Introduction and Theoretical Background

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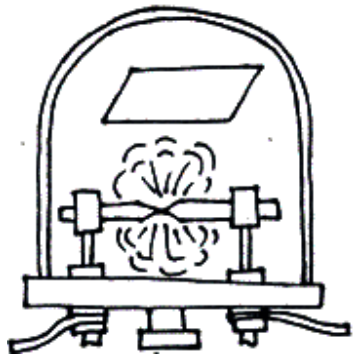
Outline

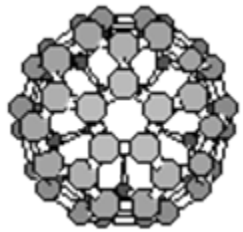
- Introduction
  - **Nanocarbon pioneers**
  - **What is so special about carbon nanotubes?**
- Theoretical tools
  - **Computational tools**
  - **State of the art of computer simulations**
- Morphology
  - **Relationship to graphite**
  - **Classification of nanotubes**
  - **Structure of nanocarbons and Euler's Theorem**
  - **Polymorphism due to high-temperature synthesis**
  - **Carbon and non-carbon nanotubes**
- Electronic structure and conductivity
  - **Morphology determines conductivity**
  - **Band structure and density of states**
  - **Ballistic and diffusive conduction**
  - **Beware of contacts!**
- Mechanical properties
  - **Graphitic sp^2 versus diamond sp^3 bonding**
  - **High Young's modulus**
- Chemical and thermal resilience, and thermal conductivity
  - **Chemical resilience**
  - **Thermal stability**
  - **High thermal conductivity**
  - **Thermal contraction**
- Summary and Conclusions

Introduction

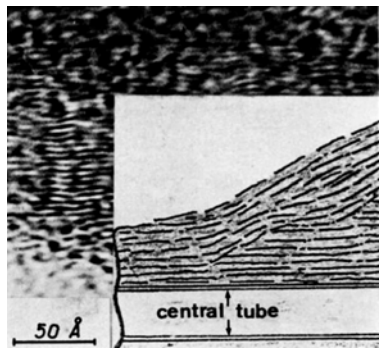
Nanocarbon pioneers

- The C_{60} 'buckyball' and other fullerenes:
  - successful synthesis
  - potential applications:
    - lubrication
    - superconductivity





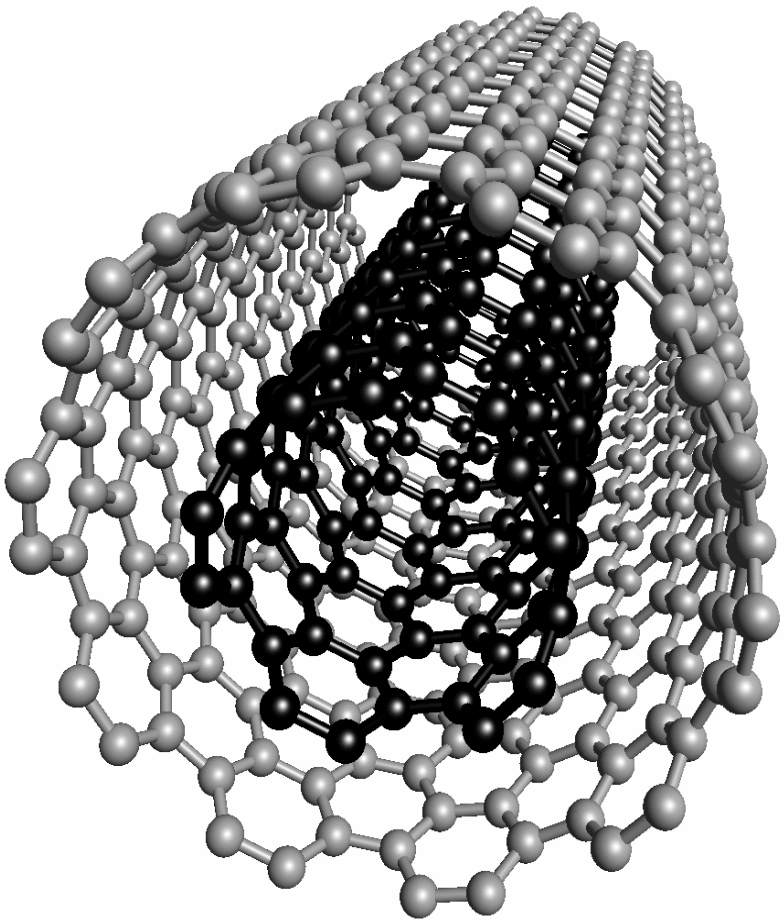
- Nanotubes:
  - successful synthesis
  - potential applications:
    - composites
    - Li-ion batteries
    - medication delivery
    - EMI shielding
    - flat-panel displays
    - super-capacitors
    - fuel cells
    - hydrogen storage



Nanotubes in the core of carbon fibers:
A. Oberlin, M. Endo, and T. Koyama, J. Cryst. Growth **32**, 335 (1976)

Nanotubes on the cathode in carbon arc:
S. Iijima, Nature **354**, 56 (1991)

What is so special about carbon nanotubes?

