Electronic properties of nanotubes

Xavier Blase

CNRS and Université Lyon I, France

Books:

M. Endo, S. Iijima, M.S. Dresselhaus, *Carbon nanotubes*, Pergamon Press, Elsevier, 1996.

M.S. Dresselhaus, G. Dresselhaus, P.C. Eklund, *Science of fullerenes and carbon nanotubes*, Academic Press, San Diego, California, 1996.

T.W. Ebbessen, *Carbon nanotubes: preparation and properties*, CRC Press Inc., Boca Raton, Florida, 1997.

R. Saito, G. Dresselhaus, *Physical properties of carbon nanotubes*, Imperial College Press, London, 1998.

P.J.F. Harris, *Carbon nanotubes and related structures*, Cambridge University Press, Cambridge, 1999.

D. Tománek and R.J. Enbody, *Science and application of nanotubes*, Kluwer Academic, Plenum Publishers, New York, 1999.

S. Reich, C. Thomsen, J. Maultzsch, *Carbon nanotubes: basic concepts and Physical properties*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2004.

A.Loiseau, P. Launois, P. Petit, S. Roche, J.-P. Salvetat, *Understanding carbon nanotubes: from basic properties to applications*, Lecture Notes in Physics 677, Springer-Verlag, Berlin, Heidelberg, 2006.

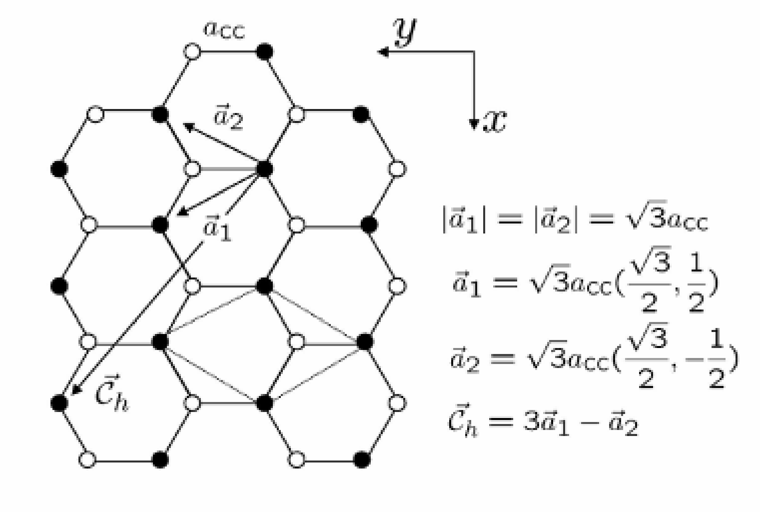
Much material in these lecture notes are extracted from:

J.-C. Charlier, X. Blase, S. Roche, « *Electronic and transport properties of nanotubes* »,
Rev. Mod. Phys. (submitted)

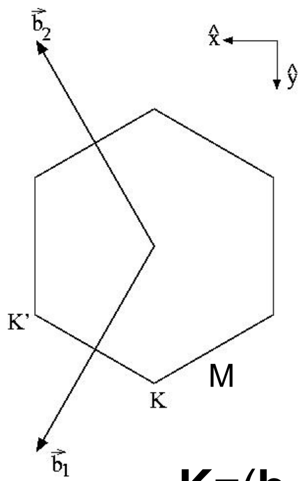
Outlines

Outlines (2)

Graphene sheet: electronic structure



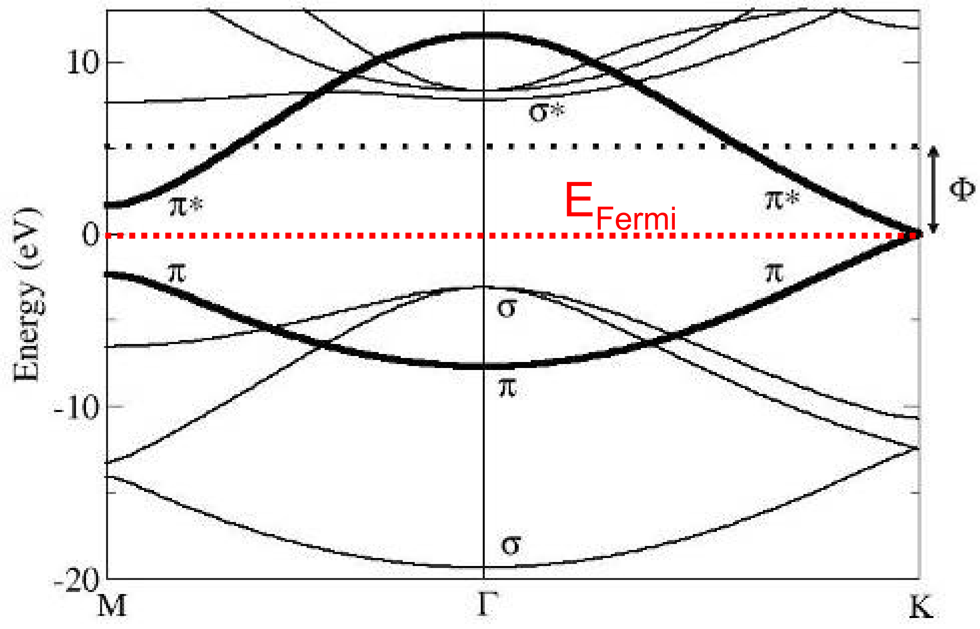
$\mathbf{a}_i.\mathbf{b}_j = 2\pi\ \delta_{ij}$



$\mathbf{b}_1 = b(1/2,\sqrt{3}/2)$
$\mathbf{b}_2 = b(1/2,-\sqrt{3}/2)$
with $b= 4\pi/a\sqrt{3}$
and $a=a_{CC}\sqrt{3}$

$\mathbf{K}=(\mathbf{b}_1-\mathbf{b}_2)/3$

Graphene band structure (*ab initio*)

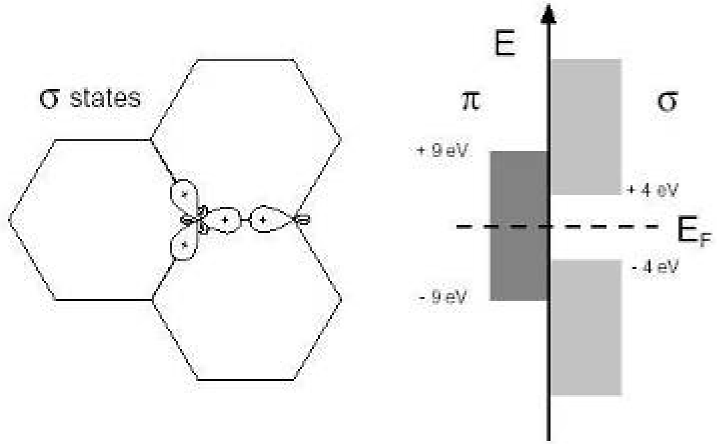


(Φ = work function (bands above are badly described)

Graphene is a semimetal with gap closing at the corners of the Brillouin zone (points K and K')

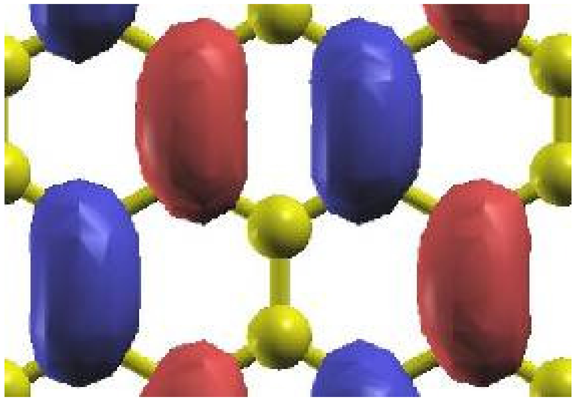
Isolated graphene sheet: Wallace, PR **71**, 622(1947); Novoselov *et al., Science* **306**, 666 (2004); Zhang *et al., Nature* **438**, 201 (2005).

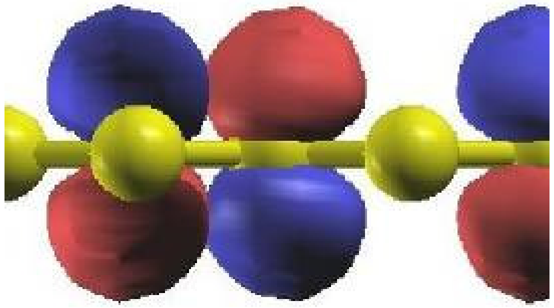
Graphene σ and π states



Courtesy: F. Ducastelle, Springer-Verlag 2006.

π-state: linear combination of p_z orbitals
Odd with respect to graphene plane symmetry

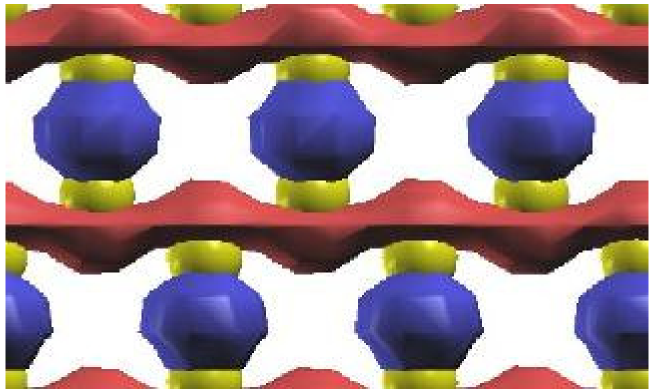


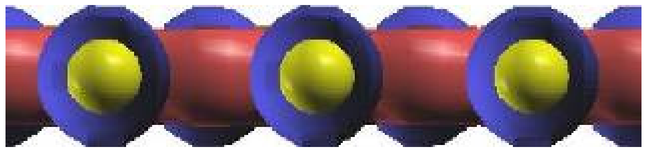


Red: (+) sign
Blue: (-) sign

Courtesy: M.-V. Fernández-Serra

σ linear combination of s, p_x and p_y
Even with respect to planar symmetry





The (orthogonal) π–π* tight-binding model (1)

$$\Psi(\vec{k},\vec{r}) = c_A(\vec{k})\tilde{p}_z^A(\vec{k},\vec{r}) + c_B(\vec{k})\tilde{p}_z^B(\vec{k},\vec{r}) \quad \text{(Bloch state)}$$

$$\left\{ \tilde{p}_z^{A/B}(\vec{k},\vec{r}) = \frac{1}{\sqrt{N_{\text{cells}}}}\sum_{\vec{\ell}} \mathrm{e}^{\mathrm{i}\vec{k}.\vec{\ell}} p_z^{A/B,\vec{\ell}} \text{ with: } p_z^{A/B,\vec{\ell}} = p_z(\vec{r}-\vec{r}_{A/B}-\vec{l}) \quad \text{(Bloch basis)} \right.$$

$$det \begin{pmatrix} \mathcal{H}_{AA}-E & \mathcal{H}_{AB} \\ \mathcal{H}_{BA} & \mathcal{H}_{BB}-E \end{pmatrix} = 0 \quad \Rightarrow$$

$$\mathcal{H}_{AA}(\vec{k}) = \frac{1}{N_{\text{cells}}}\sum_{\vec{\ell},\vec{\ell}'} \mathrm{e}^{\mathrm{i}\vec{k}.(\vec{\ell}'-\vec{\ell})}\langle p_z^{A,\vec{\ell}} \mid \mathcal{H} \mid p_z^{A,\vec{\ell}'}\rangle = \langle p_z^{A,0}|\mathcal{H}|p_z^{A,0}\rangle$$

$$\mathcal{H}_{AB}(\vec{k}) = \frac{1}{N_{\text{cells}}}\sum_{\vec{\ell},\vec{\ell}'} \mathrm{e}^{\mathrm{i}\vec{k}.(\vec{\ell}'-\vec{\ell})}\langle p_z^{A,\vec{\ell}} \mid \mathcal{H} \mid p_z^{B,\vec{\ell}'}\rangle = -\gamma_0\alpha(\vec{k})$$

$$\alpha(\vec{k}) = (1+\mathrm{e}^{-\mathrm{i}\vec{k}.\vec{a_1}}+\mathrm{e}^{-\mathrm{i}\vec{k}.\vec{a_2}}) \quad \text{and:} \quad \gamma_0 = \langle p_z^{A,0}|\mathcal{H}|p_z^{B,0}\rangle$$

(1)

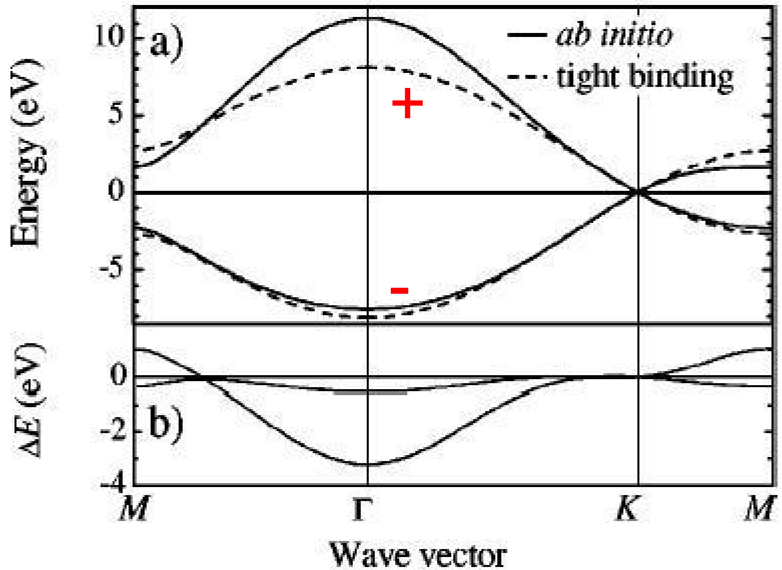
$$\boxed{\begin{aligned} E_\pm(\vec{k}) &= \pm\gamma_0\sqrt{3+2\cos(\vec{k}.\vec{a_1})+2\cos(\vec{k}.\vec{a_2})+2\cos(\vec{k}.(\vec{a_1}-\vec{a_2}))} \\ E_\pm(k_x,k_y) &= \pm\gamma_0\sqrt{1+4\cos\frac{\sqrt{3}k_xa}{2}\cos\frac{k_ya}{2}+4\cos^2\frac{k_ya}{2}} \quad \text{with: } \gamma_0 \sim 2.7-2.9\text{eV} \end{aligned}}$$

One verifies that: $E_\pm(\mathbf{k}=\mathrm{K})=0$ with $\mathbf{K} = (\mathbf{a}_1-\mathbf{a}_2)/3$

Reminder: cos(a+b)=cos(a)cos(b)-sin(a)sin(b)

The (orthogonal) $\pi-\pi^*$ tight-binding model (2)

$\gamma = 2.7$ eV



From: Reich et al., PRB ***66****, 035412 (2002)*

In reality, π and π^* bands are not symmetric with respect to zero energy. A better fit, including the non-zero overlap matrix elements $S=\langle p_z^A|p_z^B\rangle$, and including 2nd or 3rd nearest neighbor inter-action restore this asymmetry.

