the strip to get a CNT!**



(Dresselhaus et al. 1999)

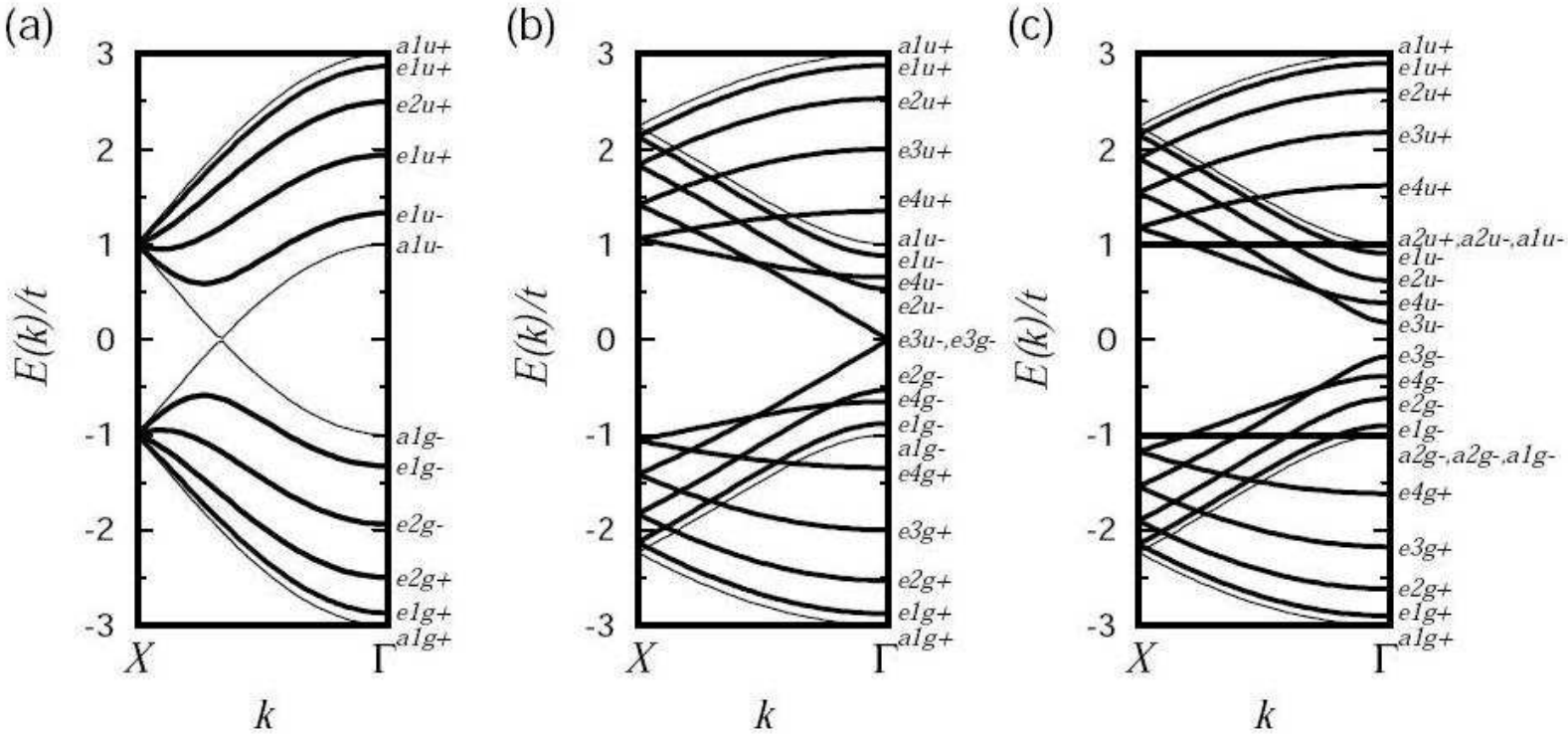
- **What will be the radius of the CNT? And what will be the band structure?**

One Electron Theory of CNTs

- **Key idea: Component of crystal momentum can take any value along the axis of the tube, but can take only quantized values along the direction of the chiral vector...this is much like the "angular momentum" quantization in the case of the free electron nanotube...thus $\boldsymbol{k} \cdot \boldsymbol{C} = 2\pi N$.**
- **Thus, CNT bands can be obtained by "slicing" the graphene band structure! For every slice, we will get two dispersion curves from π sheet and π^* sheet!**
- **If it so happens that one of the slices passes through the corner of the BZ, then we will have metallic tubes (zero gap), else semi-conducting! In fact, a tube will be metallic if $(n-m)/3$ is an integer!**