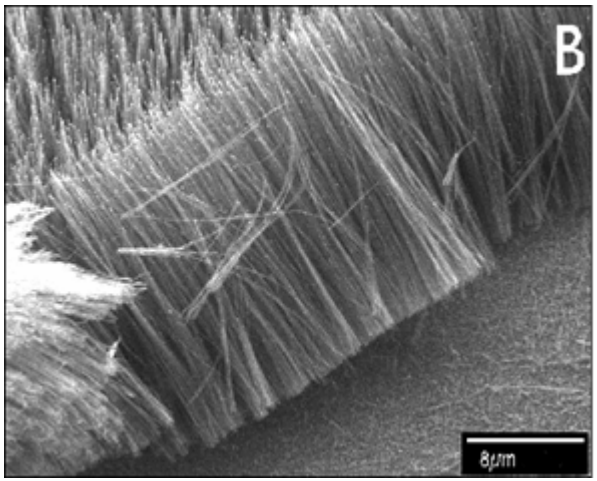


- 1-20 nm diameter
- Atomically perfect
- Chemically inert
- 100 times stronger than steel
- Extremely high melting temperature
- Ideal (ballistic) conductors of electrons, or insulators
- Ideal heat conductors

Unique properties of nanotubes lead to unique applications

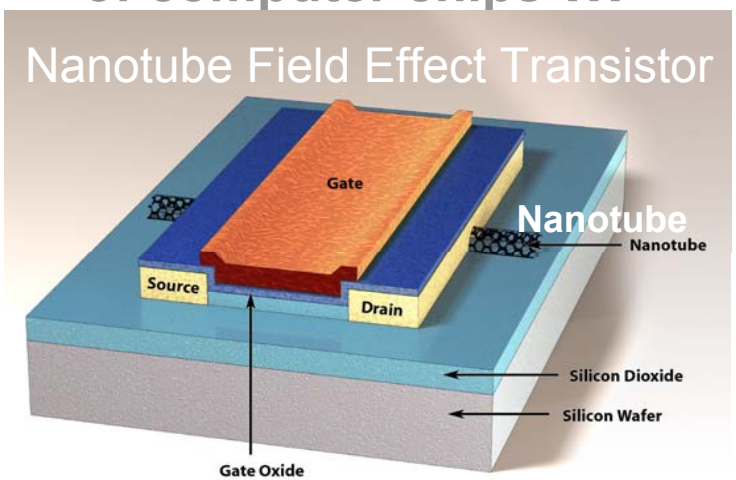
- Sharp and long (<1 cm): large aspect ratio $1:10^6$ – field emission, electrically conductive composites
- Highest current density 10^9 A/cm^2 – Vias, Field Emitters
- Ballistic electron transport – Field Effect Transistors
- Highest Young's modulus, ~1TPa – fibers, composites
- Highest thermal conductivity, 4000 W/(m·K) – composites
- Large electrode potential range/surface area – sensors, supercapacitors