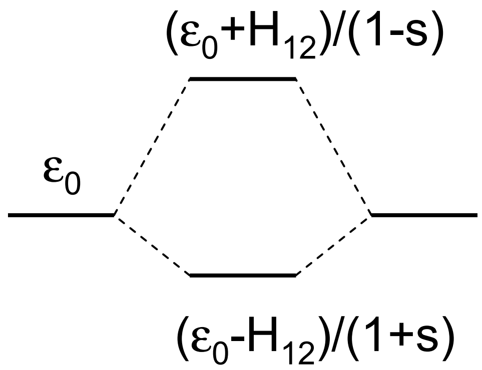
Exercice: H_2 molecule

One orbital $|s_1\rangle$ on atom 1
One orbital $|s_2\rangle$ on atom 2

Solution: $|\phi\rangle = \alpha |s_1\rangle + \beta |s_2\rangle$

Solve for eigenvalue λ:

$|H-\lambda S|=0 \quad H_{ij}=\langle s_i|Hs_j\rangle \; S_{ij}=\langle s_i|s_j\rangle$



$\varepsilon_0=\langle s_1|Hs_1\rangle$ and $s=\langle s_1|s_2\rangle$

Rolling a graphene sheet onto a SW nanotube

Create a tube by cutting along OB and AB' direction and folding OB onto AB'

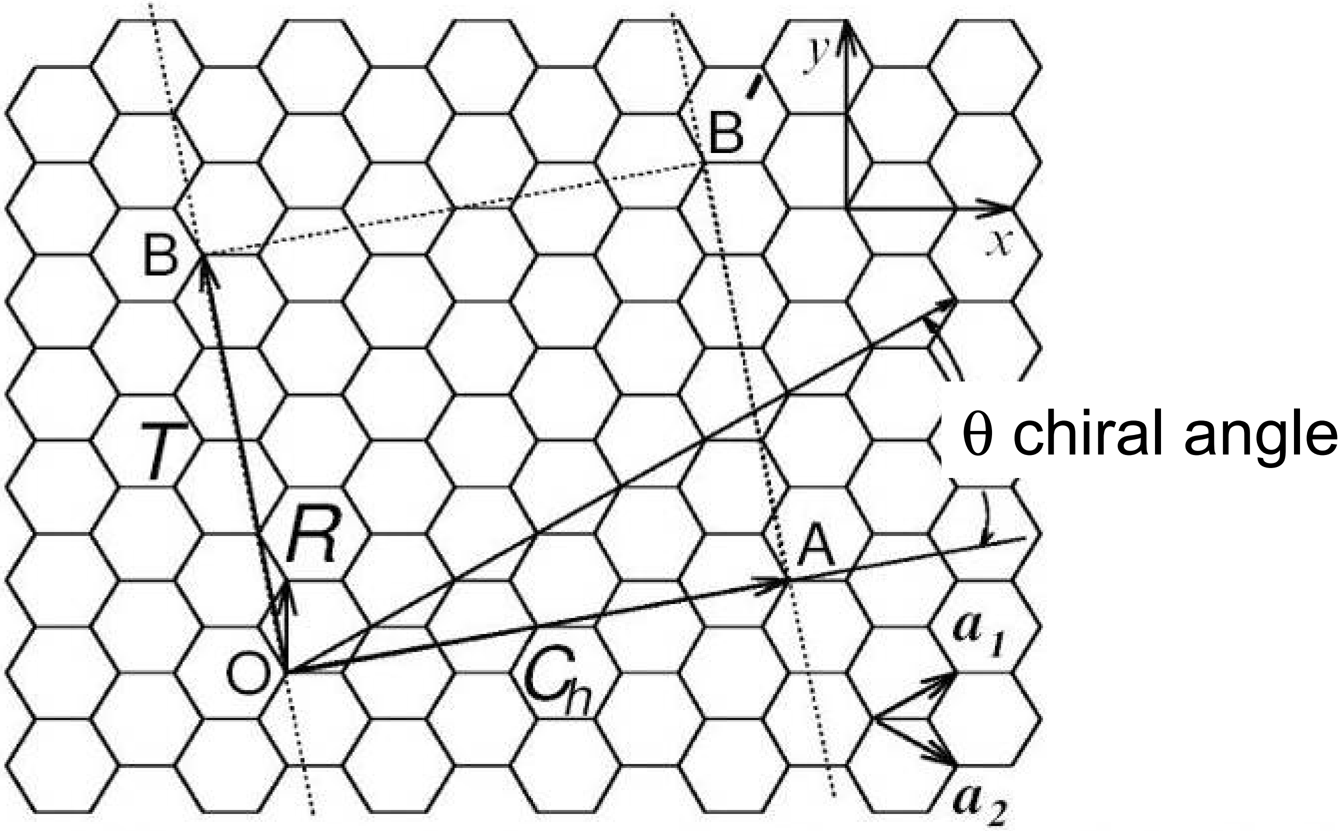
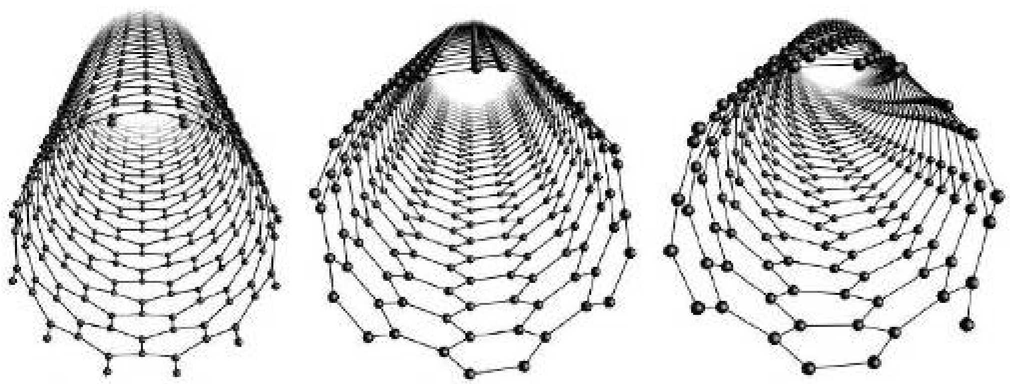


Figure 1. The unrolled honeycomb lattice of a nanotube. When we connect lattice sites O and A, and sites B and B', a nanotube can be constructed. $\overrightarrow{OA}$ and $\overrightarrow{OB}$ define the chiral vector $\mathbf{C}_h$ and the translational vector $\mathbf{T}$ of the nanotube, respectively. The rectangle $OAB'B$ defines the unit cell for the nanotube. The figure is constructed for an $(n, m) = (4, 2)$ nanotube [2].

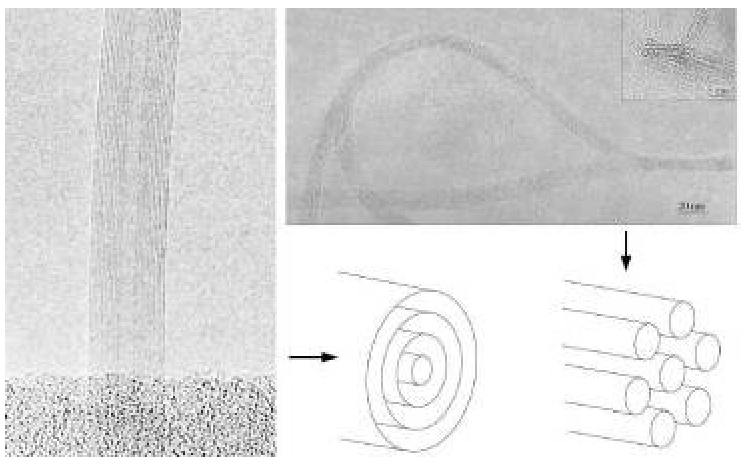
From: Dresselhaus/Ecklund, Advances in Physics **49**, 705 (2000)

Single-wall (SWNTs), multiwall (MWNTs) and bundles

zigzag armchair helical

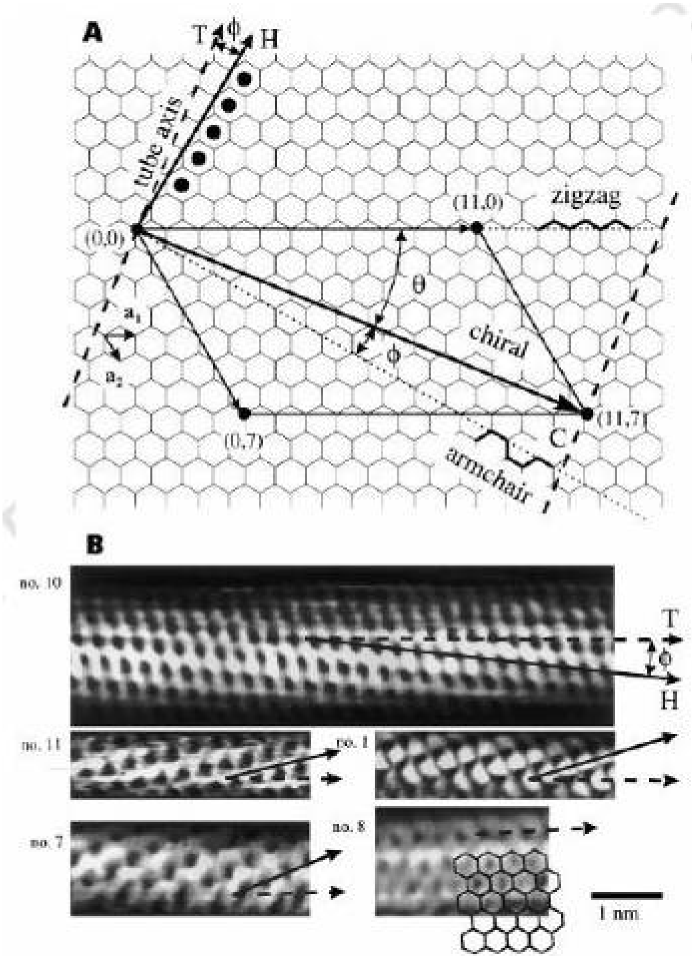


(12,0) (6,6) (6,4)



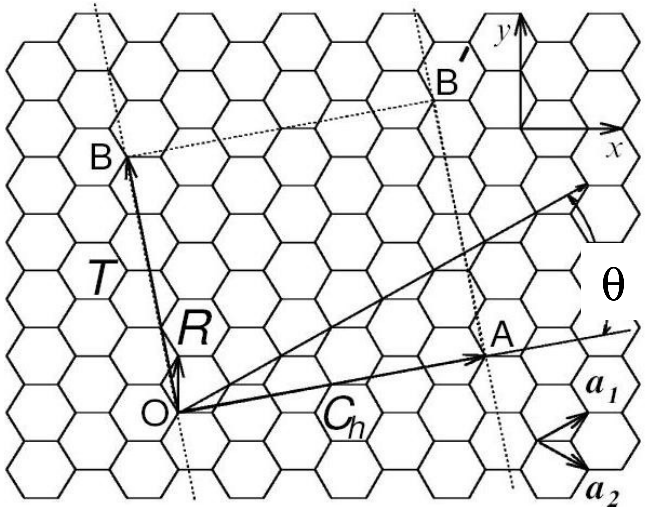
bundle

multiwall



(Wildöer *et al., Nature* **391**, 59 (1998))

The indices (n,m) define completely the nanotube



⇨ $d_t = |\vec{C}_h| / \pi = \frac{a}{\pi}\sqrt{n^2 + nm + m^2}$ diameter

⇨ **T** $= t_1 \mathbf{a}_1 + t_2 \mathbf{a}_2$, $t_1 = (2n+m)/N_R$ and $t_2 = (2m+n)/N_R$

N_R largest common divisor of (2n+m) and (2m+n)

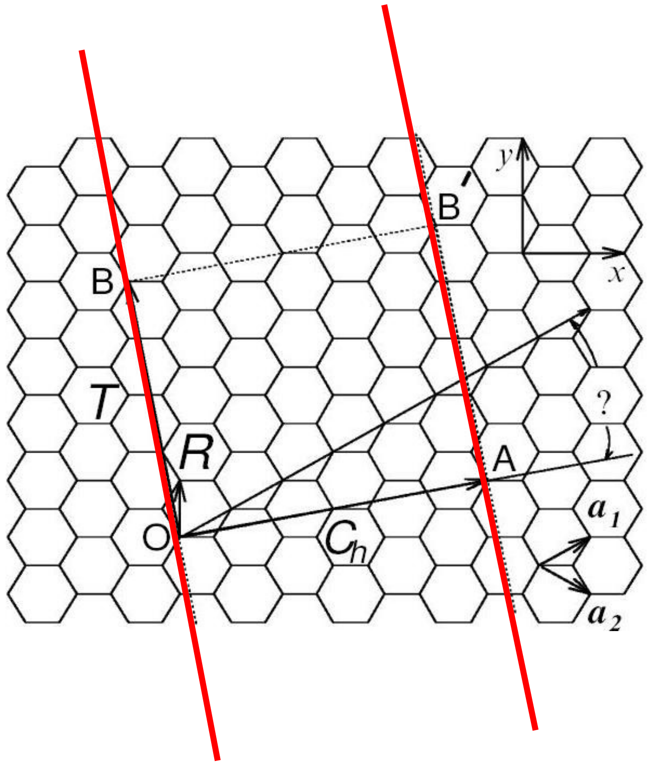
⇨ $t = |\vec{T}| = \sqrt{3}a\sqrt{n^2 + nm + m^2}/N_R$ Unit cell length along axis