One Electron Theory of CNTs

- **Energy dispersions**

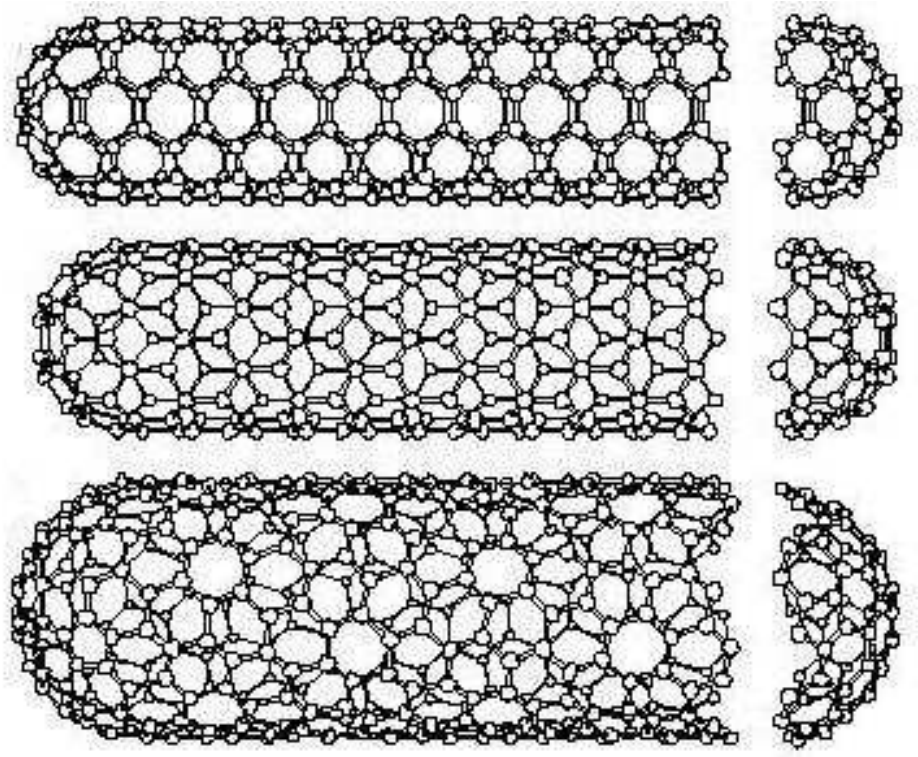


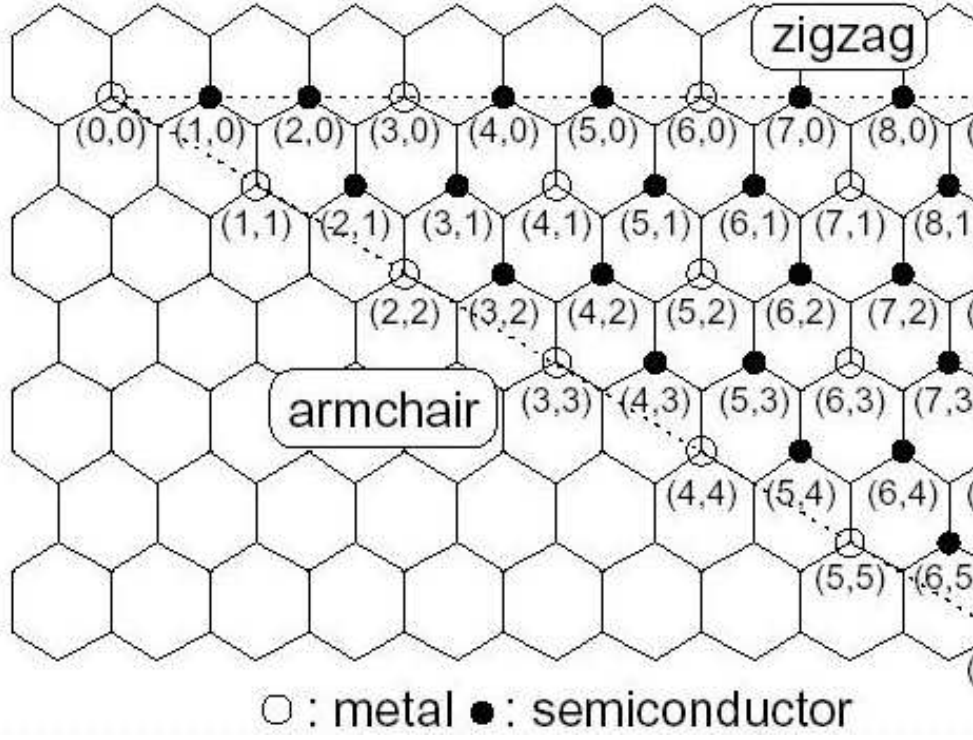
(Dresselhaus et al. 1999)

