From Graphene to Nanotubes

Zone Folding and Quantum Confinement at the Example of the Electronic Band Structure

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Outline

1 Introduction

2 Going from Graphene to Nanotubes in k-space
- Real and k-space of Graphene
- Real and k-space of Nanotubes

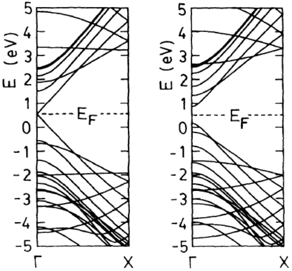
3 Electronic Band Structure of Nanotubes
- Zone Folding Approximation
- Limits of Zone Folding

4 Summary

Motivation

interesting electronic behavior

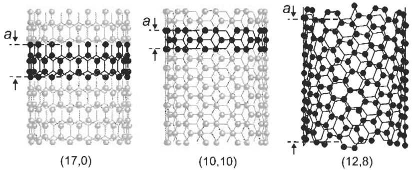
- about 1/3 of possible nanotubes are (quasi) metallic depending on geometric structure



Hamada et al: Phys Rev Lett **68** 1579 (1992)

high degree of complexity

- ∞-number of realizable tubes
- large number of atoms in unit cell possible
  → efficient tool needed



Reich et al: Carbon Nanotubes, Wiley (2004)

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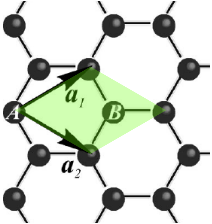
Real and k-space of Graphene

real space

- 2 atomic unit cell
- lattice basis vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ with $\|\mathbf{a}_1\| = \|\mathbf{a}_2\| = a_0$ and $a_0 = 2.461\,\text{Å}$

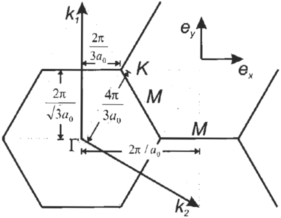
Reich et al: Carbon Nanotubes, Wiley (2004)



Reich et al: Phys Rev B **66** 035412 (2002)

k-space

- reciprocal lattice basis vectors $\mathbf{k}_1$ and $\mathbf{k}_2$
- K-point at $\frac{1}{3}(\mathbf{k}_1 - \mathbf{k_2})$, $\left(\frac{1}{3}\mathbf{k}_1 + \frac{2}{3}\mathbf{k_2}\right)$ and $\left(\frac{2}{3}\mathbf{k}_1 + \frac{1}{3}\mathbf{k_2}\right)$



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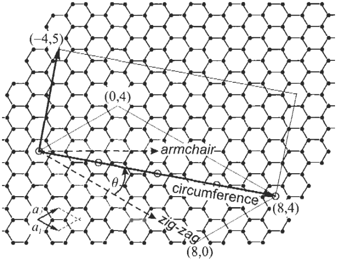
Unitcell of Nanotubes in Real Space

- chiral vector
  $\mathbf{c} = (n_1, n_2) \equiv n_1\mathbf{a}_1 + n_2\mathbf{a}_2$
- lattice vector
  $\mathbf{a} = \left(-\frac{2n_2+n_1}{nR}, \frac{2n_1+n_2}{nR}\right)$



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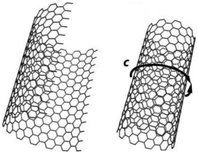
where

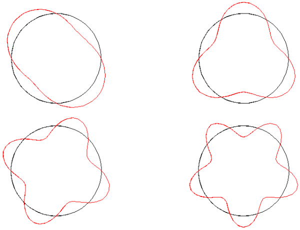
- n greatest common divisor of n_1, n_2
- $R = \begin{cases} 3 \text{ if } 3 \mid \frac{n_1-n_2}{n} \\ 1 \text{ else} \end{cases}$

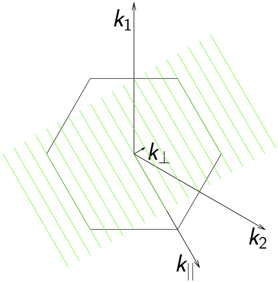


Thomsen et al: Light Scat in Sol IX **108** (2007)