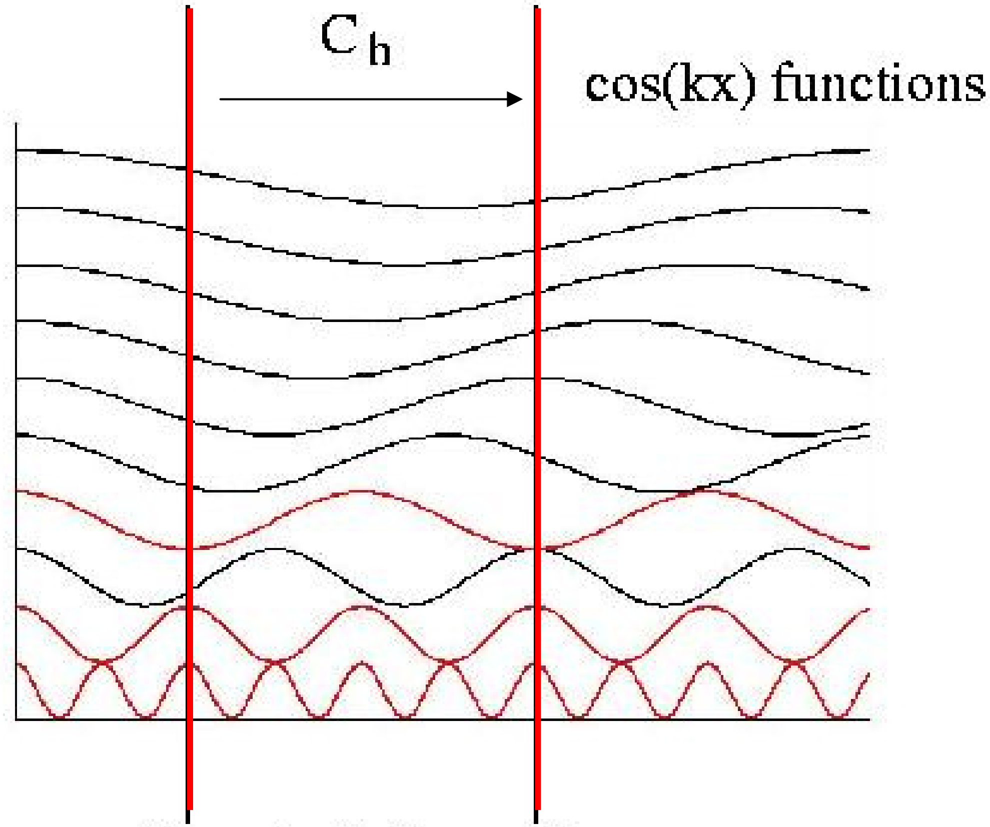
⇨ $N_C = 4(n^2 + nm + m^2)/N_R$ Number of atoms in unit cell

⇨ $\cos\theta = \frac{\vec{C}_h \cdot \vec{a}_1}{|\vec{C}_h||\vec{a}_1|} = \frac{2n+m}{2\sqrt{n^2 + nm + m^2}}$ Chiral angle (cosine)

Zone-folding and k-vector selection (schematic)

The wavefunctions must be single-valued around the tube circumference:

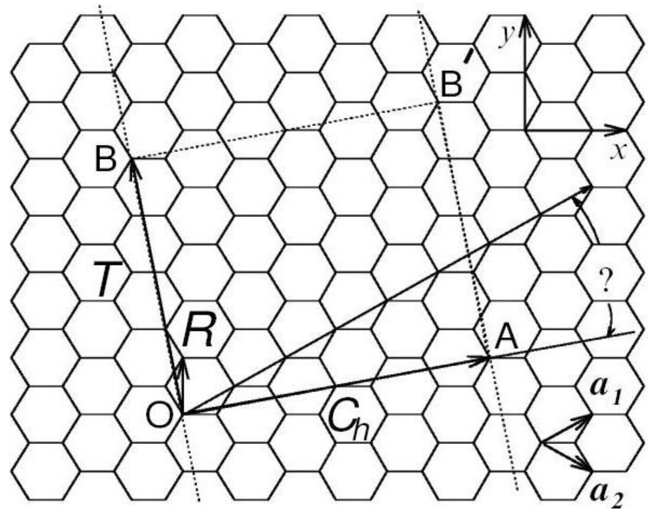




In red: $k.C_h = q\,2\pi$ (or $q\lambda = C_h$)

Graphene bands selection and folding

The boundary conditions around the tube circumference (wavefunctions single valued) imposes the condition



$$\Phi_{\mathbf{k}}(\mathbf{r}+\mathbf{C}_h)=e^{i\mathbf{k}.\mathbf{C}_h}\Phi_{\mathbf{k}}(\mathbf{r})=\Phi_{\mathbf{k}}(\mathbf{r})$$

Bloch relation

$$\mathbf{k.C}_h = 2\pi \text{ q, q integer}$$

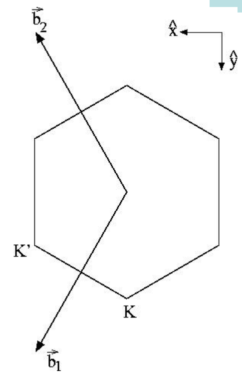
Defines parallel lines of allowed **k**-vector with $2\pi/C_h$ spacing in reciprocal space:

$$\mathbf{k}^{\text{allowed}} = q\,\mathbf{B}_1 + k_\perp\,\mathbf{B}_2\,,\ -\pi/T < k_\perp < \pi/T$$

$\mathbf{A}_1=\mathbf{C}_h$ and $\mathbf{A}_2=\mathbf{T}$

$\mathbf{B}_i{}^*\mathbf{A}_j=2\pi\,\delta_{ij}$

Nanotubes can be either metallic or semiconducting



$\mathbf{K} = (\mathbf{b}_1 - \mathbf{b}_2)/3$ (corner of the hexagonal BZ with zero gap)

$\mathbf{C}_h = n\mathbf{a}_1 + m\mathbf{a}_2$ and $\mathbf{a}_i.\mathbf{b}_j = 2\pi\,\delta_{ij}$

$\mathbf{K.C}_h = 2\pi\,(n\text{-}m)/3$ => if (n-m)=3l, l integer then **K** is allowed

(n-m)=3l, l integer => metallic tubes
(n-m)=3l±1 => semiconducting tube

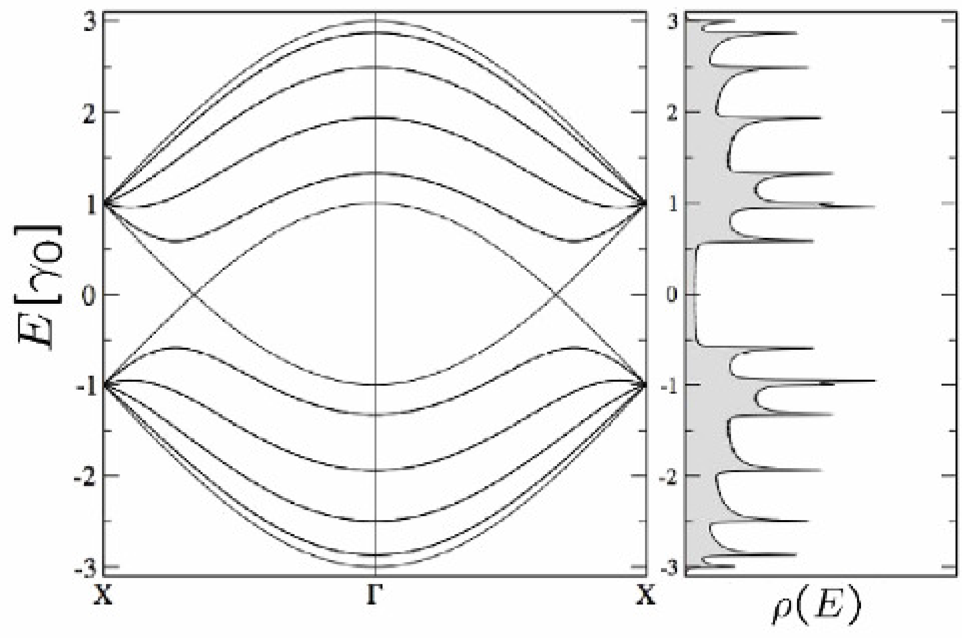
- Armchair tubes are always metallic
- Zigzag (n,0) tubes are metallic if n multiple of 3
  => e.g. (12,0) is metallic, (13,0) is semiconducting

1/3 of tubes are metallic, 2/3 are semiconducting

Hamada, Sawada, Oshiyama, PRL 68, 1579 (1992)
Saito, Fujita, Dresselhaus, Dresselhaus, PRB 46, 1804 (1992)

Armchair (n,n) tubes (π–π* band folding model)

(5,5) tube

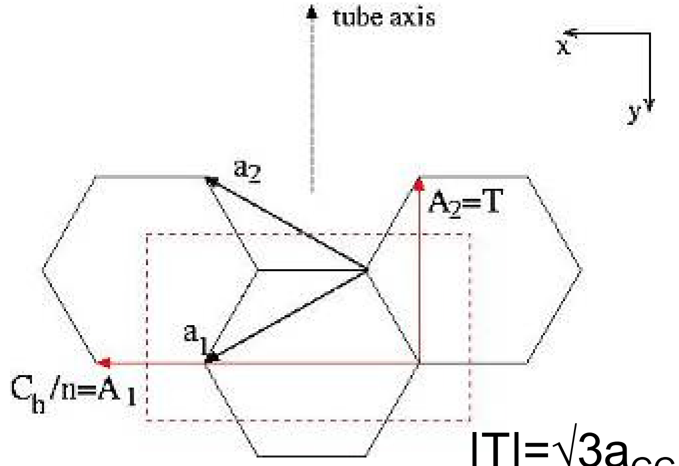


(X=π/T)

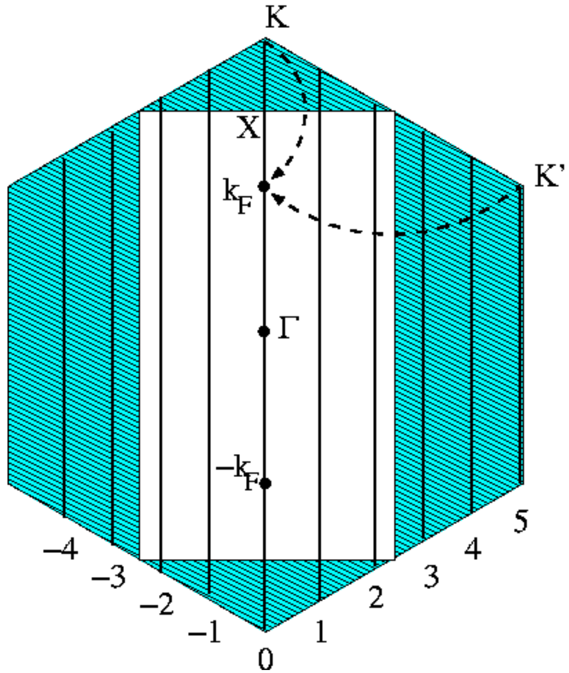
In armchair tubes, k_F occurs at 2/3 of ΓX (where K is folded)

In a metallic tube, at the Fermi level:

$$\rho(\varepsilon_F) = 2\sqrt{3}a_{cc}/(\pi\gamma_0|\vec{C}_h|)$$



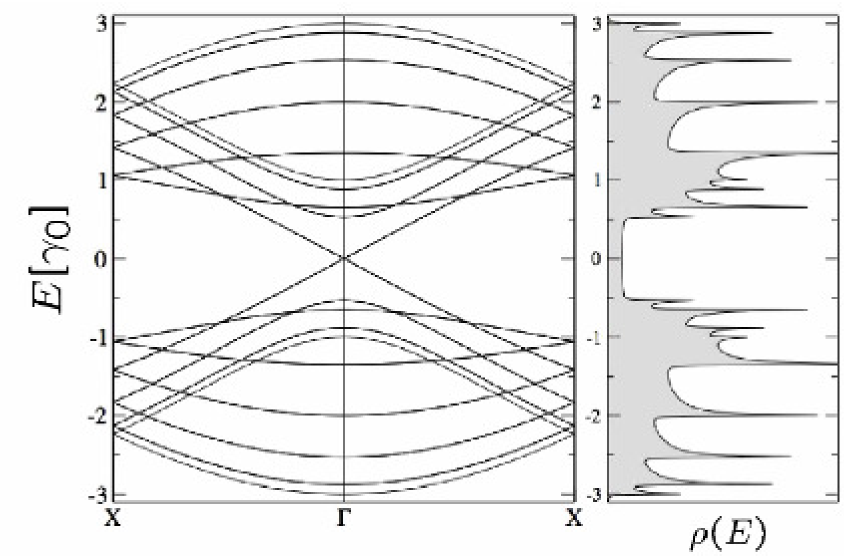
$|T|=\sqrt{3}a_{CC}$



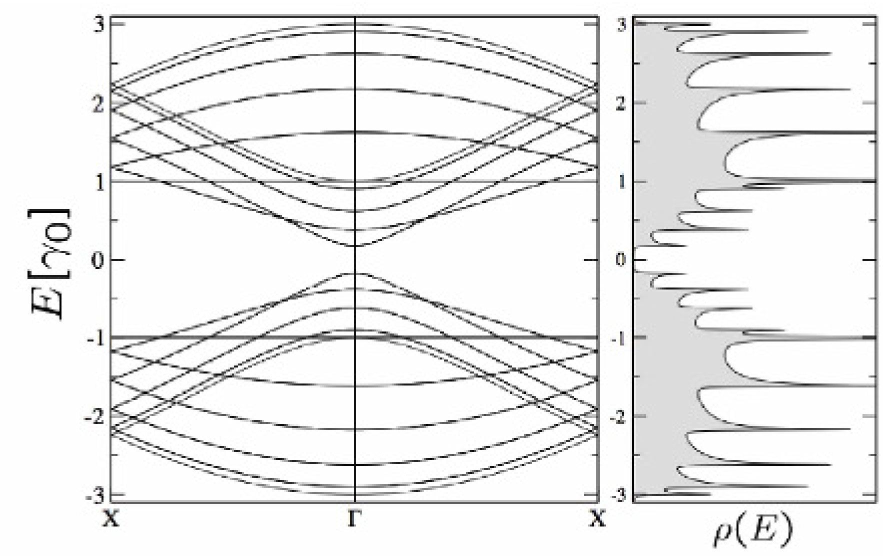
In white, BZ associated with **C_h**/n and **T**