Nanotubes grow by decomposing carbon compounds …

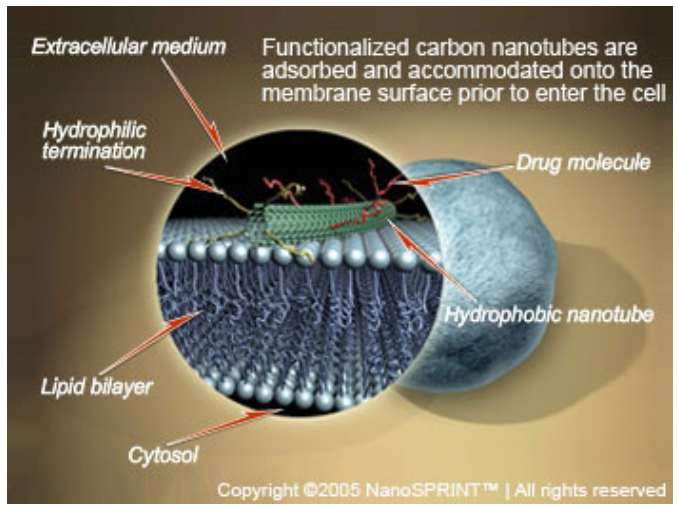


… to make bright flat-panel displays …

… field-effect transistors for the next generation of computer chips …



… or deliver drugs



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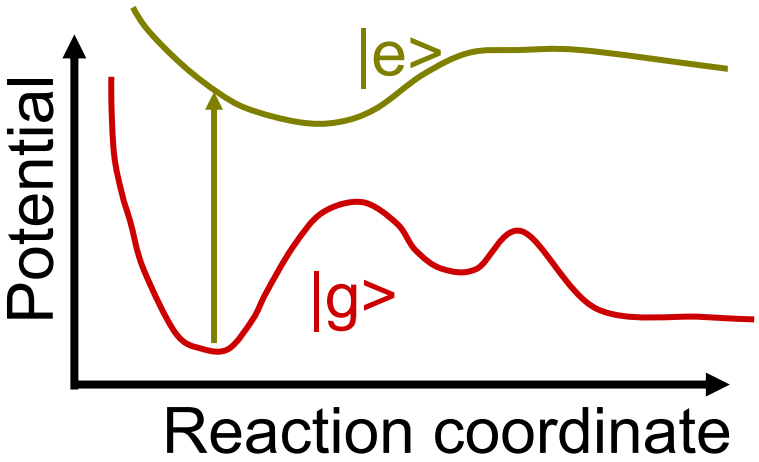
Theoretical tools

Computational tools

- **High-end calculations (no adjustable parameters):**
  - Total energy and electronic structure calculations based on the *ab initio* Density Functional formalism
  - Time evolution of electronic wave functions: Time-Dependent Density Functional formalism
  - Optical properties: Self-energy equation yields electron binding energies (GW approximation), Bethe-Salpeter equation also describes excitons
  - Atomic motion: Molecular dynamics simulations with electrons in the ground and excited state
- **Parametrized atomic-scale calculations:**
  - Tersoff-Brenner potential structure and deformation energies
  - Tight-binding formalism for energy and electronic structure
  - Hückel formalism (single-band tight-binding) for basic electronic structure
- **Continuum claculations:**
  - Continuum elasticity theory for deformation energies

Ground-state versus excited-state calculations

What approach to use?



Excited state dynamics:

Solve the time-dependent problem

$$i\hbar \frac{d\psi_n}{dt} = \hat{H}\psi_n = \varepsilon_n \psi_n$$

Density Functional Theory

(codes including SIESTA, VASP, CASTEP, GAUSSIAN, etc.)

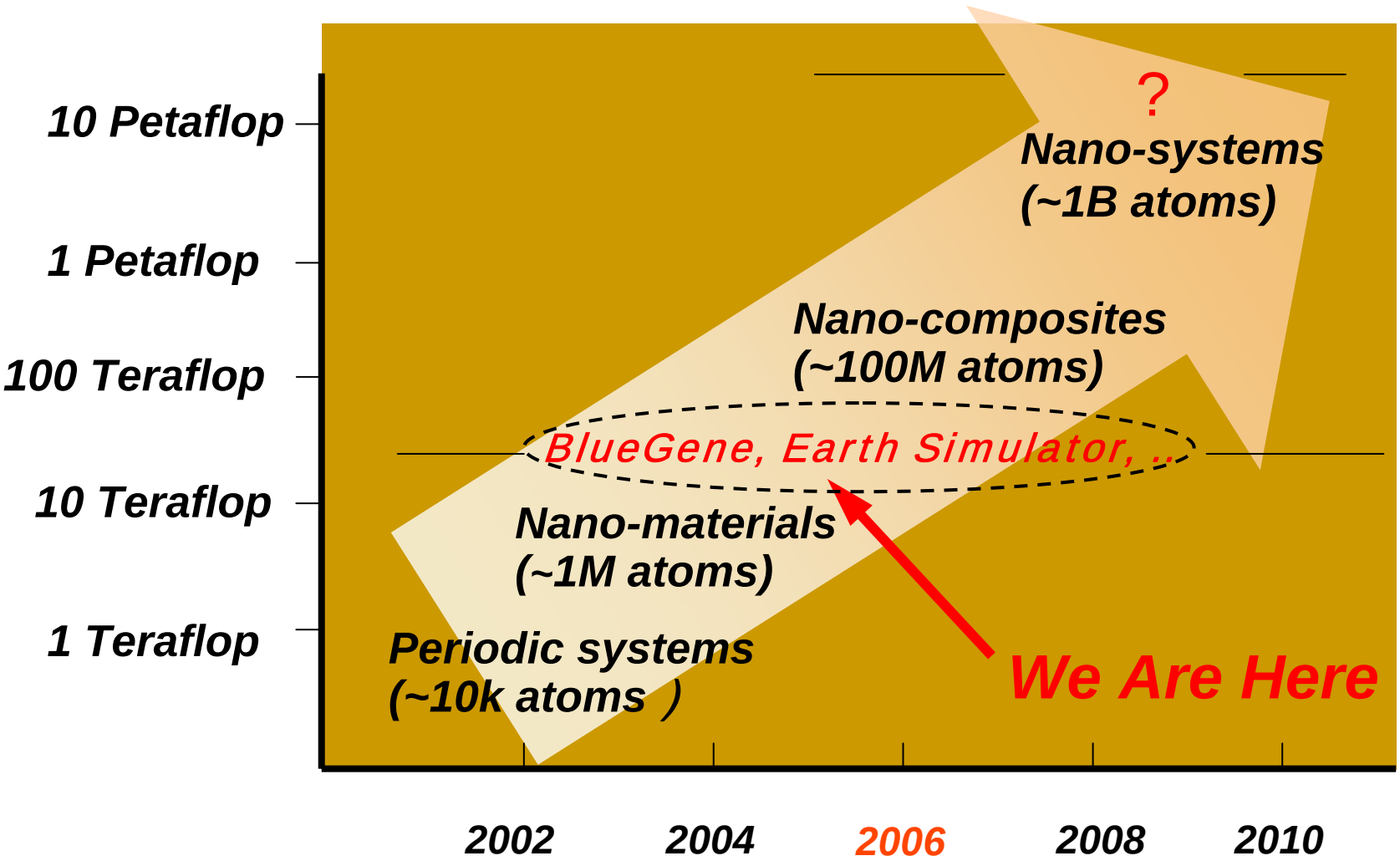
FPSEID (ef-psai-di:)