- **For "large" diameter** d**,** $E_{gap} \sim \frac{1}{d}$**!**

One Electron Theory of CNTs

- **CNT Chirality – Metal or Semiconductor**

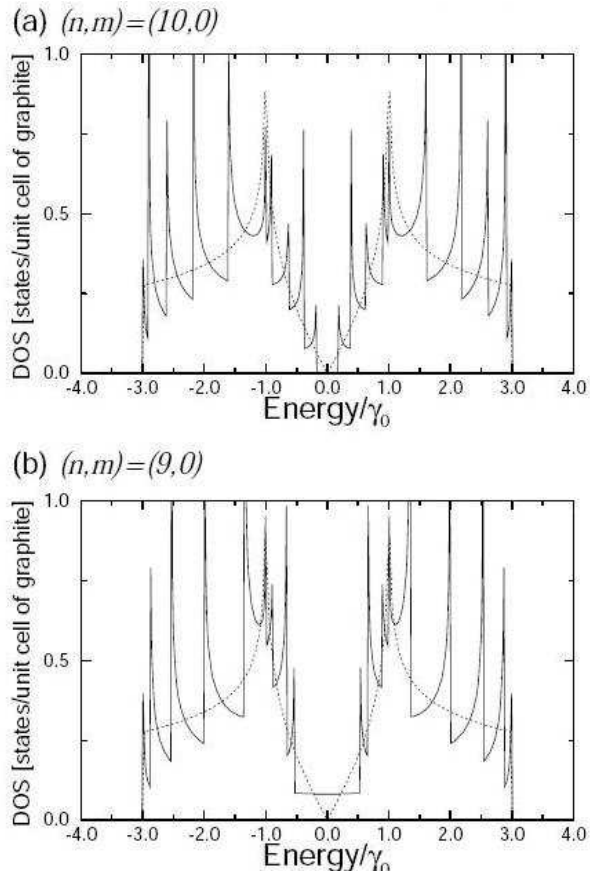




(Dresselhaus et al. 1999)

One Electron Theory of CNTs

- **DOS of CNTs**

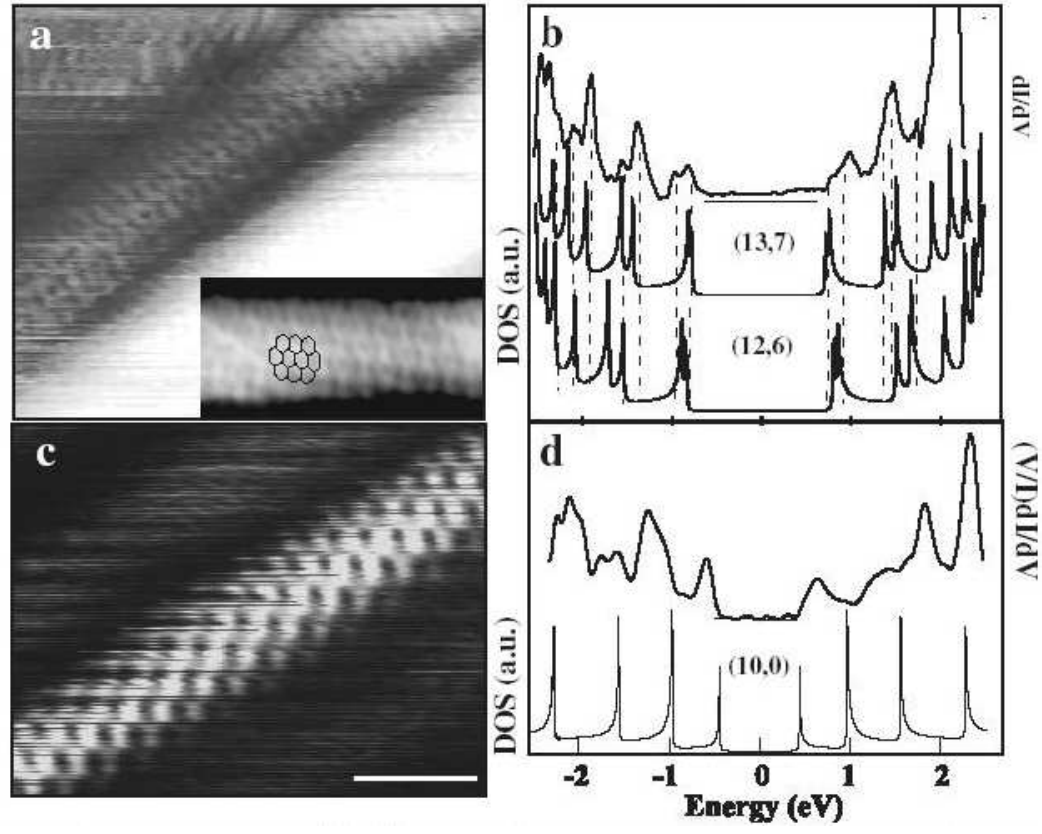


(Dresselhaus et al. 1999)