Zigzag (n,0) tubes (π–π* band folding model)

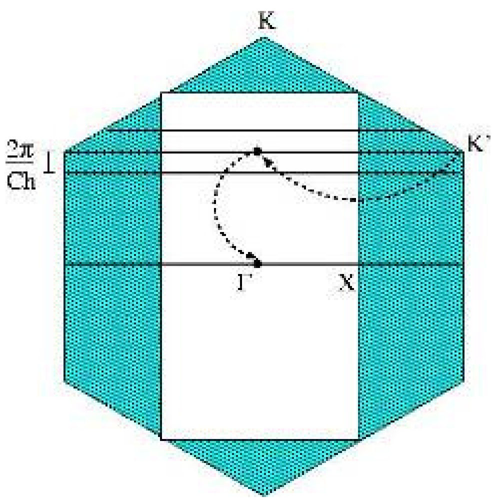
(9,0) tube



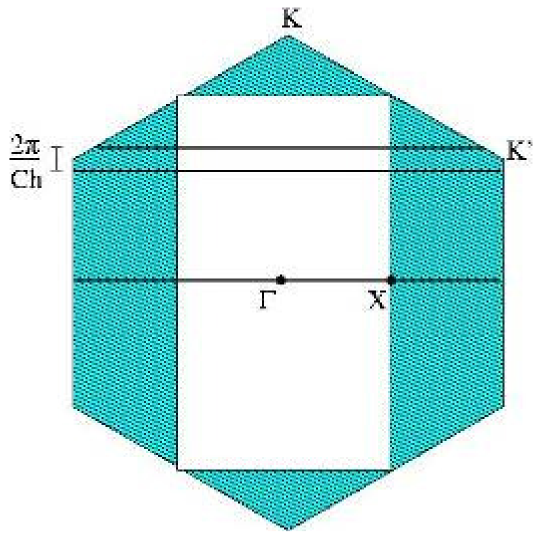
(10,0) tube



The band gap (zero when n is multiple of 3) is at zone-center Γ

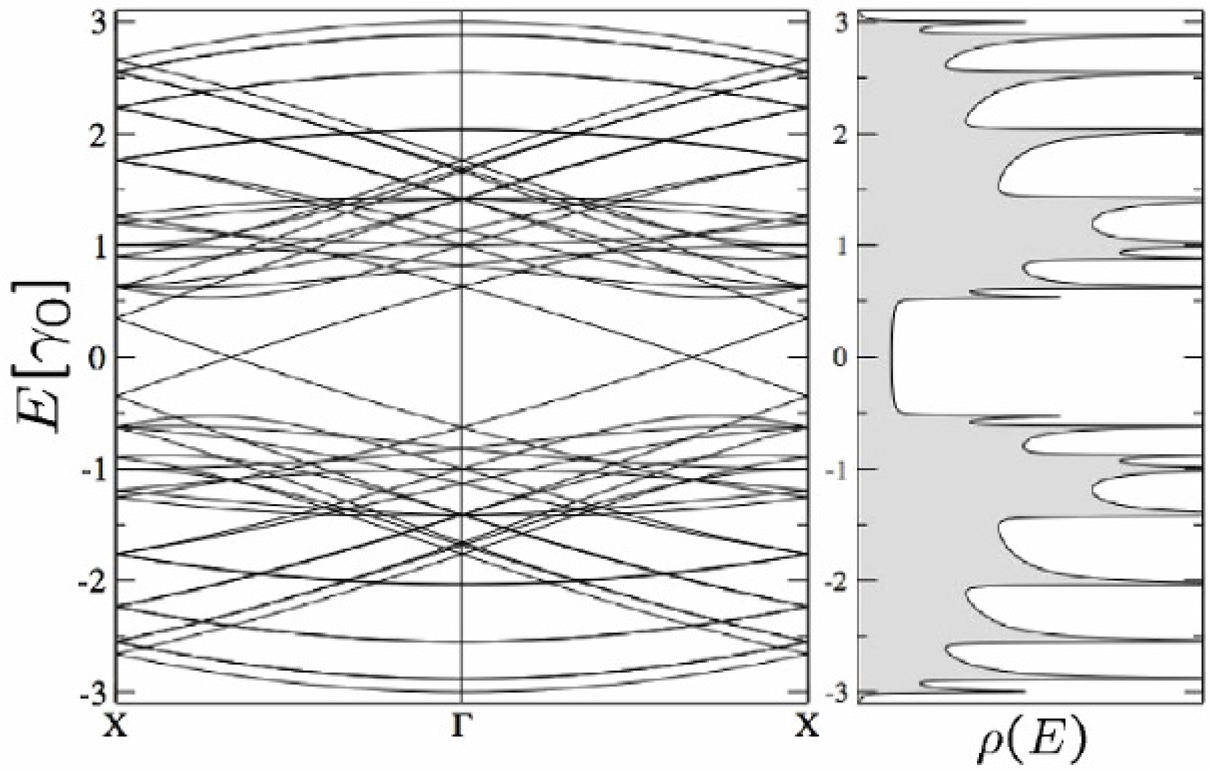


A few allowed lines around K



Chiral tubes (π–π^* zone-folding model)

(8,2) tube



In the general case of achiral (n≠m≠0) tubes, the band gap (which can be zero if n-m=3l) occurs at Γ or 2/3 ΓX as well

Charlier, Lambin, PRB **57**, R15037 (1998)
Reich, Thomsen, PRB **62**, 4273 (2000)

Comparing band folding and ab initio calculations

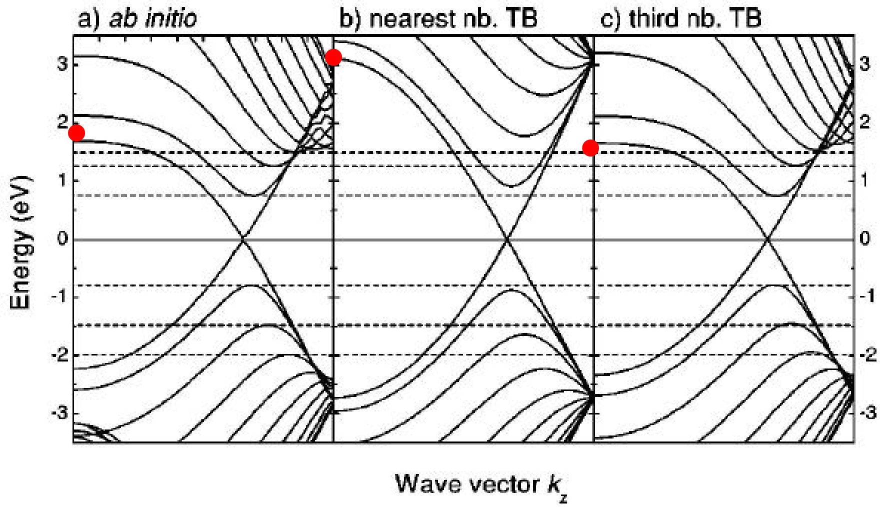


FIG. 4. Band structure of a (10,10) armchair nanotube. (a) *Ab initio* calculation. (b) Nearest-neighbor tight-binding calculation with $\gamma_0 = -2.7$ eV. (c) Third-nearest-neighbor tight-binding calculation with parameters obtained from a fit to the optical energy range; see Table I. The dashed lines denote *ab initio* calculated energies of the singularities in the density of states.

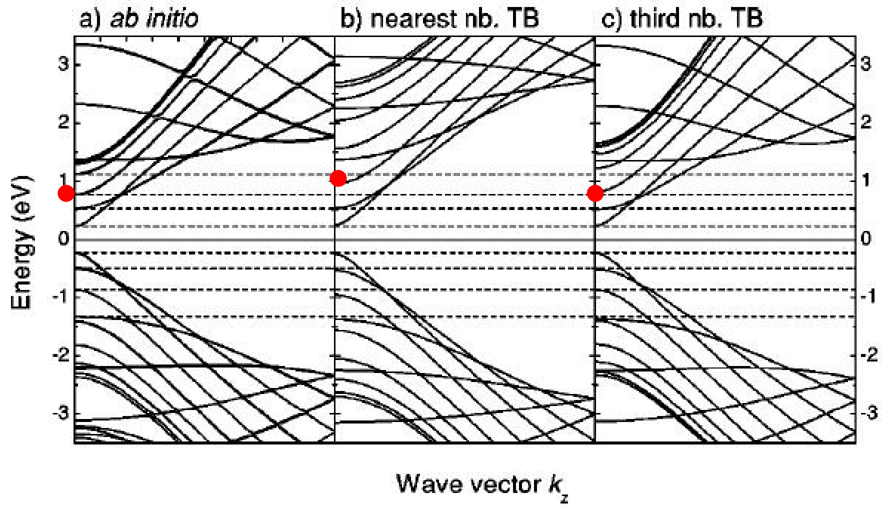


FIG. 5. Band structure of a (19,0) zigzag nanotube. (a) *Ab initio* calculation. (b) Nearest-neighbor tight-binding calculation with $\gamma_0 = -2.7$ eV. (c) Third-nearest-neighbor tight-binding calculation with parameters obtained from a fit to the optical energy range; see Table I. The dashed lines denote *ab initio* calculated energies of the singularities in the density of states.

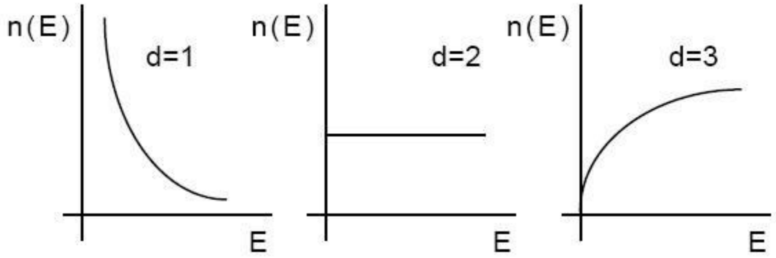
TB=tight-binding=band folding of graphene as described with TB calculations

From: Reich, Maultzsch, Thomsen, Ordejon, PRB **66**, 035412 (2002)

Electronic density of states (eDOS) in 1,2 and 3D. van Hove singularities

The density of states $\rho(E)$ - which gives the number of states $\rho(E)dE$ per energy span dE - is proportional to $1/\sqrt{E}$ close to a band extrema ($dE/dk=0$) in 1D

Behavior of DOS close to a band extremum or saddle-point ($\nabla_{\mathbf{k}}(E)=0$) in 1D, 2D and 3D:



(graph from: Loiseau et al., Understanding carbon Nanotubes, Lecture Notes in Physics **677**, Springer-Verlag, 2006)

$\nabla_{\mathbf{k}}(E)=0$ defines the « critical points » in the BZ with:

$$\rho(E) \sim \int dS/|\nabla_k E|$$

(S=constant energy surface):

$$\rho(E) = \frac{2}{\Omega}\sum_q \sum_{s=\pm} \int dk\ \delta(E - E_q^s(k)) \quad (k=k_z=k_{||})$$

$$= \frac{2}{\Omega}\sum_q \sum_{s=\pm} \int dk\ \delta(k - k_{qs}) \times \left|\frac{\partial E_q^s(k)}{\partial k}\right|^{-1}$$

with: k_{qs} roots of $E-E^s_q(k)=0$. Using linearity of bands (see next page), one finds:

$$\left|\frac{\partial E_q^s(k)}{\partial k}\right|^{-1} = \frac{2}{\sqrt{3}\gamma_0 a}\frac{\left|E_q^s(k)\right|}{\sqrt{(E_q^s)^2(k) - \varepsilon_{qs}^2}}$$

with: $\varepsilon_{qs} = \pm\pi\gamma a_{CC}|3q-n+m|/C_h$

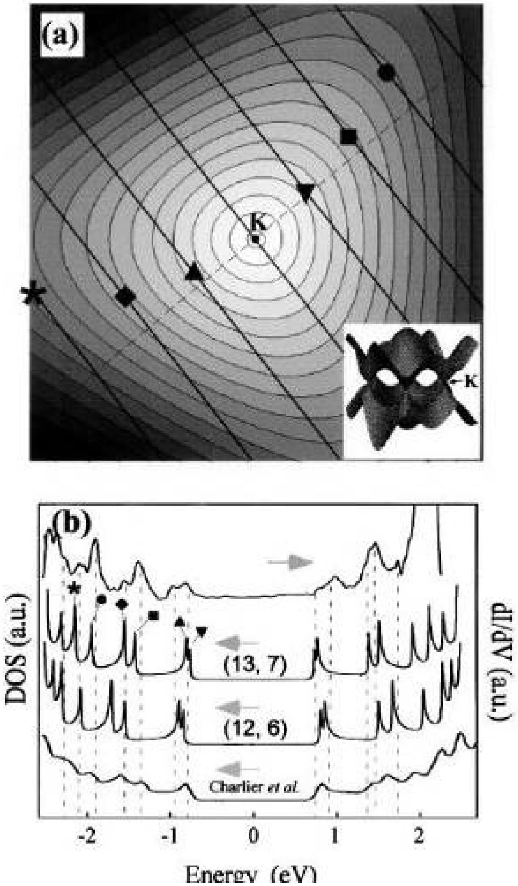
If $(3q-n+m)=0$ (metallic tube), $\varepsilon_{qs}=0$ and $\rho(E=0)=2a/\pi\gamma|C_h|$ ($a=\sqrt{3}\, a_{CC}$)

The $1/\sqrt{E}$ divergencies in the eDOS are called the van Hove singularities.