First-**P**rinciples **S**imulation tool for **E**lectron-**I**on **D**ynamics

- Based on time-dependent density functional theory (TDDFT):
  *E. Runge and E. K. U. Gross, Phys. Rev. Lett. **52**, 997 (1984).*
- Computational details for real-time MD simulations:
  Sugino & Miyamoto PRB 59, 2579 (1999) ; ibid, B 66, 89901(E) (2002),
  using the Suzuki-Trotter split operator method to compute the time-propagator

Need massively parallel computer architectures and suitable algorithms distribute load over processors for speed-up

State of the art computer simulations



Computational Nanotechnology Laboratory: Earth Simulator, Tokyo

www.nytimes.com

The New York Times ON THE WEB

April 20, 2002

Japanese Computer Is World's Fastest, as U.S. Falls Back

By JOHN MARKOFF

SAN FRANCISCO, April 19 — A Japanese laboratory has built the world's fastest computer, a machine so powerful that it matches the raw processing power of the 20 fastest American computers combined and far outstrips the previous leader, an I.B.M.-built machine.

Cost: $500,000,000
Maintenance: $50,000,000/year

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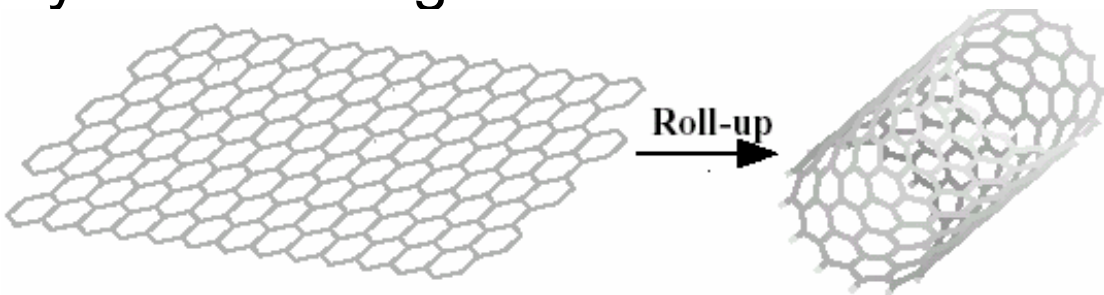
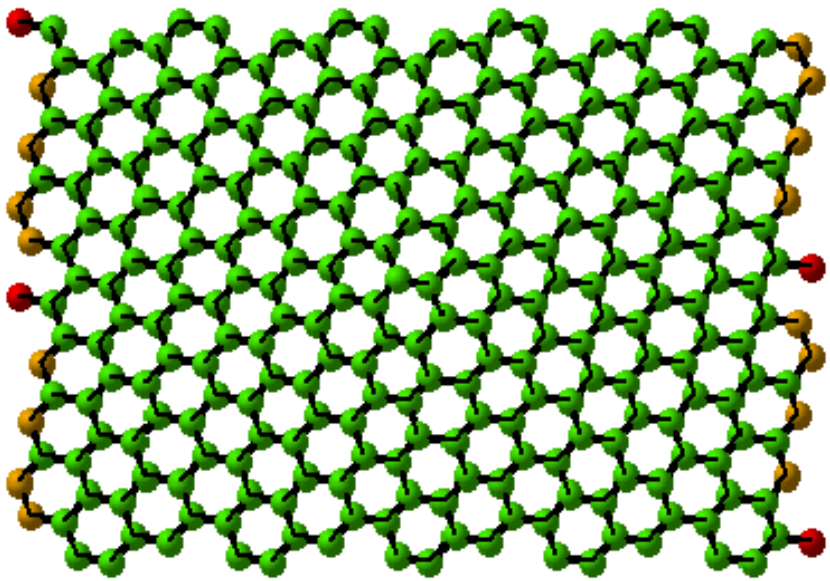
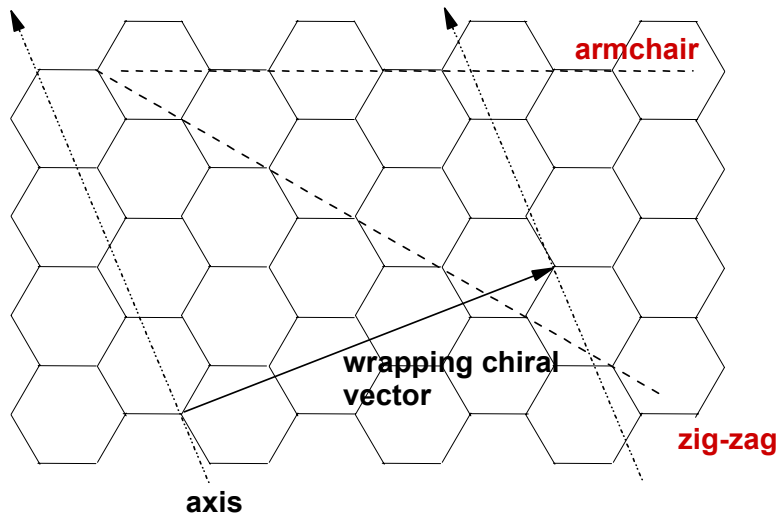
Morphology

