Carbon Nanotubes\textsuperscript{a} – Electronic Properties

Vijay B. Shenoy
(shenoy@physics.iisc.ernet.in)

Centre for Condensed Matter Theory
Indian Institute of Science

\textsuperscript{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

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

(Harris 2001)
Carbon: More Nanotubes

(Harris 2001)
CNTs – Wonder Materials?

“Amazing” Properties of CNTs
- “Interesting” electronic properties
- High elastic stiffness (≈5–10 × 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 $H |\psi\rangle = i\hbar \frac{\partial |\psi\rangle}{\partial t}$
- Stationary 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 $\Sigma$.

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 $n$)

$$E(k, n) = E_0 \epsilon_{k,n} = \frac{\hbar^2}{2m_e R^2}(k^2 + n^2)$$
A “Free Electron” Theory of CNTs

- **Chemical Potential (Fermi Energy)** $\epsilon_f$

- **“Size Parameter”** $\rho = \sum R^2$: $\epsilon_f$ 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 semiconducting? (Now you begin to fear hair-loss!)
Free Electron needs Repair

Electrons are not really free!

They move in a periodic potential

\[ V(r) = \sum_{R} V_a(r - R) \]

Schrödinger equation

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

What are allowed \( E \)s and associated \( \psi \)s?

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

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

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 $\psi_+$ state is “located closer to the atom”!
1D Solid – Simple Arguments

Clearly, $\psi_+^{-}$ 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

$$\psi_{\pm}(x) = \left( C_k^{\pm} + C_{k-G}^{\pm} e^{-iGx} \right) e^{ikx}$$

$u_{\pm}(x)...lattice$ periodic
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

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

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 \( \pi \)-bonding!
- Tight binding Hamiltonian

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

\( l,m, \text{ Bravais lattice index, } \alpha,\beta \text{ basis index, } t \text{ is the } p_z-p_z \text{ } \pi \text{ overlap integral} \)
Graphene Band Structure

- There are two bands...the $\pi$ band and $\pi^*$ 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

![Graph showing transport properties of graphite]

Dutta 1953

- Ready to tackle CNTs
Structure of CNTs

- CNT = Rolled Up Graphene Sheet

- CNT: Defined chiral vector (Bravais lattice vector)
  \[ C = ma_1 + na_2 \]

(Avouris et al. 2003)
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!

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 \( k \cdot C = 2\pi N \).

Thus, CNT bands can be obtained by “slicing” the graphene band structure! For every slice, we will get two dispersion curves from \( \pi \) sheet and \( \pi^* \) 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: Simples 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
  \[ \mathcal{H} = \epsilon_d c_d^\dagger c_d + U n_d^\dagger n_d^\dagger + \sum_k \left( V_k c_d^\dagger c_k^\sigma + \text{h. c.} \right) + \sum_k \epsilon_k c_k^\dagger c_k^\sigma \]

- 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

\[ \mathcal{H}_{RKKY} = \sum_{\langle ij \rangle} \mathcal{J}(|R_i - R_j|) S_i \cdot S_j, \quad \mathcal{J}(r) = \frac{T(k_{Fr})}{(k_{Fr})^d} \]

- \( T( \ ) \) – 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** $\Sigma$

- **Energy States**
  \[ E_{\epsilon_{k,n}} = \frac{\hbar^2}{2m_e R^2} (k^2 + n^2) \]

- **Chemical Potential (Fermi Energy)** $\epsilon_f$

\[ \rho = \Sigma R^2: \epsilon_f \text{ Specified by } N_f, \{k_{f,n}\} \]
RKKY Interaction in Nanotubes

- **Kondo \( s - d \) Hamiltonian: Impurity – Conduction Electron Interaction**

\[
H_{sd} = -J \int dx d\theta \mathbf{s}(x, \theta) \cdot \mathbf{S}(x, \theta),
\]

\[
(\mathbf{S}(x, \theta) = \sum_p \mathbf{S}_p \delta(x - x_p) \delta(\theta - \theta_p))
\]

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

\[
H_{RKKY} = \sum_{\langle ij \rangle} J(x_i - x_j, \theta_i - \theta_j) \mathbf{S}_i \cdot \mathbf{S}_j
\]
RKKY Interaction in Nanotubes

- Impurity Spin-Polarises Conduction Electrons; “Felt” by Another Impurity
- RKKY Interaction (Dimensionless)

\[ \mathcal{J}(x, \theta) = \frac{1}{(2\pi)^2} \sum_{m=-\infty}^{\infty} dq \ e^{i(qx+m\theta)} \chi^s(q, m) \]

- Spin Susceptibility (Polarisation Bubble)

\[ \chi^s(q, m) = \sum_{n=-N_f}^{N_f} \int_{-k_f n}^{k_f n} dk \left( \frac{1}{\epsilon_{k-q,n-m} - \epsilon_{k,n}} + \frac{1}{\epsilon_{k+q,n+m} - \epsilon_{k,n}} \right) \]

- 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 $\rho$ (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 $\rho \ (= \sum R^2)$ – 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 $x$

![Graph showing the comparison between Exact and Asymptotic functions.](image)
Physics of Non-Periodic Modulation

**Intraband and Interband P-H Excitations**

\[ (k', m) \]

\[ (k, m) \]

\[ \epsilon \]

\[ \epsilon_f \]

\[ k \]

\[ k' \]

\[ k_m \text{ and } k_n : \text{Not Integer Multiples} \]

*Both Intra- and Interband Excitations Lead to Non-Periodicity*
RKKY Interaction in Nanotubes

Summary:
\[ J(x, \theta) \sim \frac{T(x, \theta)}{x} \] at “Large” \( x \)

\( T(x, \theta) \) – Size Dependent Non-Periodic Function

Implications:
- CNTs – Possible Systems for 1D Spin Glasses
- CNT Spintronics – May be Not(??)

Acknowledgments

Thanks to:

- H. R. Krishnamurthy
- N. Ravishankar
- Anonymous Reviewer, PRB
- Members of Strong-Correlations Discussion Group

Research funded by:

Indian National Science Academy, Young Scientist Programme
A Final Thought

सृष्ट्वमदं सृष्ट्वमिदं सृष्ट्वमात्सृष्ट्वममुदच्यते ।
सृष्ट्वमस्य सृष्ट्वमादाय सृष्ट्वममवावशिष्यते ॥ ॥

नॉनोपनिषद्