- **Can any of these be checked experimentally?**

Experiment vs. Theory

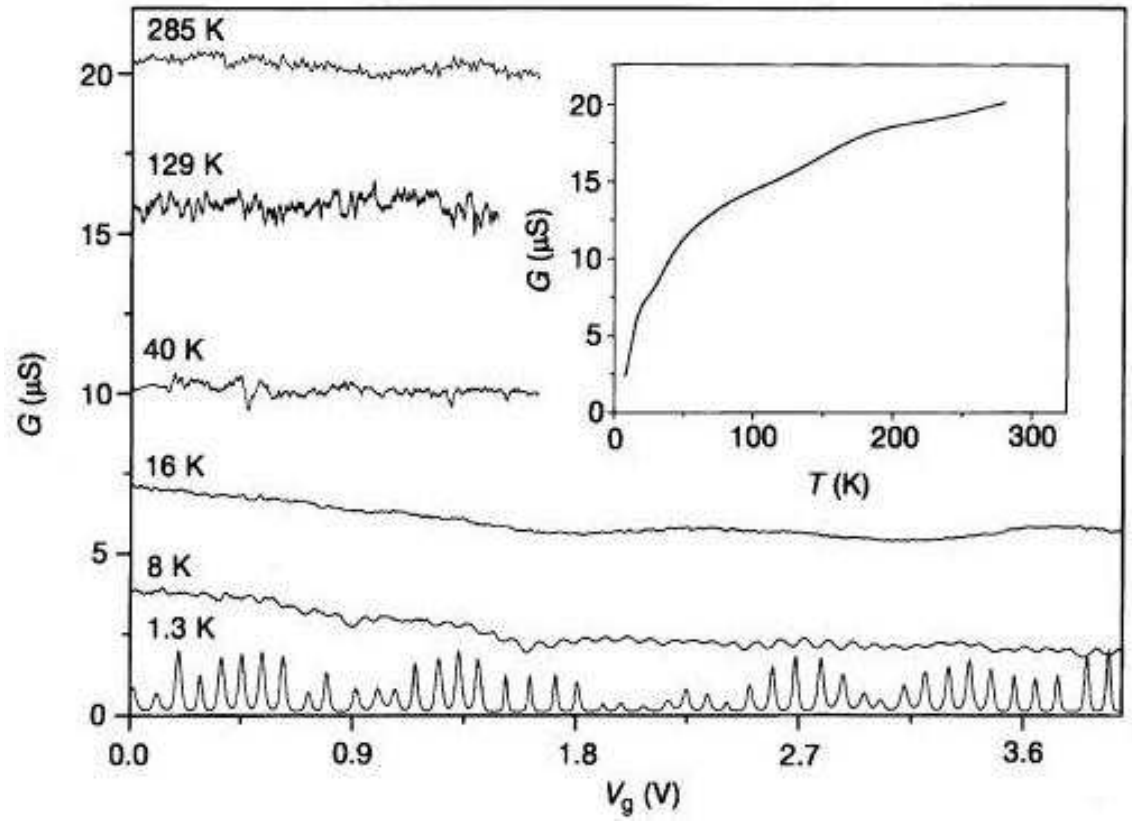
- **Scanning Tunneling Microscopy of Nanotubes**



(Odom et al. 2002)

- **Excellent Agreement with One Electron Theory (Really?)**

"Strange" Metallic Properties



(Bockrath et al. 1999)

- **Coulomb Blockade**
- **Luttinger Liquid Behaviour**

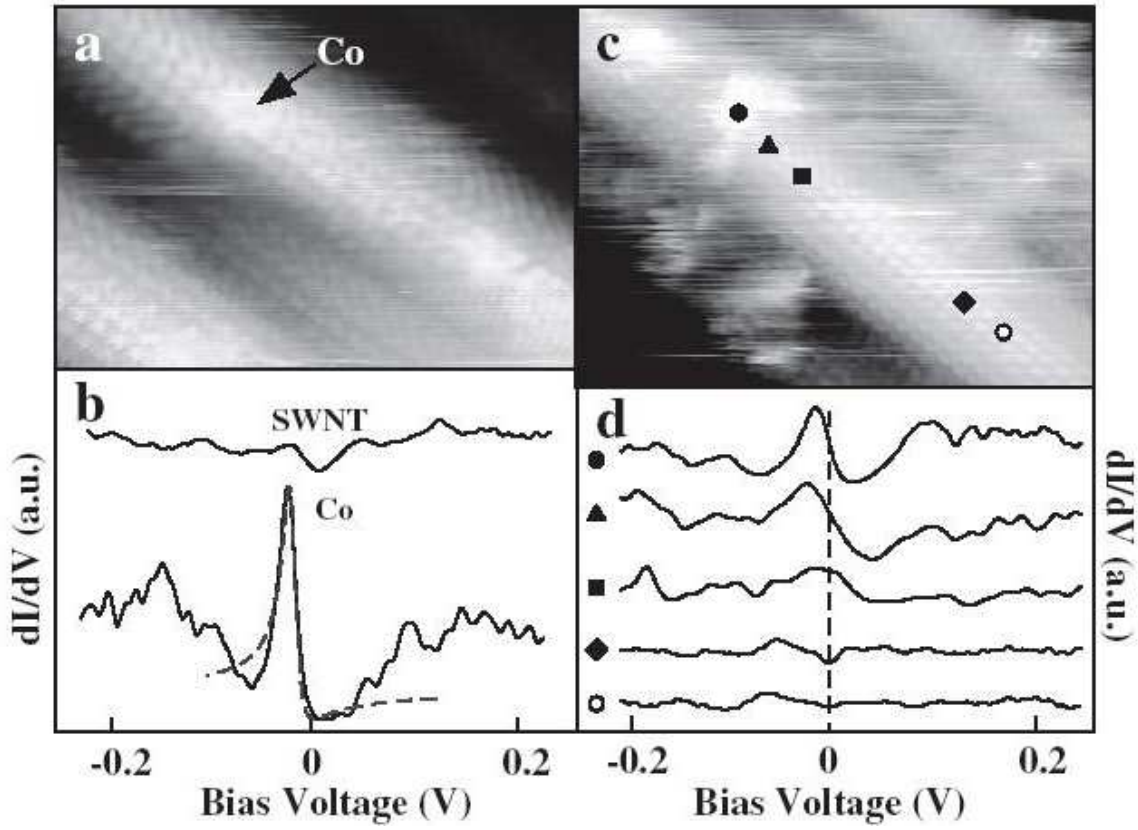
Summary

- **CNTs are wonder materials...may be?**
- **CNT : Simplet model – roll up of graphene sheets!**
- **Can understand overall electronic properties!**

What will you do with CNTs?