Relationship to graphite

- A nanotube is formed by rolling up a graphene layer to a contiguous tube

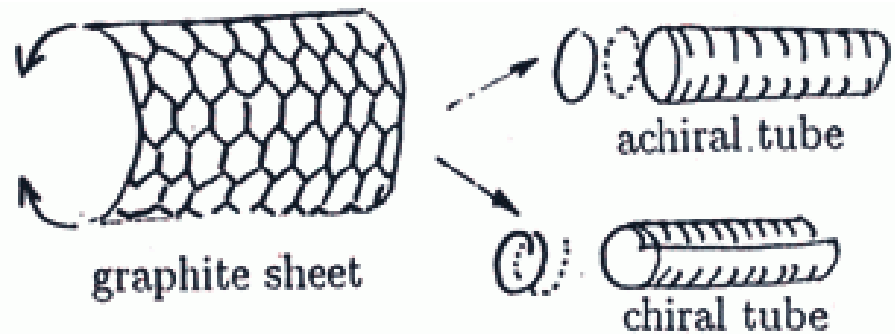




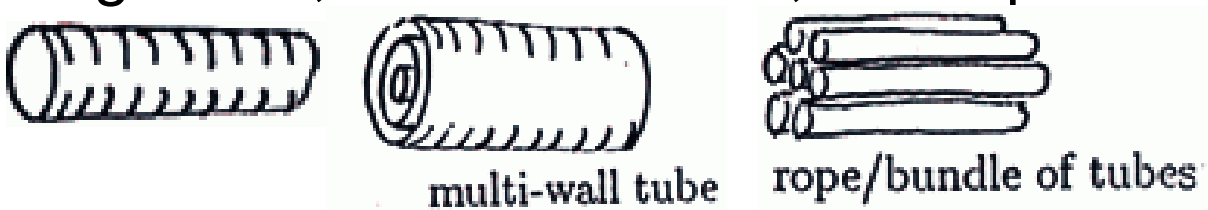


Classification of nanotubes

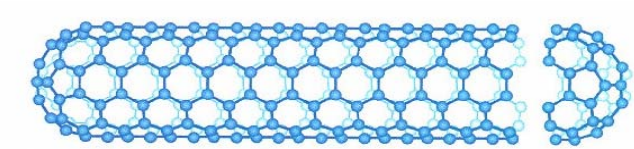
- Achiral and chiral nanotubes



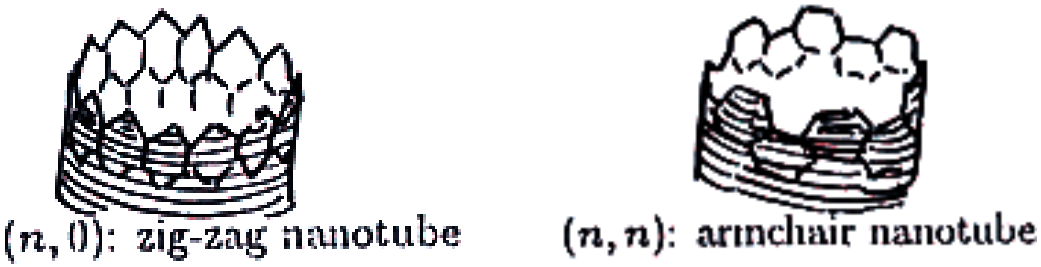
- Single-wall, multi-wall tubes, and ropes