- diameter $d = \frac{\|\mathbf{c}\|}{\pi} = \frac{a_0}{\pi}\sqrt{n_1^2 + n_2^2 + n_1 n_2}$
- # graphene unit cells: $q = \frac{\|\mathbf{a}\|\|\mathbf{c}\|}{a_0\sqrt{3}/2} = \frac{2}{nR}\left(n_1^2 + n_2^2 + n_1 n_2\right)$

Quantum Confinement and Boundary Conditions





along tube axis

one dimensional reciprocal lattice

- $k_t \in \left]-\frac{\|\mathbf{k}_{||}\|}{2}, \frac{\|\mathbf{k}_{||}\|}{2}\right]$ with $\mathbf{k}_{||} = \frac{2\pi}{\|\mathbf{a}\|}\hat{\mathbf{a}}$

perpendicular to tube axis

due to rolled up structure, periodic boundary conditions are exact

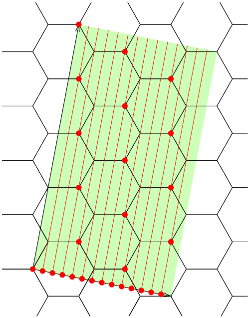
finite scale yields quantization of allowed k-values $e^{i\mathbf{k}_\perp \mathbf{c}} = 1$ yields $\mathbf{k}_{\perp,m} = \frac{2\pi}{\|\mathbf{c}\|} m\hat{\mathbf{c}}$

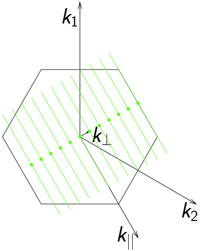
Number of Modes

what is the maximal value of the quantum number m?

- projecting tube unitcell on **c**-axis $\Rightarrow$ q equidistant intersections
- m is limited by $e^{i\mathbf{k}_\perp \alpha \hat{\mathbf{c}}} = e^{i(\mathbf{k}_\perp + \Delta\mathbf{k}_\perp)\alpha\hat{\mathbf{c}}}$
- smallest physical period in real space given by $\alpha = \frac{\|\mathbf{c}\|}{q}$ $\Rightarrow \|\Delta\mathbf{k}_\perp\| = \frac{2\pi}{\|\mathbf{c}\|/q}$

$$m = -\frac{q}{2} + 1, -\frac{q}{2} + 2, \ldots, 0 \ldots, \frac{q}{2}$$





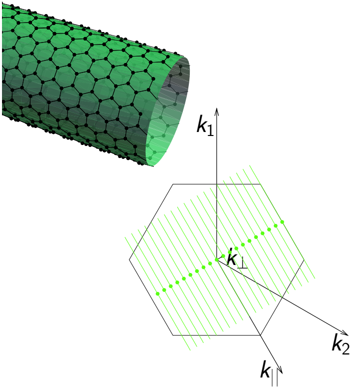
Examples

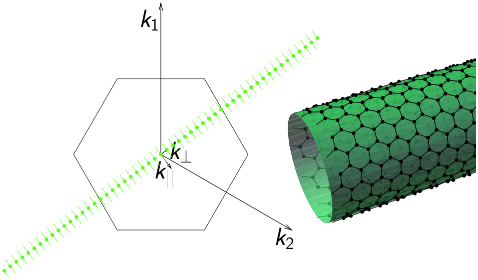
(10,10) tube

- $d = \frac{a_0}{\pi}\sqrt{10^2 + 10^2 + 10^2}$
  $= 1.357\,\text{nm}$
- $q = \frac{2}{10\cdot 3}(10^2 + 10^2 + 10^2) = 20$

(12,8) tube

- $d = \frac{a_0}{\pi}\sqrt{12^2 + 8^2 + 12\cdot 8}$
  $= 1.366\,\text{nm}$
- $q = \frac{2}{4\cdot 1}(12^2 + 8^2 + 12\cdot 8) = 152$





tube models created with: Blinder: Carbon Nanotubes, Wolfram Demonstrations Project