Magnetic Impurities and CNTs

- **Scanning Tunneling Microscopy of Magnetic Clusters**



Co Clusters (Odom et al. 2002)

- **Kondo Clouds!**

Background: Magnetic Impurities in Metals

- **May (Fe in Cu) or May Not(Fe in Al) Retain Moment – Anderson Model**

$$\mathcal{H} = \epsilon_d c^\dagger_{d\sigma} c_{d\sigma} + U n_{d\uparrow} n_{d\downarrow} + \sum_k \left(V_k c^\dagger_{d\sigma} c_{k\sigma} + \textbf{h. c.} \right) + \sum_k \epsilon_k c^\dagger_{k\sigma} c_{k\sigma}$$

- **Magnetic Impurity Physics**
  - **High Temperature : "Free Moments" Interacting via RKKY (Local Moment Regime)**
  - **Low Temperature : "Quenching" of Moments by Conduction Electrons (Strong Coupling Regime – Kondo Effect)**
- **Recent Interest in RKKY – Spintronics Materials**

RKKY Interaction

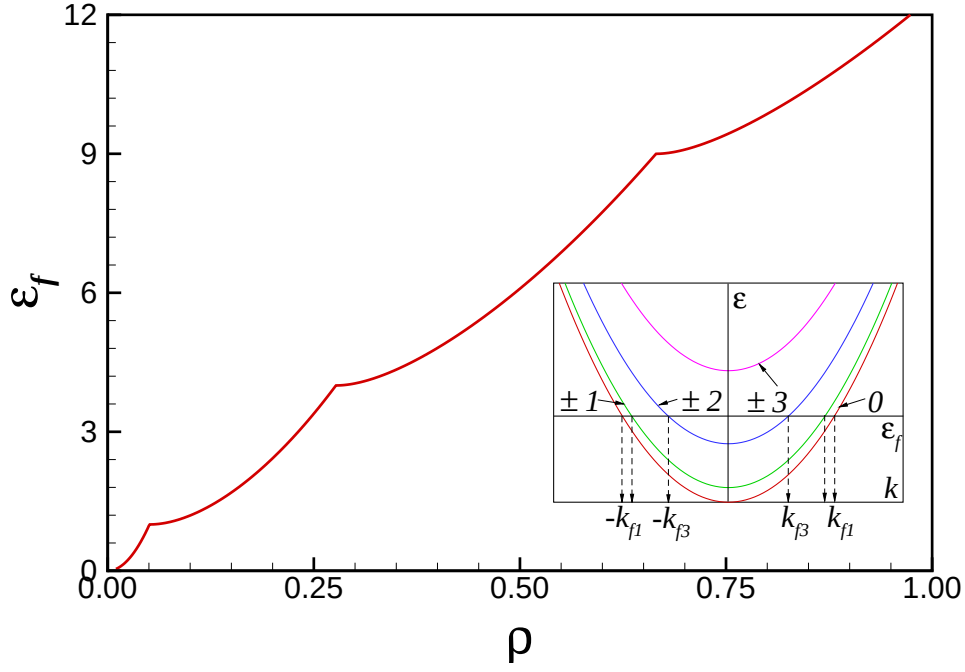
- **RKKY = Ruderman-Kittel-Kasuya-Yoshida**
- **Conduction Electron Mediated Magnetic Impurity Interaction**

$$\mathcal{H}_{RKKY} = \sum_{\langle ij \rangle} \mathcal{J}(|\boldsymbol{R}_i - \boldsymbol{R}_j|)\boldsymbol{S}_i \cdot \boldsymbol{S}_j, \qquad \mathcal{J}(r) = \frac{T(k_F r)}{(k_F r)^d}$$

- $T(\ )$ **– Periodic Function (**$\cos()$ **in 1 and 3-D,** $\sin()$ **in 2D)**
- **Question(s) :**
  - **What is the RKKY Function for a Single-Walled NT?**
  - **What are the "Dimensionality" Effects?**

"Free Electron" Model of Metallic Nanotubes

- **Cylinder of Radius R with Electron Density Σ**
- **Energy States $E_\circ \epsilon_{k,n} = \frac{\hbar^2}{2m_e R^2}(k^2 + n^2)$**
- **Chemical Potential (Fermi Energy) ϵ_f**