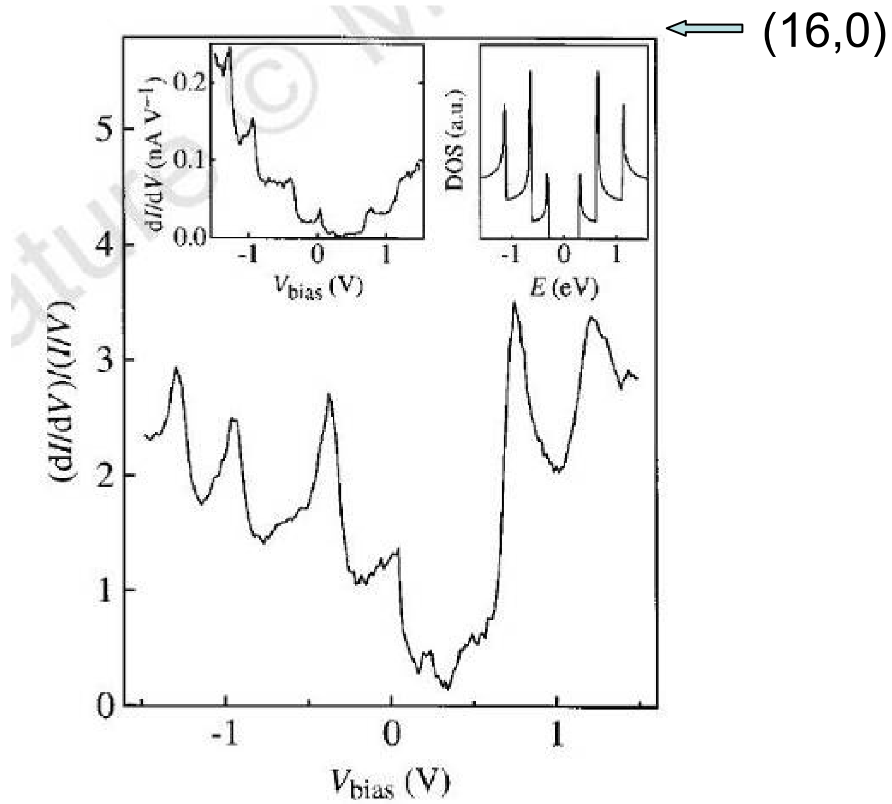
Reminder: $\delta(g(x)) = \Sigma_{x0}\ \delta(x-x_0)/g'(x_0)$, x_0 roots of $g(x)=0$

Experimental STS measurements of eDOS

The eDOS is roughly proportional to (dI/dV)(V/I) in a STS measurement. This has allowed experimental verification of the vHs structuration of the eDOS of nanotubes



Kim *et al.*, PRL **82**, 1225 (1999)

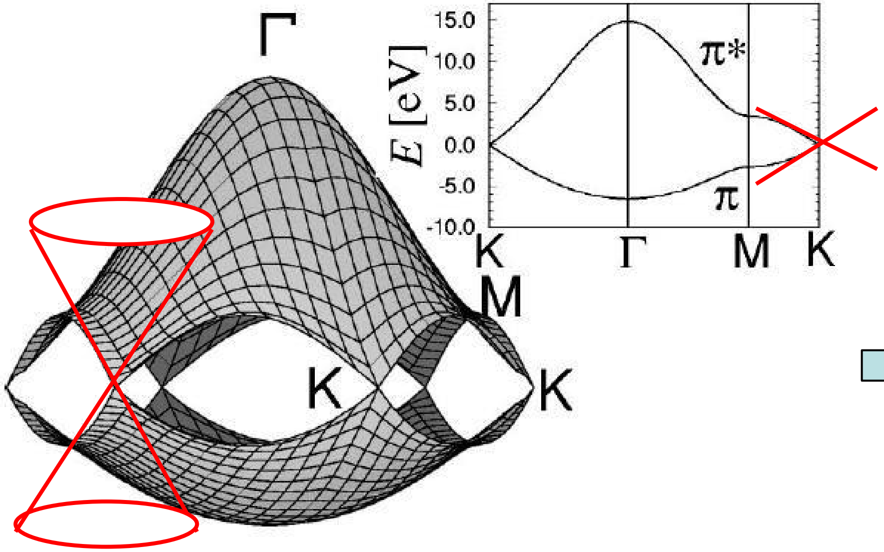


Wildöer *et al.*, *Nature* **391**, 59 (1998)

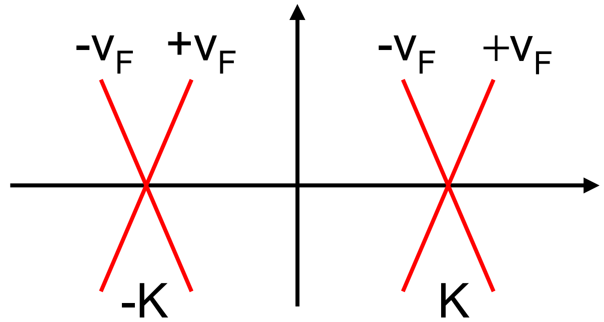
+ Odom *et al.*, *Nature* **391**, 62 (1998); Venema *et al.*, PRB **62**, 5238 (2000); Avramov *et al.*, CPL **370**, 597 (2003)

The approximation of linear bands around k_F and its consequences

(Fig: Saito et al., PRB **61**, 2981 (2000))



Armchair tube



In the vicinity of **K**=(**b**$_1$-**b**$_2$)/3, one writes: **k**=**K**+δ**k**=(δk_x, $4\pi/3a+\delta k_y$) and a Taylor expansion of Eq.(1) yields for a metallic tube:

$$E_{\pm}(\delta k) \simeq \pm\frac{\sqrt{3}a}{2}\gamma_0 \parallel \delta\vec{k} \parallel \quad \xrightarrow{v=\nabla_k E/h} \quad v_F = \sqrt{3}a\gamma_0/2\hbar = \tfrac{3}{2}a_{cc}\gamma_0/\hbar \quad (\sim 8.10^5 \mathrm{ms}^{-1})$$

In the case of a semiconducting tube, the Taylor expansion of (1) with the condition

$\delta\vec{k} = (2\pi/|C_h|)(q \pm 1/3)\vec{\kappa_\perp} + k\vec{\kappa_\parallel}$ yields:

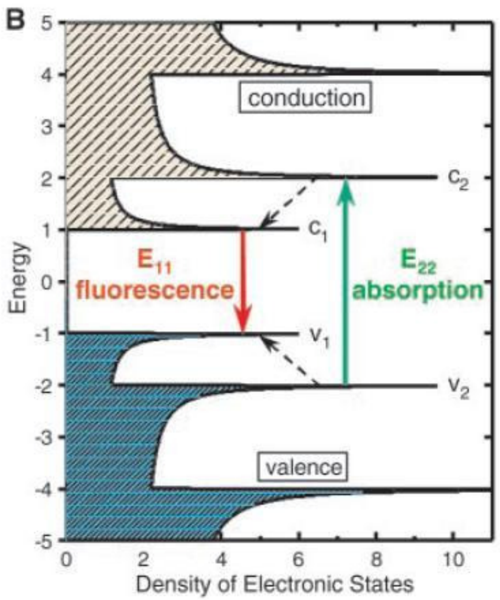
$$E_q^{\pm}(\delta\vec{k}) \simeq \pm\frac{\sqrt{3}a}{2}\gamma_0\sqrt{\left(\frac{2\pi}{|\vec{C_h}|}\right)^2\left(q\pm\frac{1}{3}\right)^2 + k^2}$$

First paper (graphene): Wallace, PR **71**, 622(1947).

Linearity of bands : the band gap is inversely proportional to diameter

From the previous equation, in a semiconducting tube:
(d_t tube diameter)

$$\boxed{\Delta E_g^1 = \frac{2\gamma_0 a_{cc}}{d_t}}$$

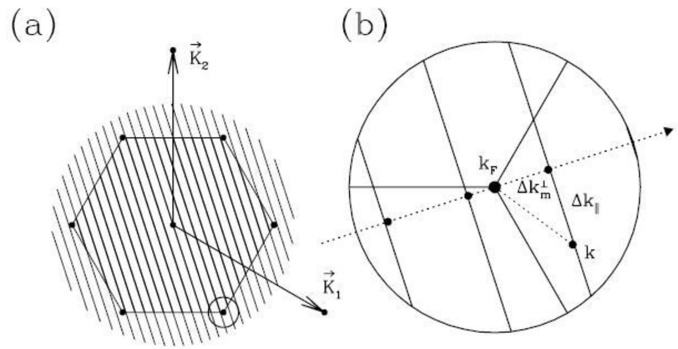


(Fig: Bachilo et al., Science **268** (2002))

Similar results can be obtained for energy gaps between vHs in the eDOS => universal eDOS functional form

In particular, E_{22}/E_{11} ($E_{11}=\Delta E^1_g$) ratio is equal to two in this « linear approximation ».

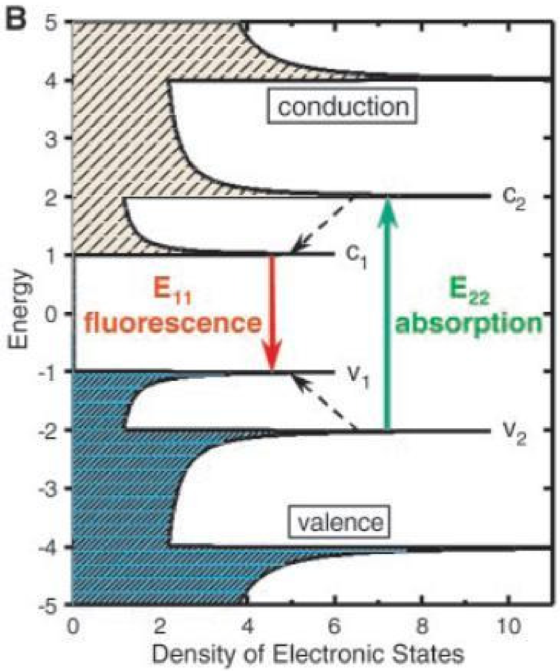
These results hold for large tubes (and therefore small gaps) so that the « allowed lines » come close to the K-points in the BZ zone.

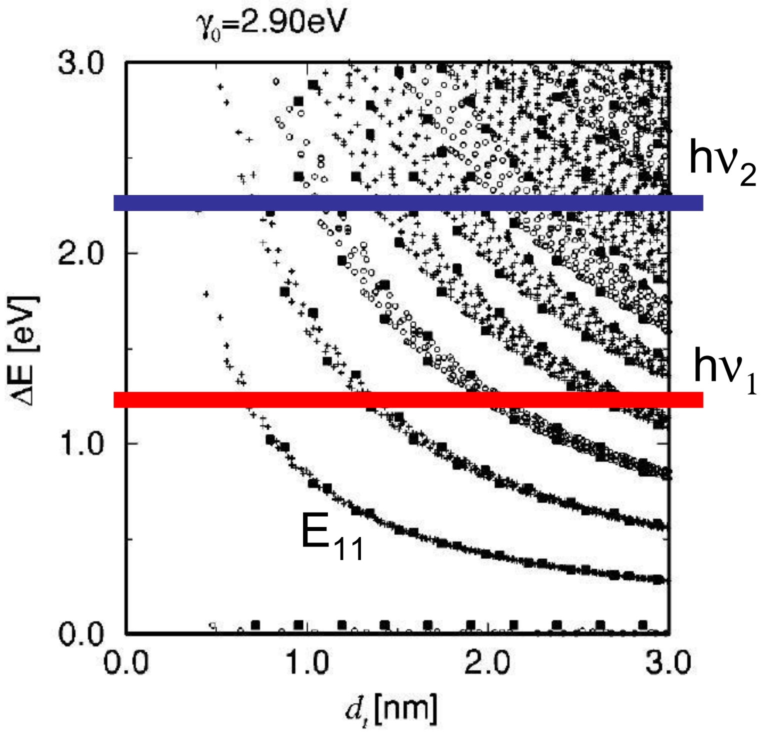


Ref: White and Mintmire, *Nature* **394**, 29 (1998); Mintmire and White, PRL **81**, 2506 (1998)

Optical properties, van Hove singularities (vHs) and Kataura's plot (see Lecture by T. Hertel)

Early interpretation of optical data identified the absorption peaks with the energy difference E_{ii} between vHs in the unoccupied and occupied bands.

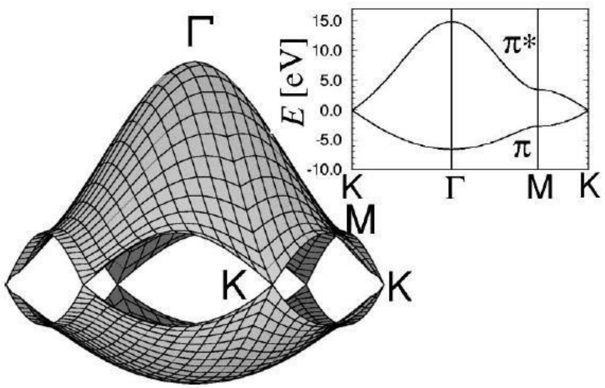




For high energy transitions, braodening of the $1/d_t$ lines: the linear approximation not so exact and the transition energies depend also on the (n,m) indices.

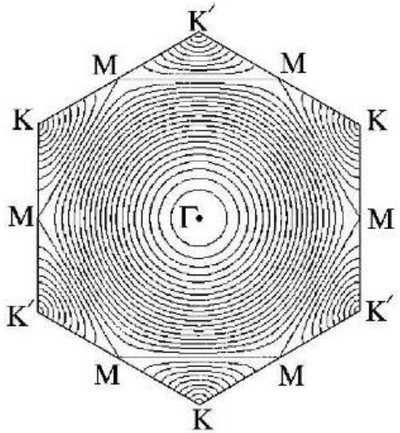
Kataura et al., Synthetic Metal **103**, 2555 (1999); Saito et al., PRB **61**, 2981 (2000); Popov+Henrard, PRB **70**, 115407 (2004); etc.