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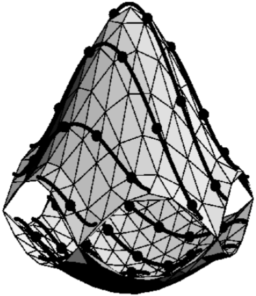
Zone Folding

calculate allowed k-states for corresponding tube

approximate band structure of carbon nanotubes by using the band structure of graphene along allowed lines in k-space



Samsonidze et al: J Nanosci Nanotech **3** (2003)

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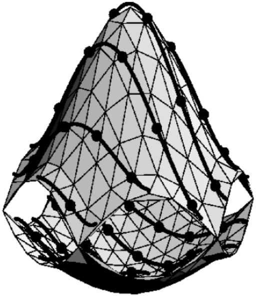
why?



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Zone Folding

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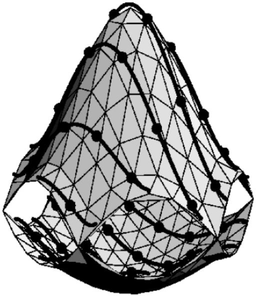
approximate band structure of carbon nanotubes by using the band structure of graphene along allowed lines in k-space

why?

- because it is simple!
  involves only once one calculation for graphene for all tubes



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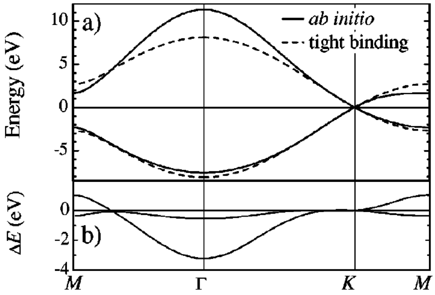
Band Structure of Graphene

- analytic expressions by tight binding model
- p_z and p_z^*-orbitals cross at K-point



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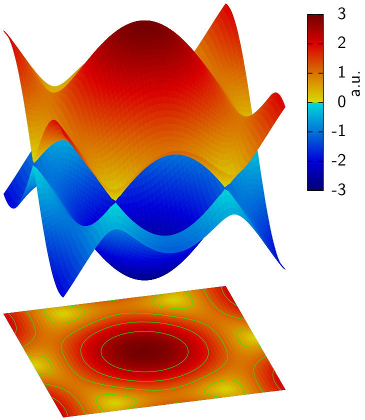
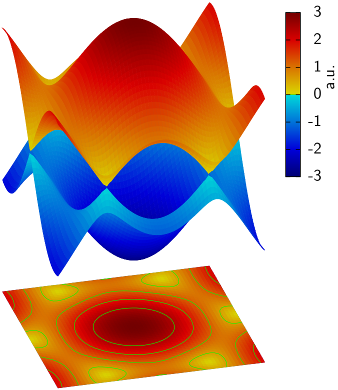


Construction

- band structure of graphene



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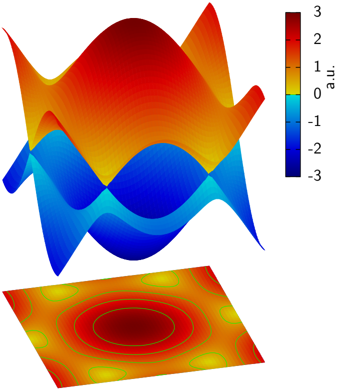
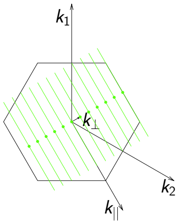


- allowed k-states [(6,6) tube]



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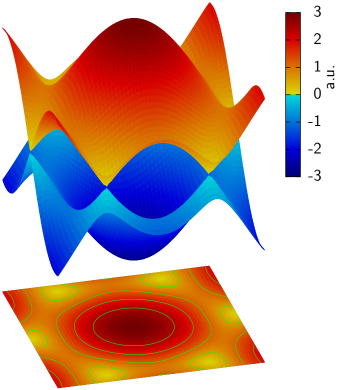