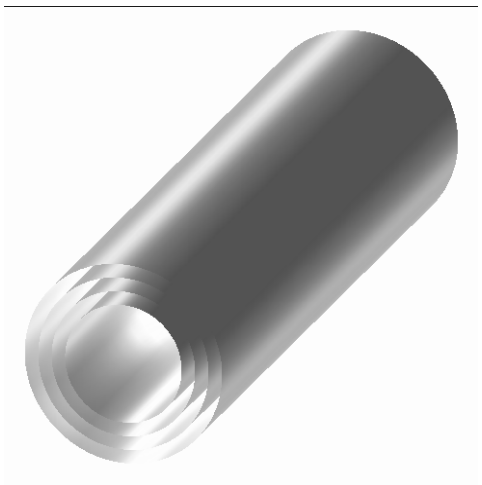
- Open-ended and capped nanotubes

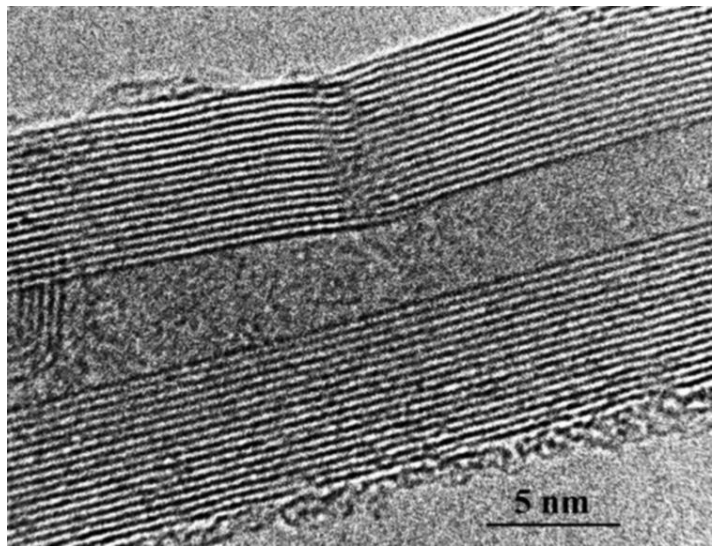


- Zigzag and armchair achiral nanotubes



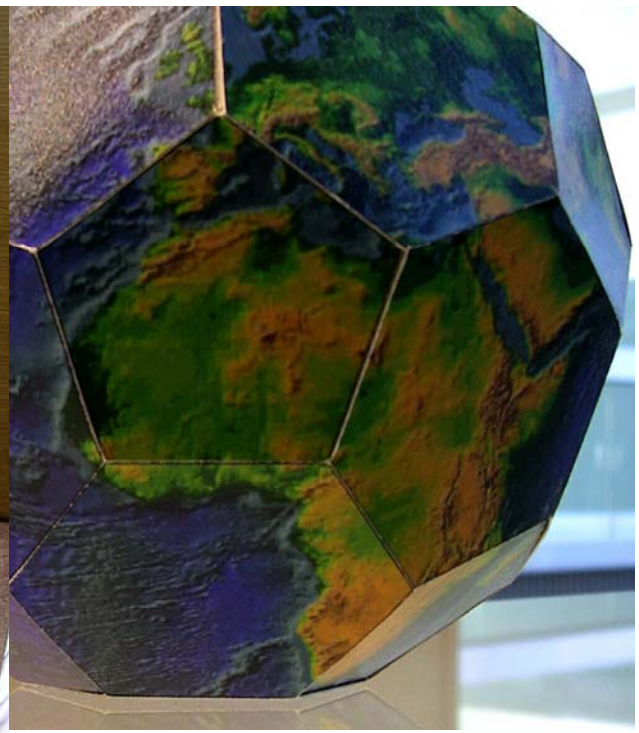
- Multi-wall tubes and scrolls





Structure of nanocarbons and Euler's Theorem

- Example 1: Objects of topological gender 0
  (polyhedra with no holes, e.g. C_{60} "buckyball")



Objects of topological gender 0

(polyhedra with no holes, e.g. C_{60} buckyball")

- **C – E + F = 2 Euler's Theorem**
  - C = number of Corners
  - E = number of Edges
  - F = number of Faces
- Assume only pentagons, hexagons in the structure
  - p = number of pentagons (5 corners)
  - x = number of hexagons (6 corners)