Trigonal warping and broadening of E_{ii} lines in Kataura's plot

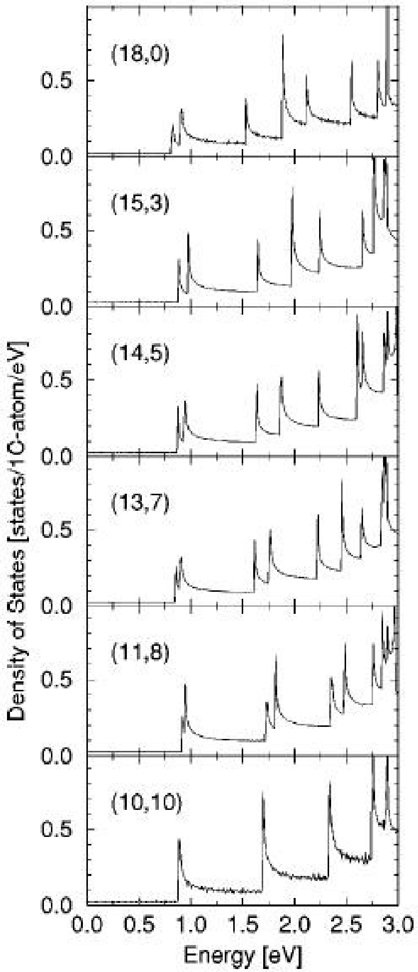


Energy bands are not linear away from E_F

$E(k) \neq \pm v_F\,|k-k_F|$ if $E(k) - E_F > \varepsilon$



Iso-energy levels around K become trigonal when crossing MM lines.



Observe splitting of vHs peaks (maximum for metallic zigzag tubes).

(nanotubes of similar diameter 1.3-1.4 nms)

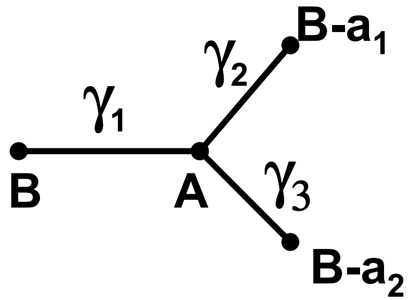
As a result, E_{ii} do not depend only on tube diameter for high-energy transitions ! Complicate the reading of the Raman, optical, etc. data.

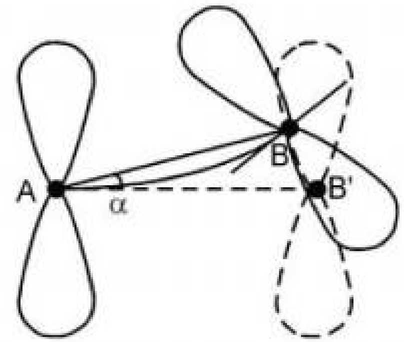
Ref: Saito et al., PRB **61**, 2981 (2000)

Deviations from band folding: curvature effects

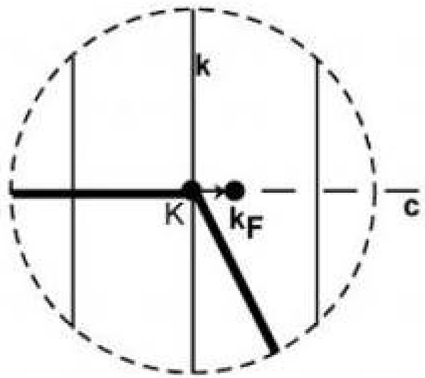
The **k**-point at which valence and conduction bands do overlap in graphene is conditioned by the annulation of:

$$H_{AB}(\mathbf{k}) \sim \gamma_1 + e^{-ik.a1}\,\gamma_2 + e^{-ik.a2}\,\gamma_3$$





(Fig: Ouyang *et al., Science* 2001)



In planar graphene, $\gamma_1 = \gamma_2 = \gamma_3 = \gamma_0 \Rightarrow$ bands cross at K

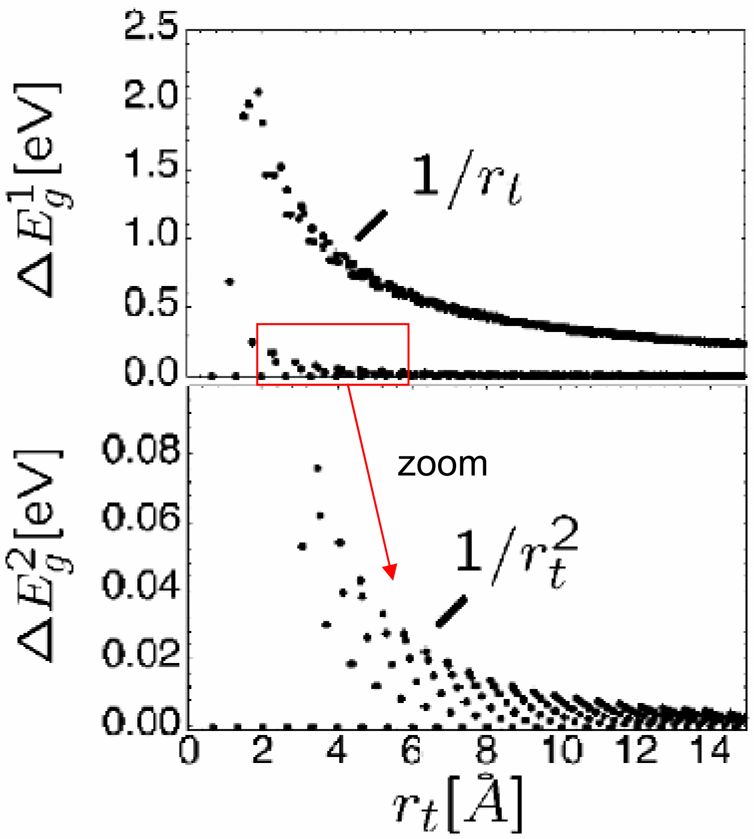
In nanotube, bonds parallel and perpendicular (or with an angle) with the tube axis are non-equivalent => $\gamma_1 \neq \gamma_2 \neq \gamma_3$

➡ The **k**-point which cancels $H_{AB}(\mathbf{k})$ is shifted away from the zone-corners **K**.

Armchair tube : this point is shifted along an allowed line => remains metallic
Metallic non-armchair: shifted off the allowed lines => opens a small band gap

Curvature effects and secondary gaps in « metallic » non-armchair tubes

Theory



$$\Delta E_g^2 = \frac{3\gamma_0 a_{cc}^2}{4 d_t^2}$$

X cos(3θ)

(chiral angle; θ=0 for zigzag)

Kane and Mele, PRL **78**, 1932 (1997)
Kleiner and Eggert, PRB **64**, 113402 (2001)

Experiment

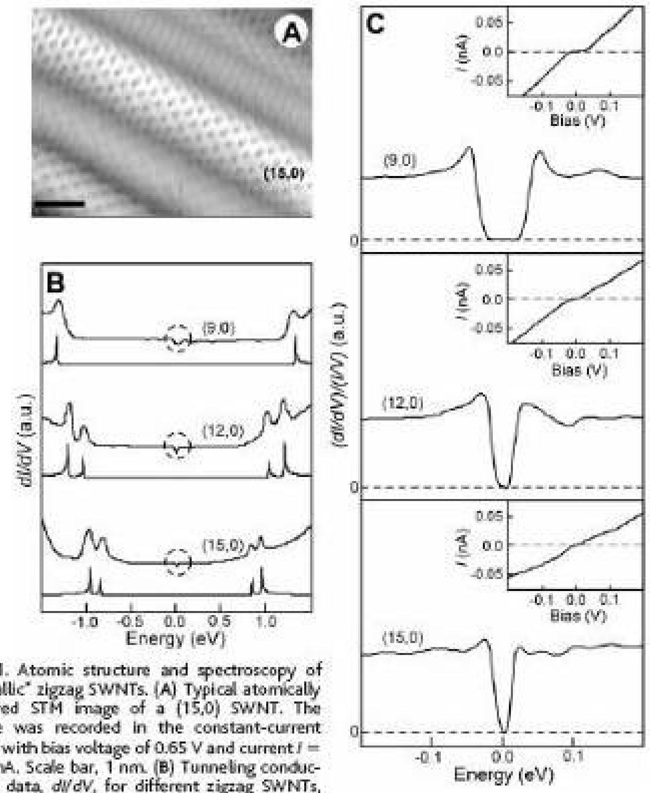
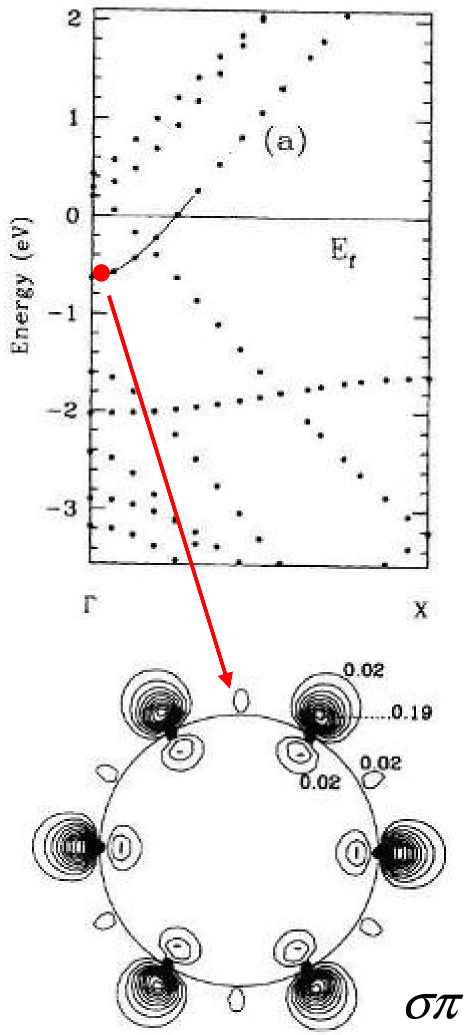


Fig. 1. Atomic structure and spectroscopy of "metallic" zigzag SWNTs. (A) Typical atomically resolved STM image of a (15,0) SWNT. The image was recorded in the constant-current mode with bias voltage of 0.65 V and current I = 0.15 nA. Scale bar, 1 nm. (B) Tunneling conductance data, dI/dV, for different zigzag SWNTs, with corresponding calculated DOS shown below each experimental curve (a.u., arbitrary units). The data were recorded as the in-phase component of I directly by a lock-in amplifier with a 7.37-kHz modulation signal of 2 mV peak-to-peak amplitude to the bias voltage. The new features in the low-energy region of the (9,0), (12,0), and (15,0) tubes are highlighted by dashed circles. (C) Typical high-resolution normalized conductance $(dI/dV)/(I/V)$ curves and measured I-V curves (insets) for (9,0), (12,0), and (15,0) tubes, respectively. The $(dI/dV)/(I/V)$ curves were calculated from dI/dV and I-V data.

Ouyang *et al., Science* **27**, 292 (2001)

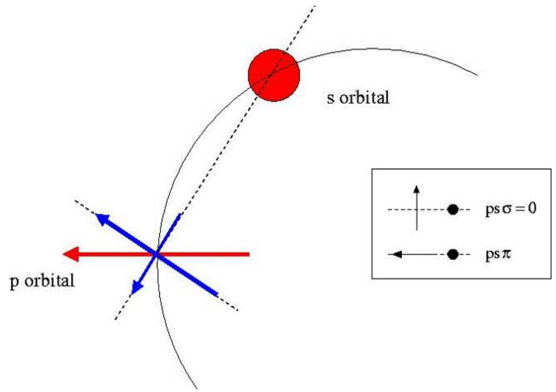
σ–π hybridization in small diameter tubes

C(6,0)

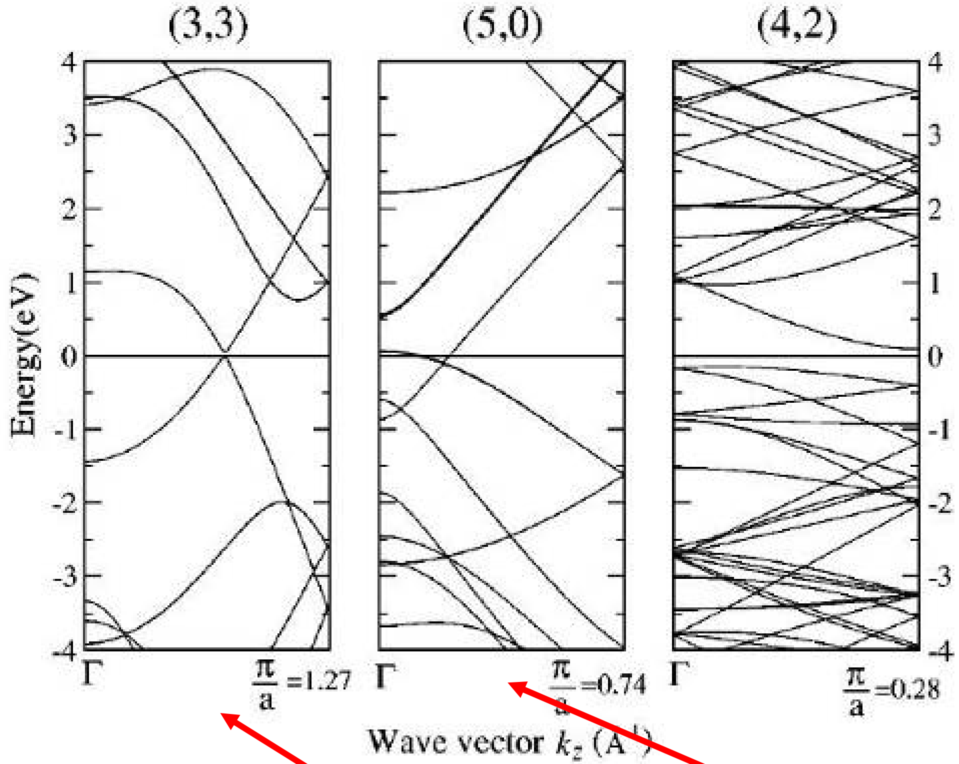


σπ hybrid

Blase et al., PRL **72**, 1878 (1994)



Ordejón et al. PRB **66**, 155410 (2002)