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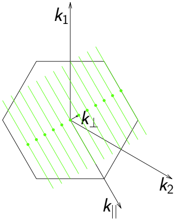
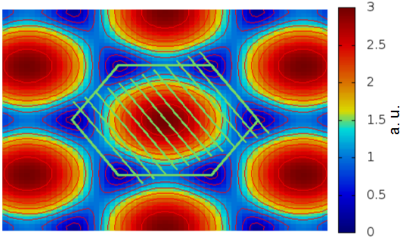
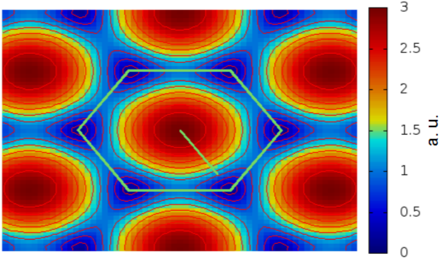


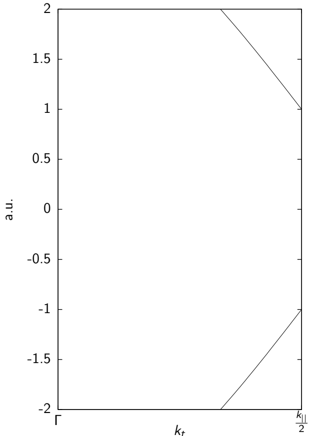
- band structure of nanotube



Closed Expression

(6,6) tube





general case

$$E(m, k_t) \quad \propto \quad \left[3 + 2\cos\left(\frac{2n_1 + n_2}{qnR} 2\pi m - \frac{n_2}{q} 2\pi k\right) + 2\cos\left(\frac{2n_2 + n_1}{qnR} 2\pi m + \frac{n_1}{q} 2\pi k\right)\right.$$

$$\left. + 2\cos\left(\frac{n_1 - n_2}{qnR} 2\pi m - \frac{n_1 + n_2}{q} 2\pi k\right)\right]^{1/2} \text{ where } k \in \left]-\frac{1}{2}, \frac{1}{2}\right]$$

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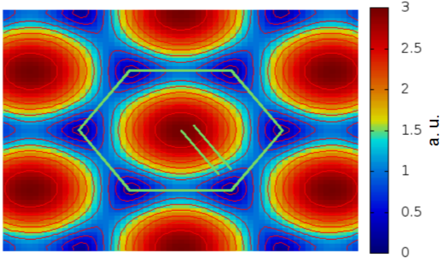

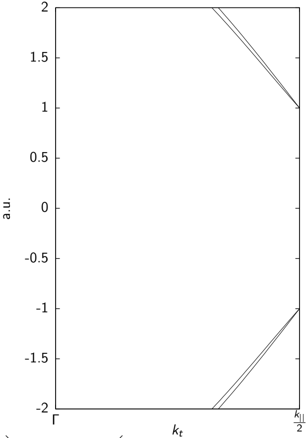

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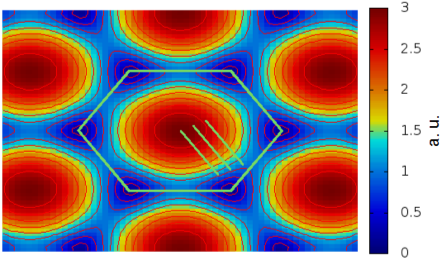

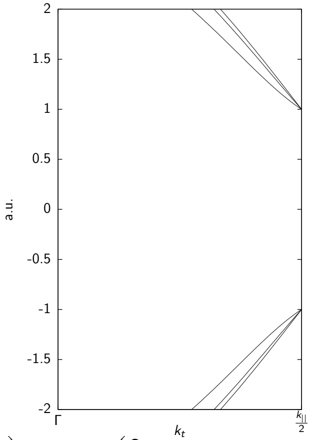

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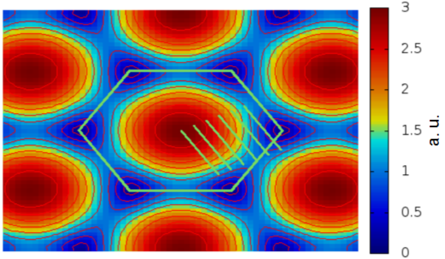