  - C = p·5/3 + x·6/3
  - E = p·5/2 + x·6/2
  - F = p + x
  - Substitute C, F, F in Euler's Theorem:
    (5/3)p + (6/3)x - (5/2)p – (6/2)x + p + x = 2
    (5/3 – 5/2 +1)p + (6/3 – 6/2 + 1) x = 2
    (1/6) p + 0x = 2
    p/6 = 2

p = 12 x=arbitrary

Objects of topological gender 0
(polyhedra with no holes, e.g. C_{60} buckyball")

- Assume also heptagons in the structure
  - p = number of pentagons (5 corners)
  - x = number of hexagons (6 corners)
  - h = number of heptagons (7 corners)

  - C = p·5/3 + x·6/3 + h·7/3
  - E = p·5/2 + x·6/2 + h·7/2
  - F = p + x + h

  - Substitute C, F, F in Euler's Theorem:
    C – E + F = 2 Euler's Theorem
    (5/3)p + (6/3)x - (5/2)p – (6/2)x + p + x = 2
    (5/3 – 5/2 +1)p + (6/3 – 6/2 + 1) x + (7/3 – 7/2 + 1) h = 2
    (1/6) p + 0x – (1/6) h = 2

p – h = 12 x=arbitrary

- Example 2: Objects of topological gender 1
  (polyhedra with one hole, e.g. “donut”)

- **C – E + F = 0 Euler’s Theorem**
  - C = number of Corners
  - E = number of Edges
  - F = number of Faces
- Assume only pentagons, hexagons in the structure
  - p = number of pentagons (5 corners)
  - x = number of hexagons (6 corners)

  - Substitute C, F, F in Euler’s Theorem:
    (1/6) p + 0x = 0
    p/6 = 0
  - no pentagons, only hexagons: perfect cylindrical segment

p = 0 x=arbitrary

Objects of topological gender 1

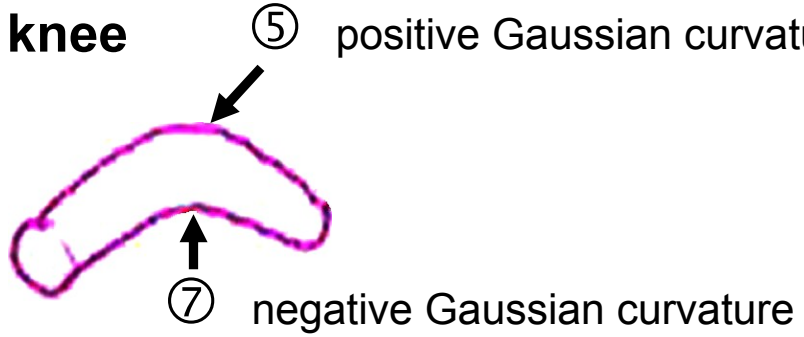
(polyhedra with one hole, e.g. “donut”)

- Assume also heptagons in the structure
  - p = number of pentagons (5 corners)
  - x = number of hexagons (6 corners)
  - h = number of heptagons (7 corners)

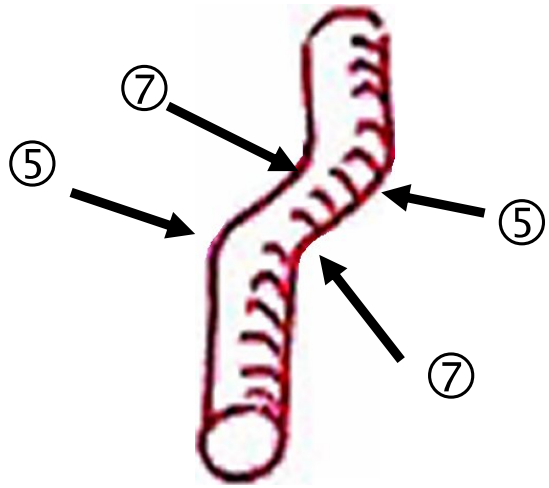
  - Substitute C, F, F in Euler’s Theorem:
    C – E + F = 0 Euler’s Theorem
    (1/6) p + 0x – (1/6) h = 0

p = h x=arbitrary

- Illustration 1: **Local curvature at a knee**

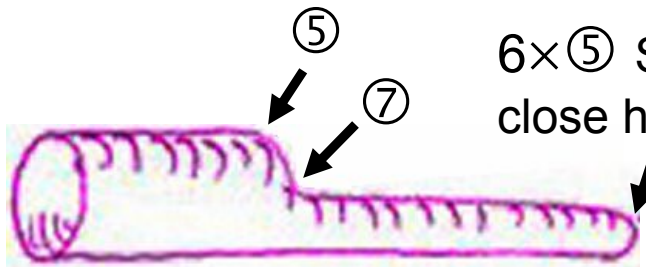


- Illustration 2: **Bent tube**



⑦- ⑤ pairs

- Illustration 3: **Tube with changing diameter**



6×⑤ Six pentagons close hemisphere

Polymorphism due to high-temperature synthesis

- Production
  - Laser ablation (LA)
  - Carbon Arc (CA)
    - Bottleneck is purification, not raw production
  - Chemical vapor decomposition (CVD)
    - Better for larger scale-up
    - Produces higher purity (‘etching’)
  - HIPCO
- Synthesis occurs at ≈1000 K, yielding mixtures of nanotubes
- Applications were critically limited by lack of production – now being fulfilled