The effect is small for amchair, important for zigzag

A (ridiculously) tiny note on symmetries in nanotubes

T. Vukovic *et al.*, Phys. Rev. B **65**, 045418 (2002).

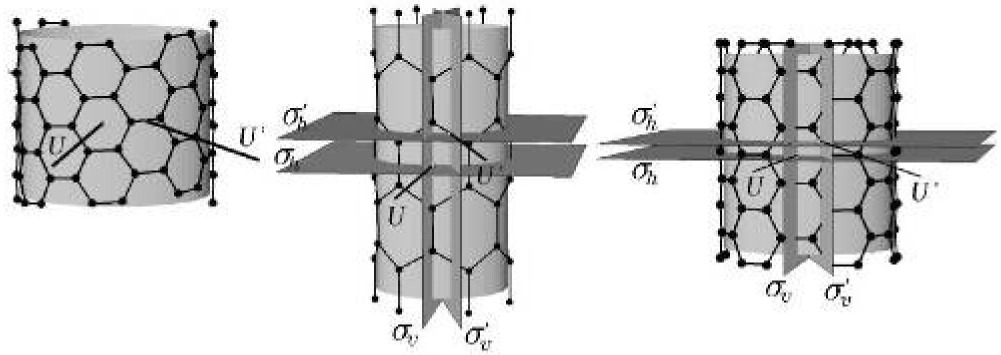
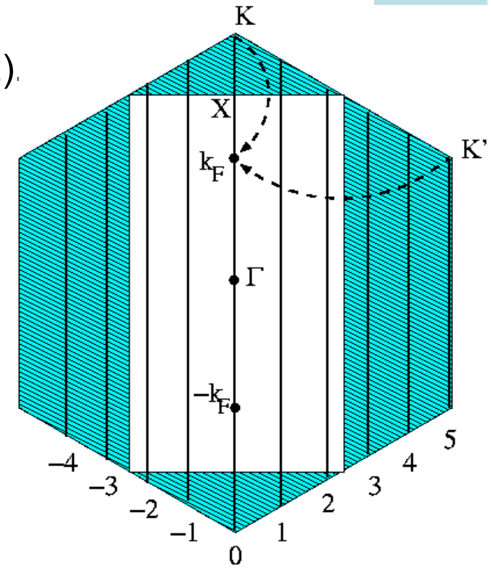


FIG. 2. Symmetries of the single-wall nanotubes: (8,6), (6,0), and (6,6). The horizontal rotational axes U and U' are symmetries of all the tubes, while the mirror planes (σ_v and σ_h), the glide plane σ_v', and the rotoreflectional plane σ_h' are symmetries of the zigzag and armchair tubes only. The line groups are $\mathbf{T}^{21}_{148}\mathbf{D}_2$ for (8,6), and $\mathbf{T}^{1}_{12}\mathbf{D}_{6h}$ for the other two tubes.



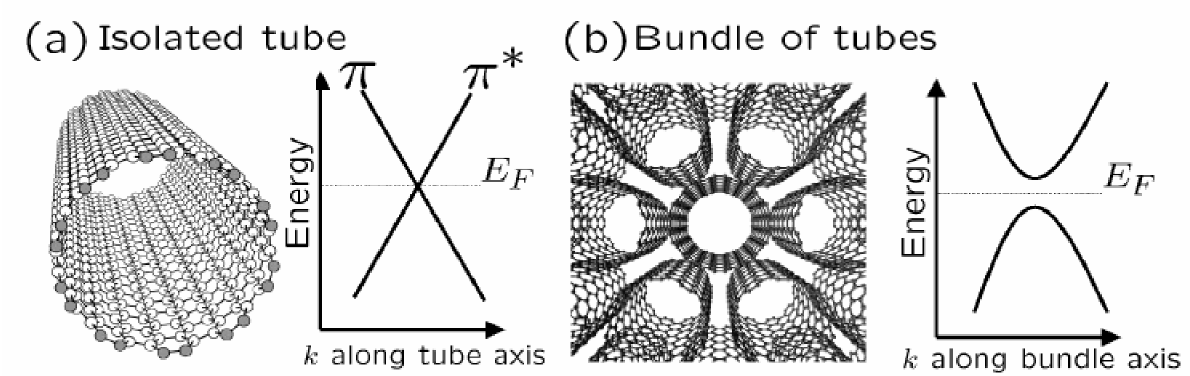
Translation group => « $k_{||}$ Bloch vector » are quantum numbers
The allowed line « q »-index is also the azimuthal quantum number
(exp(iqθ) phase factor « around » the tube).
In achiral tubes (zigzag, armchair) reflexion and glide planes => parity number

A perturbation mixes two subbands with (α,β) quantum number if it has an γ-component such that $\alpha-\beta\pm\gamma=0$

The effect of a perturbation (squashing, tube-tube interaction, substrate-tube Interaction, $\sigma-\pi$ hybridization, electric field (gate voltage), optical perturbation, etc. can be analyzed with group theory to know which bands will be affected.

Lammert+Crespi, PRB **61**, 7308 (2000); Yang+Han, PRL **85** , 154 (2000); Kim+Chang, PRB **64**, 153404 (2001); etc.

Tube-tube interactions in a SWNTs bundle



Tube-tube interactions break the tube symmetries => π–π* repulsion and opening of a gap (~0.1 eV) in metallic (10,10)

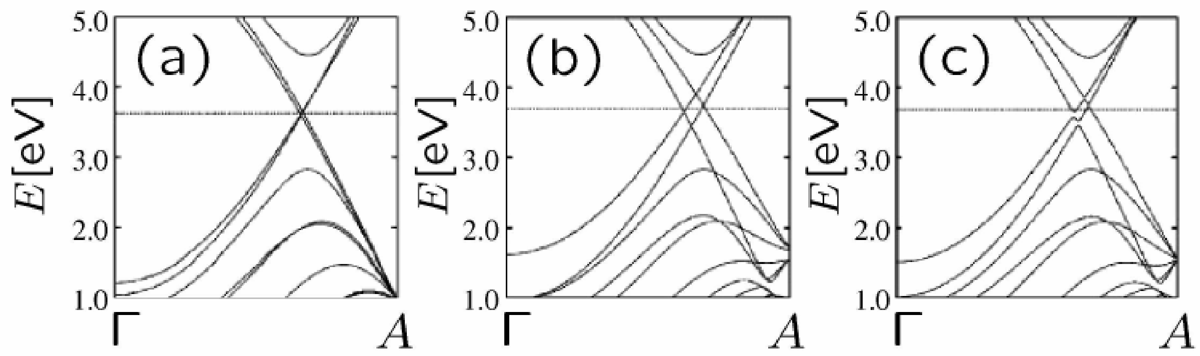
Delaney *et al., Nature* **391**, 466 (1998)
Charlier *et al*., Europhys. Lett. **29**, 43(1995)
Reich et al., PRB **65**, 155411 (2002)

Bundling can also reduce gap of semiconducting tubes through « lateral » dispersion.

(Exp: Ouyang *et al*., *Science* **292**, 702 (2001)

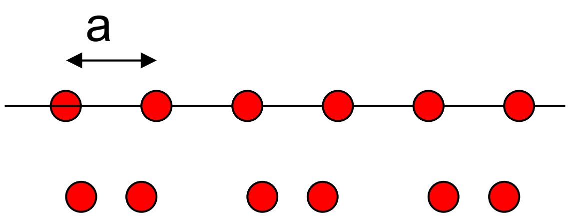
Bilayer tube: rotating the inner tube (5,5)@(10,10)

Tube-tube interaction in a MWNTs



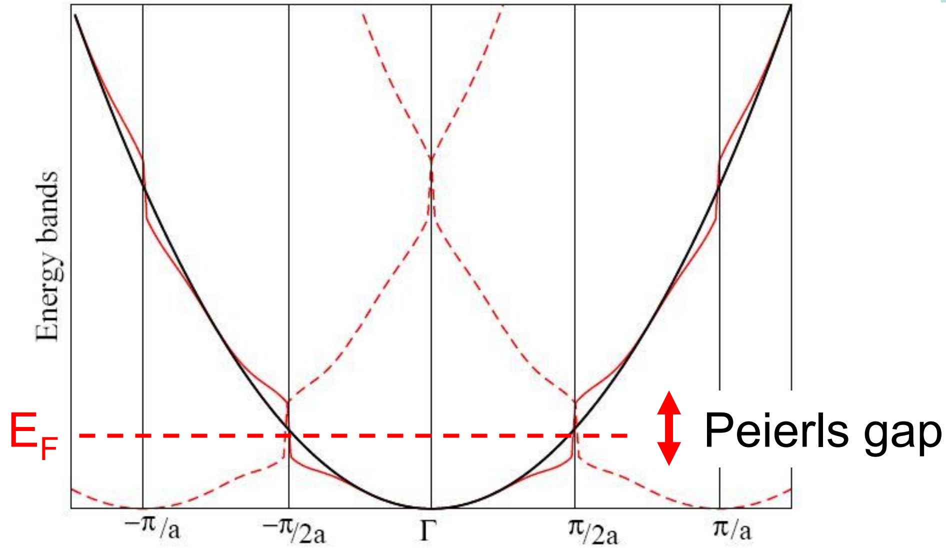
Kwon and Tománek, PRB **58**, 16001 (1998)
Lambin *et al*., Comput. Matter Sci. **2**, 350 (1994)

Peierls distorsion in CNTs



Dimerization of an atomic chain with one electron per site.

(Kittel, Intro to Solid State Physics)



General theorem : metallic 1D systems are unstable at low temperature with respect to $2k_F$ momentum lattice perturbation. It always happens : the real question is « what is the transition temperature T_{CDW} ?? » (CDW=charge density wave)

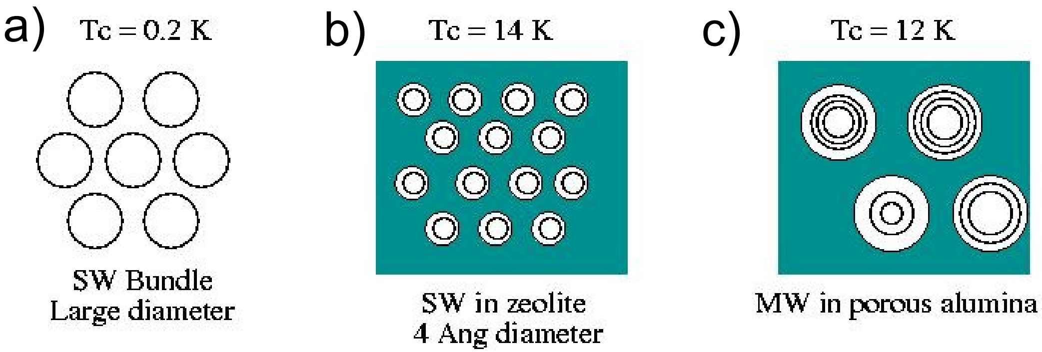
The transition temperature depends exponentially on the strength of the electron-phonon deformation potentiel associated with the lattice deformation
=> difficult to calculate it with accuracy and large dispersion in theoretical values.

(Mintmire *et al*., PRL 1992; Saito *et al*., APL 1992; Figge *et al*., PRL 2001; De Martino and Egger, PRB 2003; Sédéki *et al*., PRL 2002)

T_{CDW} much smaller than room temperature except for small diameter nanotubes (D = 4 Å) with room temperature transition predicted by ab initio calculations.

(Bohnen et al., PRL 2004; Connétable et al., PRL 2005.

Superconductivity (SC) in CNTs



Experiments:

a) Kociak *et al.*, PRL 2001
b) Tang *et al.*, Nature 2001
c) Haruyama *et al.*, PRL 2006

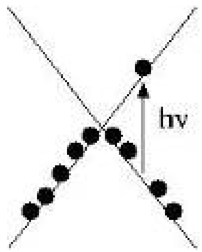
Theory:
Sédéki *et al.*, PRB 2002;
Kamide *et al*. PRB 2003;
González 2002; Alvarez+González, 2003;
González+Perfetto, 2005.

The superconducting order is difficult to observe in 1D systems for several reasons:

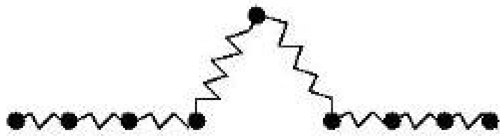
- Competition with the CDW instability **:** the electron-phonon coupling channels can either induce CDW order or SC order (cf. BCS approach). Both instabilities are notcompatible. (T.Giamarchi, Quantum physics in One Dimension, Oxford Science Pubs., 2004)
- Long-range order at finite T is impossible in 1D systems due to thermal fluctuations (see: Mermin and Wigner, PRL 17, 1133 (1966))
- Even at T=0 K, quantum fluctuations due to quantum phase slip induce a non-zero resistivity unless T=0 => smooth decay of resistivity below T_C (Langer+Ambegaokar, PR **164**, 498 (1967))

T_C increases with decreasing diameter: strength of the e-ph coupling increases due to curvature effects ($pp\pi$ => $pp\sigma$ coupling) and normalisation (1/D and 1D^2 dependence) (**Benedict et al., PRB 52, 14935 (1995))**
Bundling favors superconductivity as it reduces the 1D character (better screening of the electron-electron repulsion, Josephson coupling between tubes, etc.)

Luttinger liquid transition in CNTs (effect of electron-electron interactions)



Standard picture of an electronic excitation: one electron is excited, the others do not move.



Can you really pull on a mass without moving the other ones ?

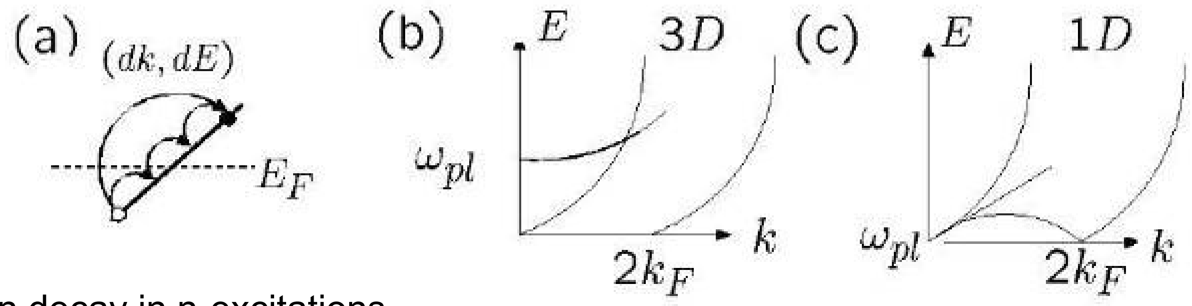
Coulomb interaction is strong in electron gaz: scattering of one electron should affect collectively all the others

Collective excitations: plasmons, spinons

In 3D systems, Pauli principle says that close to E_F, single-particle excitations are possible:

=> $1/\tau^{ee} \approx (E-E_F)^2$ (Fermi liquid theory, Nozières-Pines, 1964).