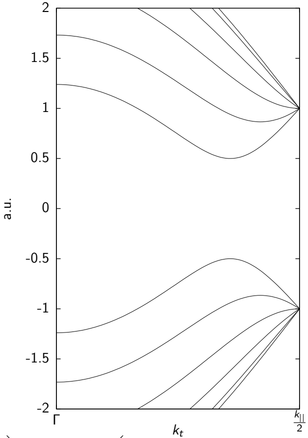

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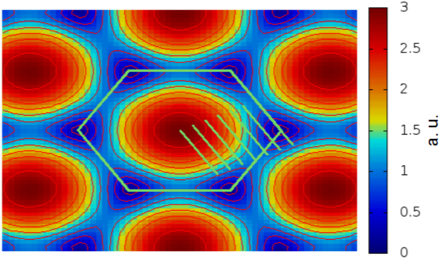

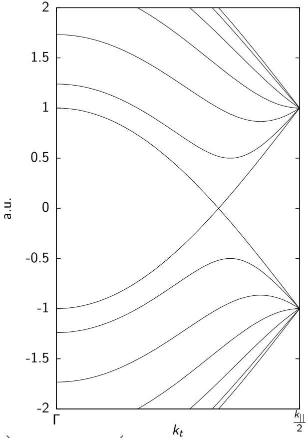

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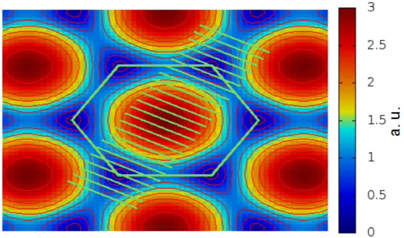
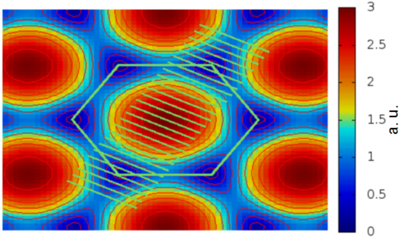
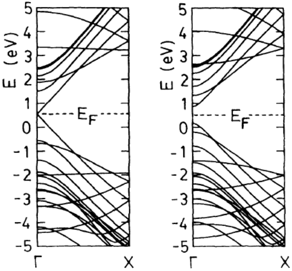
Examples: (12,0) and (13,0)







Hamada et al: Phys Rev Lett **68** 1579 (1992)

Electronic Classification

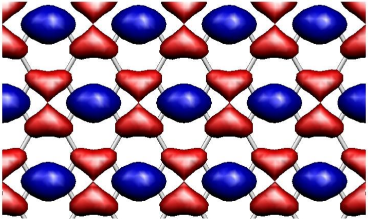
metallic tubes

- from quantization condition: K-point allowed if $2\pi z = \mathbf{K}\mathbf{c} = \frac{1}{3}(\mathbf{k}_1 - \mathbf{k}_2)\mathbf{c} = \frac{2\pi}{3}(n_1 - n_2)$