- **"Size Parameter" $\rho = \Sigma R^2$: ϵ_f Specified by $N_f, \{k_{fn}\}$**

RKKY Interaction in Nanotubes

- **Kondo $s-d$ Hamiltonian : Impurity – Conduction Electron Interaction**

$$\mathcal{H}_{sd} = -J \int \mathbf{d}x\mathbf{d}\theta\, \boldsymbol{s}(x,\theta)\cdot \boldsymbol{S}(x,\theta),$$

$$(\boldsymbol{S}(x,\theta) = \sum_p \boldsymbol{S}_p \delta(x-x_p)\delta(\theta-\theta_p))$$

- **Second Order Perturbation Theory : Conduction Electron Energies Depend on Impurity Spin Configuration**

$$\mathcal{H}_{RKKY} = \sum_{\langle ij\rangle} \mathcal{J}(x_i-x_j,\theta_i-\theta_j)\boldsymbol{S}_i\cdot\boldsymbol{S}_j$$

RKKY Interaction in Nanotubes

- **Impurity Spin-Polarises Conduction Electrons; "Felt" by Another Impurity**
- **RKKY Interaction (Dimensionless)**

$$\mathcal{J}(x,\theta) = \frac{1}{(2\pi)^2} \sum_{m=-\infty}^{\infty} \int_{-\infty}^{\infty} \mathbf{d}q\, e^{i(qx+m\theta)} \chi^s(q,m)$$

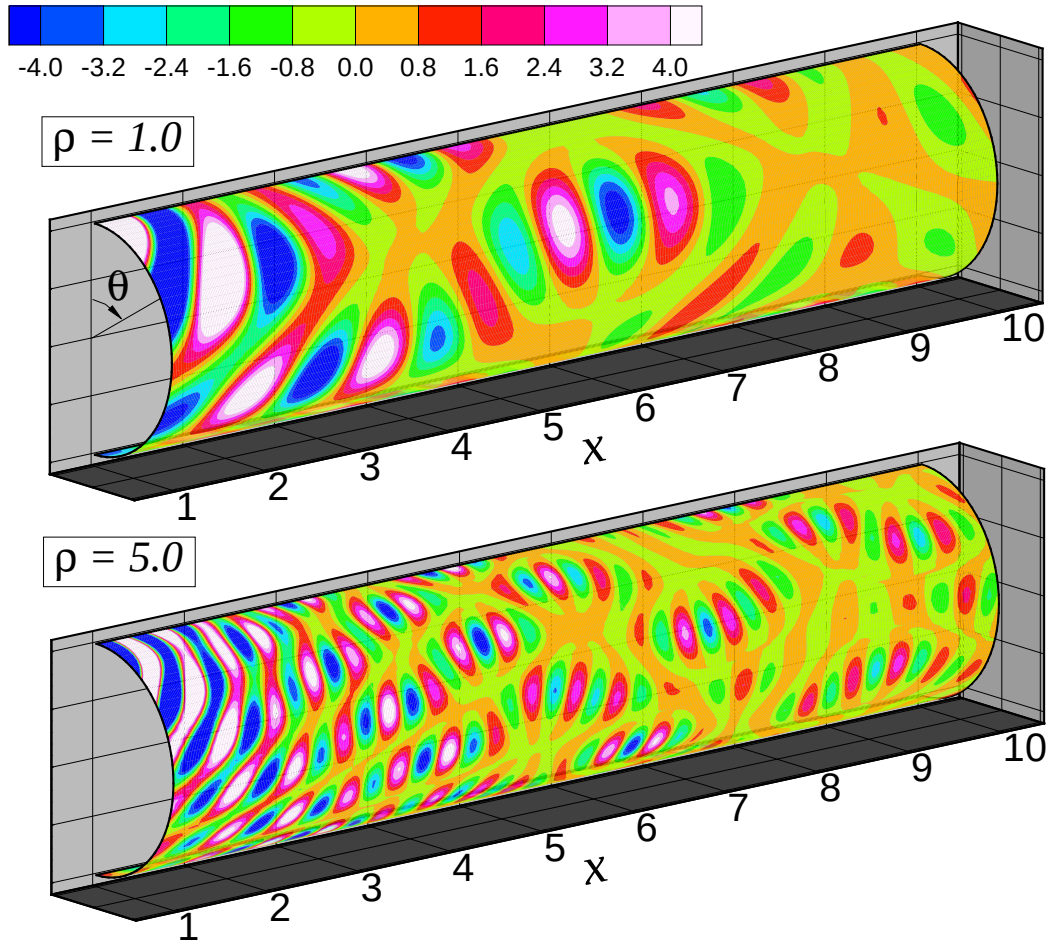
- **Spin Susceptibility (Polarisation Bubble)**

$$\chi^s(q,m) \quad = \quad \sum_{n=-N_f}^{N_f} \int_{-k_{fn}}^{k_{fn}} \mathbf{d}k \left(\frac{1}{\epsilon_{k-q,n-m} - \epsilon_{k,n}} + \frac{1}{\epsilon_{k+q,n+m} - \epsilon_{k,n}} \right)$$