This is no longer true in 1D: low energy excitations are collective excitations (plasmons, spinons)
=> Luttinger liquid behavior (Tomonaga (Nobel prize 19xx), Luttinger)

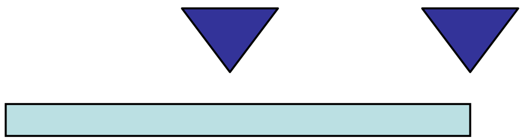


Single excitation decay in n-excitations (linearity of bands makes conservation of energy and momentum preserved)

In 3D, single particle and plasmons are decoupled.
In 1D, they are resonant.

Signature of the Luttinger liquid behavior: transport properties

Tunneling rate into LL is suppressed at low voltage and temperature as a power law.



Tunneling at center and end of nanotube

$\rho(\varepsilon) \sim |\varepsilon-\varepsilon_F|^{\alpha}$ quasiparticule eDOS $(k_BT<<V)$

$dI/dV \sim \int d\varepsilon\, \rho(\varepsilon)\, df_{FD}(\varepsilon - eV)/dV \sim |V|^{\alpha}$

$\rho(\varepsilon) \sim T^{\alpha}$ quasiparticule eDOS $(V << k_BT)$

(complicated scaling law in the intermediate regime)

$\alpha_{end} = (1/g-1)/4$

$\alpha_{bulk} = (1/g+g-2)/8$

The exponent α depends on the electron-electron interaction parameter g (0<g<1 repulsive interactions; g=1 Fermi liquid)

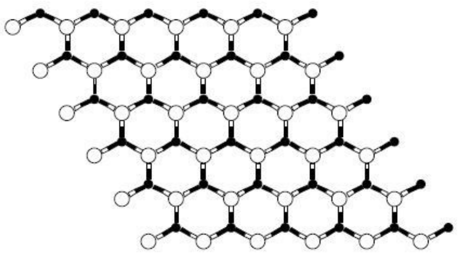
However, difficult to distinguish at low T the LL behavior with Coulomb blockade effects (Egger+Gogolin, PRL **87**, 066401 (2001))

Egger and Gogolin, PRL **79**, 5082 (1997); Kane *et al* PRL **79**, 5086 (1997); Egger, PRL **83**, 5547 (1999); Eggert PRL **84**, 4413 (2000); Lopez-Sancho *et al*. PRB **63**, 165419 (2001); Mora et al. PRB, submitted (2006) M. Bockrath *et al*., *Nature* **397**, 598 (1999); O. M. Auslaender *et al*., *Phys. Rev. Lett.* **84**, 1764 (2000); Z. Yao, et al., *Nature* **402**, 273 (1999); Gao *et al* PRL **92**, 216804 (2004); Lee *et al*. PRL **93**, 166403 (2004)

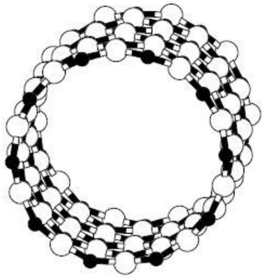
Note: A spin/charge density waves separation has been evidenced as well (Lee *et al*. PRL **93**, 166403 (2004)), providing a strong proof for a possible LL behavior.

Planar and nanotubes *h*-BN structures

BN planar sheet



BN zigzag tube



$$det\begin{pmatrix} \mathcal{H}_{AA}-E & \mathcal{H}_{AB} \\ \mathcal{H}_{BA} & \mathcal{H}_{BB}-E \end{pmatrix} = 0$$

$H_{AA} \neq H_{BB}$

At **K**, where H_{AB}=0, opening of an <u>ionicity gap</u>: $E_{gap} = |H_{AA}-H_{BB}|$

Arnaud et al., PRL 96, 026402 (2006)

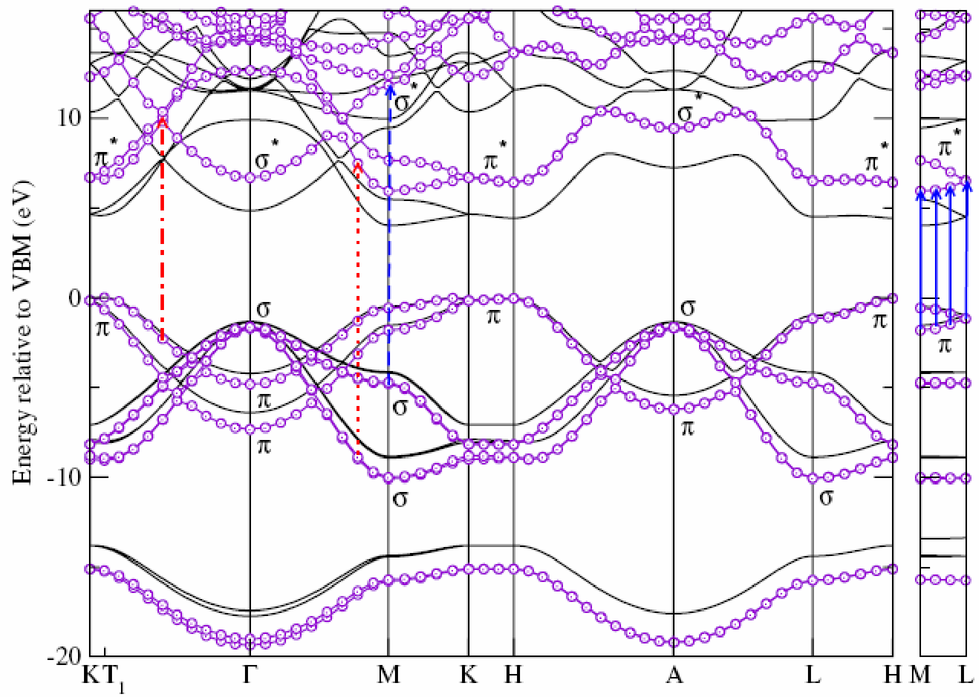
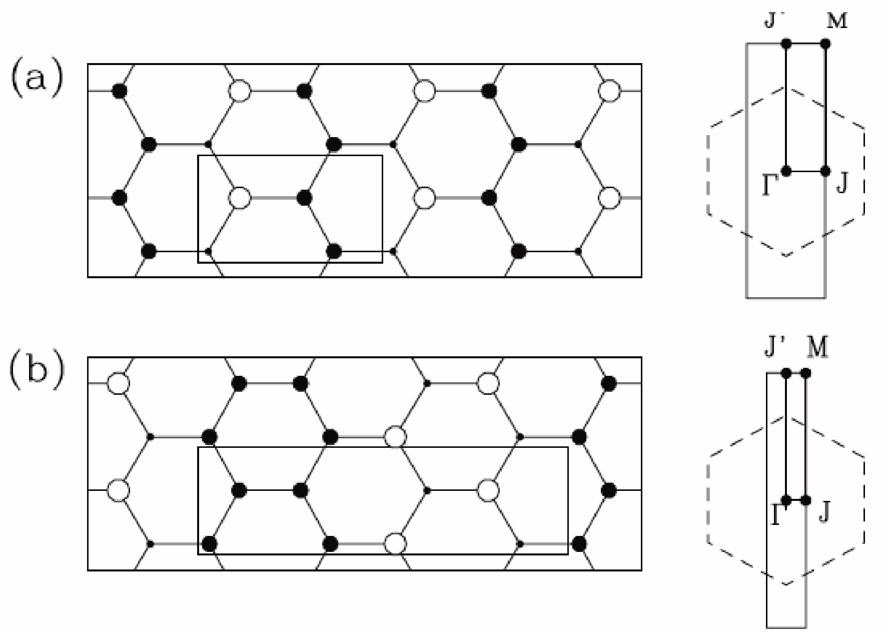


FIG. 1 (color online). Calculated electronic band structure along high-symmetry lines for bulk hexagonal boron nitride. The thin solid lines display the LDA results while the solid lines with open circles show the *GW* approximation results. The energy scale is relative to the top of the valence band maximum (VBM) located at the T_1 point near K along the Γ-K high-symmetry direction.

BN tubes synthesis: Loiseau et al. PRL **76**, 4737 (1996); Chopra et al., Science **269**, 966 (1995); etc.

BN tubes theory: Rubio et al., PRB **49**, 5081 (1994) ; Blase *et al*., Europhys.Lett. **28**, 335 (1994); ibid. PRB 51, 6868 (1995).

Photoluminescent *h*-BC_2N systems

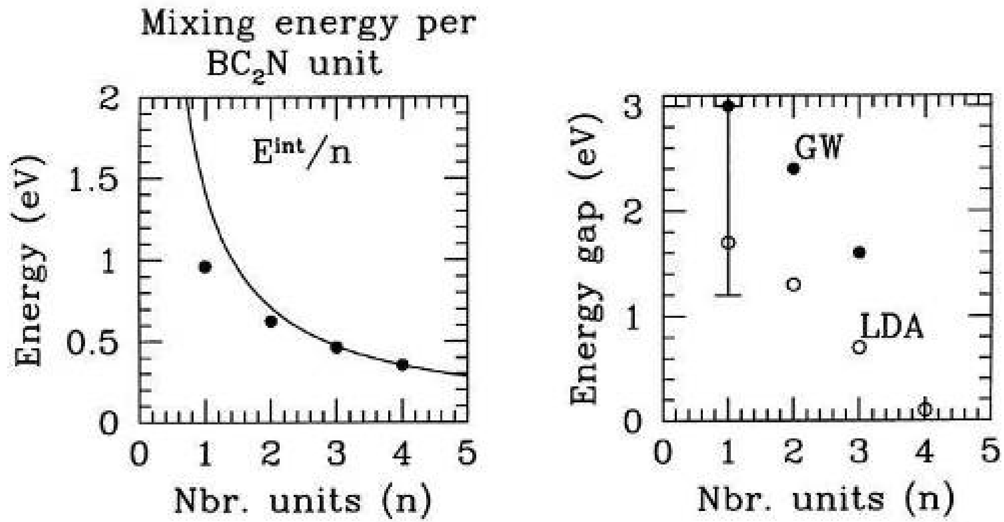


Experimental evidence of visible range photoluminescent character.

Watanabe et al., PRL **77**, 187 (1996)
Chen et al., PRL **83**, 2406 (1999)

Theory: tendency towards segregation in large pure C or BN domains.

Liu, *et al*., PRB **39**, 1760 (1988).
Blase et al., APL **70**, 197 (1997)
Blase et al., Appl. Phys. A **68**, 293 (1999)
Mazzoni et al., PRB **73**, 073108 (2006)

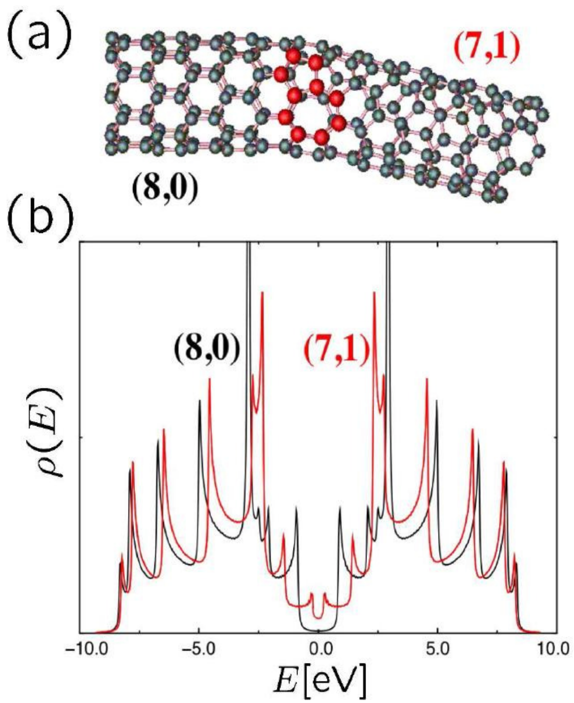


Upon segregation, band gap goes from zero to 3 eV (visible range 1.8-3 eV)

Blase et al., Appl. Phys. A **68**, 293 (1999)
Mazzoni et al., PRB **73**, 073108 (2006)

Addenda 1: tube-tube junctions

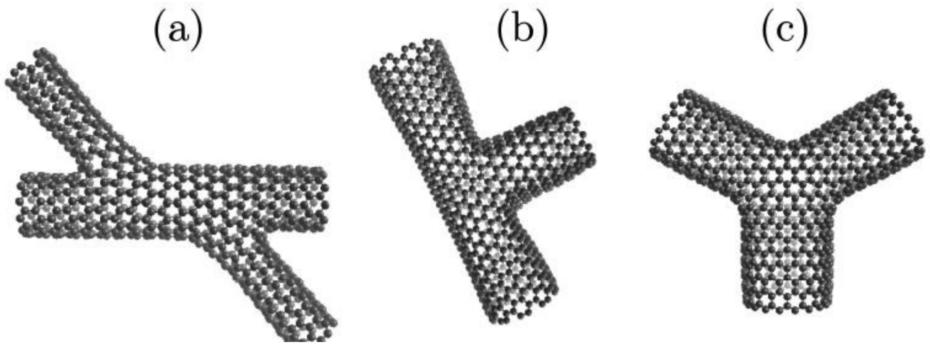
(5,7) defects can "branch" two tubes with different chiralities, that is different band gaps => rectifying junctions



Dunlap, PRB 1994; Lambin et al., CPL 1995; Saito et al., PRB 1996; Chico et al., PRL 1996.

Exp: Yao *et al*., *Nature* **402**, 273 (1999); Ouyang *et al*., Science 291, 97 (2001).

Electron beam irradiation can weld tubes to form X,Y or T junctions.



Terrones *et al*., Science 2000; PRL 2002; Meunier *et al*., APL 2002.