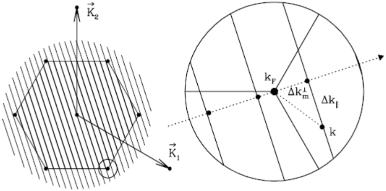
nanotube band structure contains graphene K point if $3 \mid (n_1 - n_2)$

semiconducting tubes

- all other 2/3 possible tubes are gapped



by courtesy of Prof. Dr. Reich

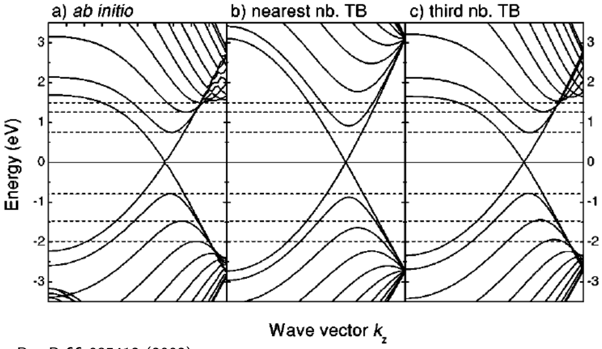


Mintmire, White: Phys Rev Lett **81** 2506 (1998)

Approximations within Zone Folding

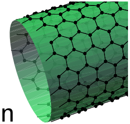
band structure of graphene

- approximation of graphene band structure directly implies deviations of obtained tube band structures



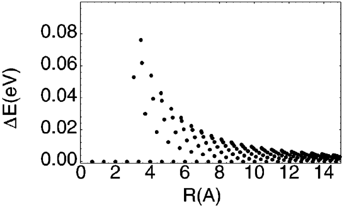
Reich et al: Phys Rev B **66** 035412 (2002)

Approximations due to Zone Folding: Curvature



geometric effects

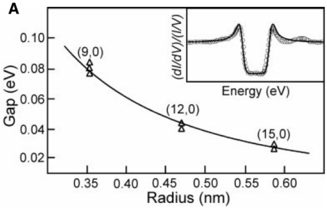
- changes bond length in **c**-direction
- shifts point of crossing bands $\rightarrow$ opens secondary gaps



Kane, Mele: Phys Rev Lett **78** 1932 (1997)

rehybridization

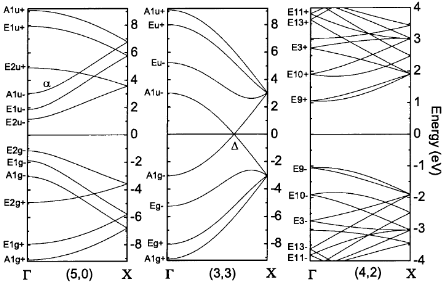
- affects higher bands
- mixing of σ and π bands due to nonorthogonality



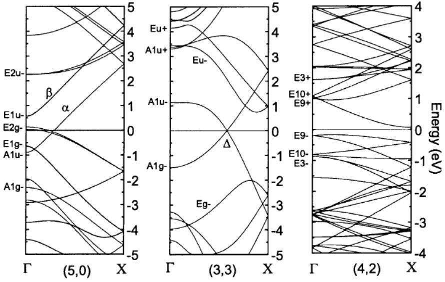
Ouyang et al: Science **292** 702 (2001)

4 Å tubes

zone folding



ab initio



Zhaoming: University of Hong Kong, PhD thesis (2004)

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Summary and Outlook

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knowledge about graphene allows approximations for nanotubes

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1/3 of possible tubes are metallic

in reality

1/3 of possible tubes are metallic or small gapped quasi metallic

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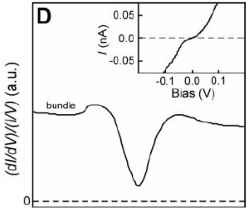
$1/3$ of possible tubes are metallic

in reality

$1/3$ of possible tubes are metallic or small gapped quasi metallic

outlook

- bundles break symmetry and e.g. open pseudogaps



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Summary and Outlook

summary

knowledge about graphene allows approximations for nanotubes

in zone folding

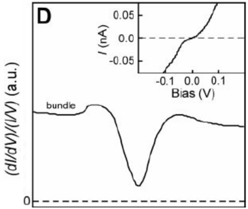
1/3 of possible tubes are metallic

in reality

1/3 of possible tubes are metallic or small gapped quasi metallic

outlook

- bundles break symmetry and e.g. open pseudogaps



Ouyang et al: Science **292** 702 (2001)

- multiwalled nanotubes
- correlations and Luttinger liquid
- applications?