- **Final Result (After Contour Integration)**

$$\mathcal{J}(x,\theta) = H_0(x) + 2 \sum_{m=1}^{\infty} \cos(m\theta) H_m(x),$$

RKKY Interaction in Nanotubes



- **Strong Angular Dependence**
- **Magnitude Falls with x (How?)**

RKKY Interaction in Nanotubes – Asymptotics

- **"Large"** x **behaviour** $\mathcal{J}^a(x,\theta) = \frac{T(x,\theta)}{x}$
- **Modulating** *Non-Periodic* **Function**

$$\frac{1}{2\pi}T(x,\theta) = \sum_{n=-N_f}^{N_f} \frac{\cos(k_{fn}x)}{k_{fn}} +$$

$$\sum_{m=1}^{M} \cos(m\theta) \left[\sum_{n=-N_f}^{N_f} \Theta(-\alpha_+) \left(\frac{\cos((k_{fn} - \sqrt{|\alpha_+|})x)}{k_{fn} - \sqrt{|\alpha_+|}} + \frac{\cos((k_{fn} + \sqrt{|\alpha_+|})x)}{k_{fn} + \sqrt{|\alpha_+|}} \right) \right.$$

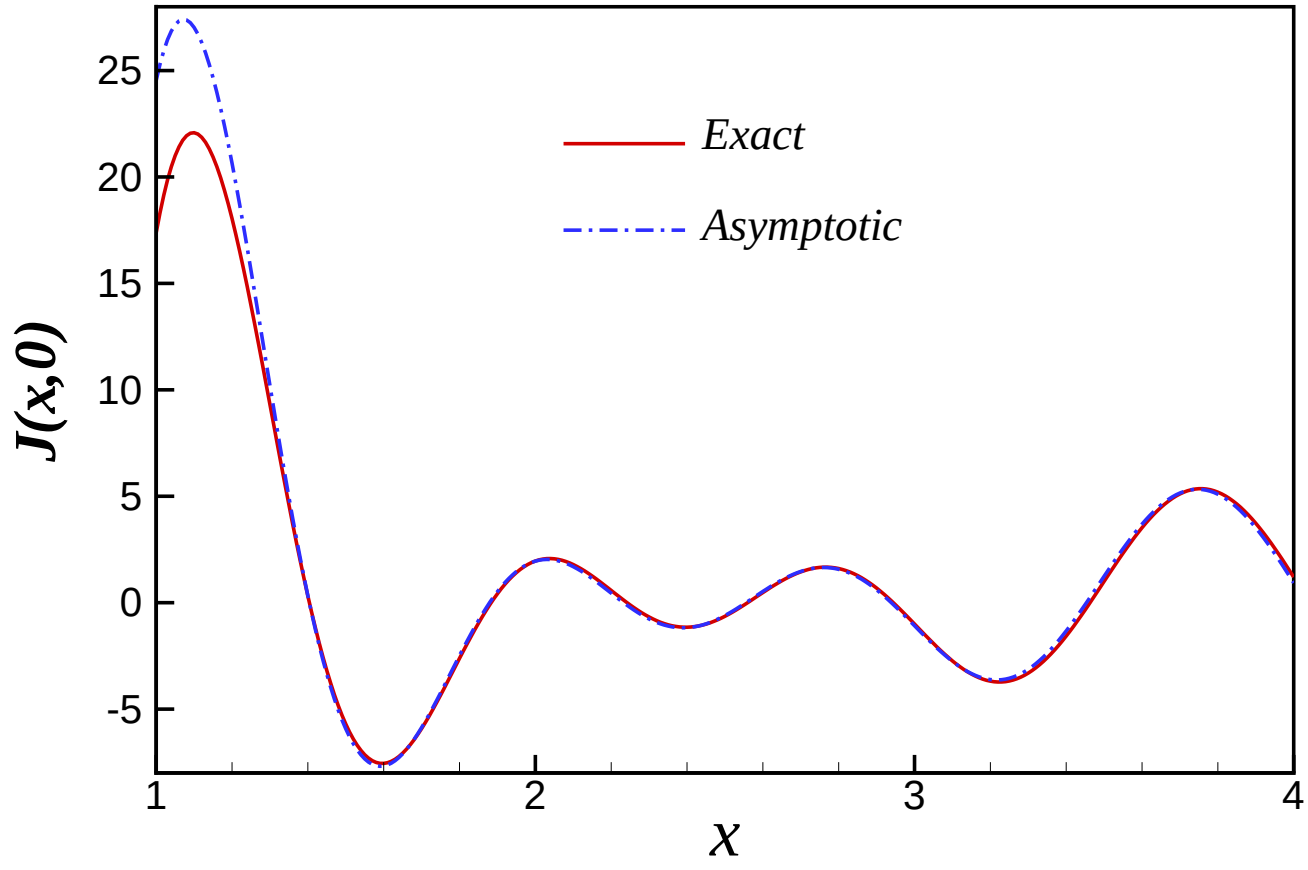
$$\left. + \sum_{n=-N_f}^{N_f} \Theta(-\alpha_-) \left(\frac{\cos((k_{fn} - \sqrt{|\alpha_-|})x)}{k_{fn} - \sqrt{|\alpha_-|}} + \frac{\cos((k_{fn} + \sqrt{|\alpha_-|})x)}{k_{fn} + \sqrt{|\alpha_-|}} \right) \right]$$

$$(\alpha_\pm = (n \pm m)^2 - \epsilon_f, \quad M = N_f + \sqrt{\epsilon_f})$$

- $T(x,\theta)$ **Depends on** ρ **(**$= \Sigma R^2$**) – Size Determines Modulating Function**

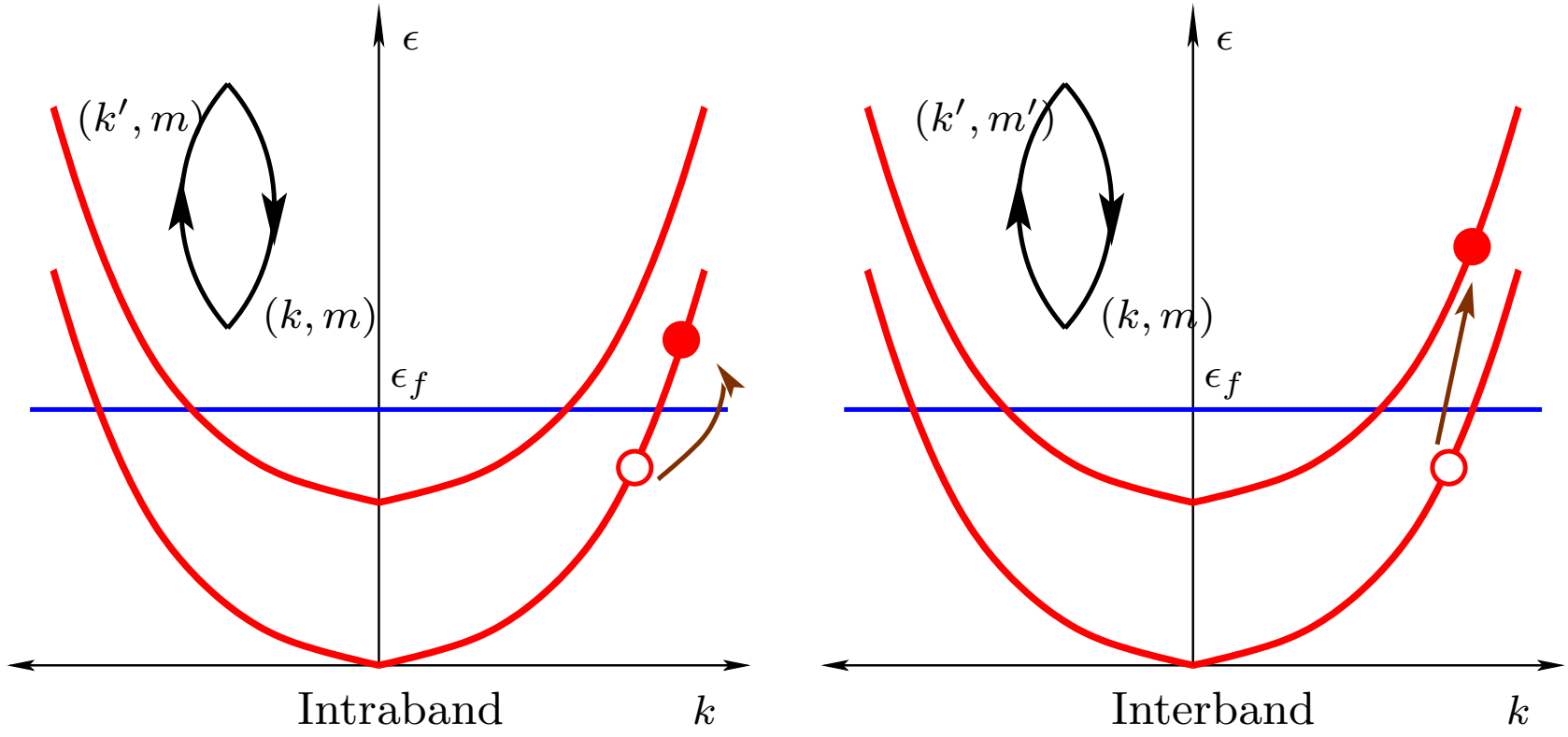
RKKY Interaction in Nanotubes – Asymptotics

- $\mathcal{J}(x,\theta) \sim T(x,\theta)/x$ **at "Large"** x
- $T(x,\theta)$ **– Non-Periodic Function of** x



Physics of Non-Periodic Modulation

- *Intra*band and *Inter*band P-H Excitations



- k_{fm} *and* k_{fn} *: Not Integer Multiples*
- *Both* **Intra- and Interband Excitations Lead to Non-Periodicity**

RKKY Interaction in Nanotubes

- **Summary:**
  - $\mathcal{J}(x,\theta) \sim T(x,\theta)/x$ **at "Large"** x
  - $T(x,\theta)$ **– Size Dependent Non-Periodic Function**
- **Implications:**
  - **CNTs – Possible Systems for 1D Spin Glasses**
  - **CNT Spintronics – May be Not(??)**

Reference: **Shenoy, V.,** *Physical Review B*, **71, 125431 (2005).**

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A Final Thought

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