Carbon and non-carbon nanotubes

- Not only sp^2 carbon (graphite), but many other layered systems form nanotubes
- Examples: BN, BC_3, MoS_2, $MoSe_2$, WS_2, WSe_2, …
- Electronic properties and diameter depend strongly on the system (e.g. ***all*** BN nanotubes are wide-gap semiconductors)

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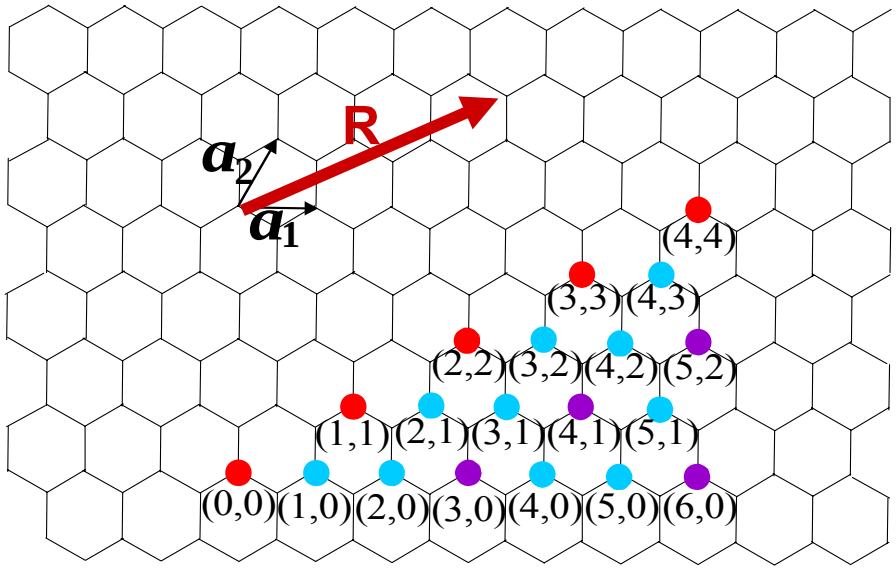
Electronic structure and conductivity

Morphology determines conductivity



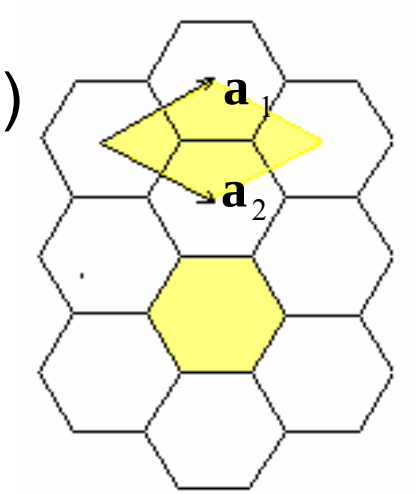
Chiral vector $\mathbf{R}=n\mathbf{a}_1+m\mathbf{a}_2$ defines uniquely the (n,m) nanotube

- *metal:* *n=m*
- *semimetal:* *n-m=3p*
- *semiconductor:* *n-m≠3p (p is integer)*

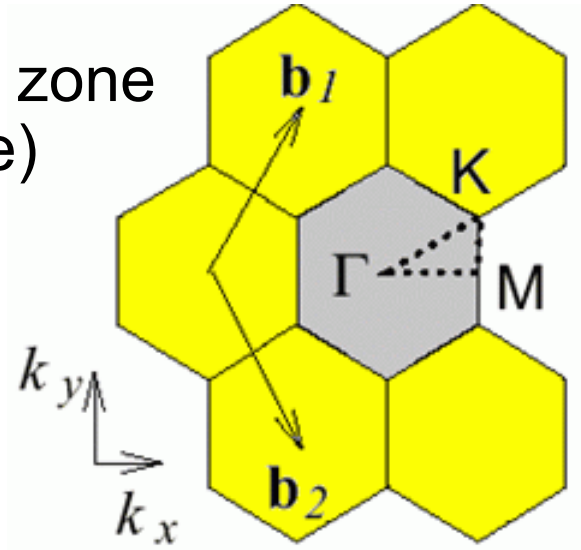
• Large ***variation in conducting behavior*** in all-carbon nanotubes

Electronic structure of graphite

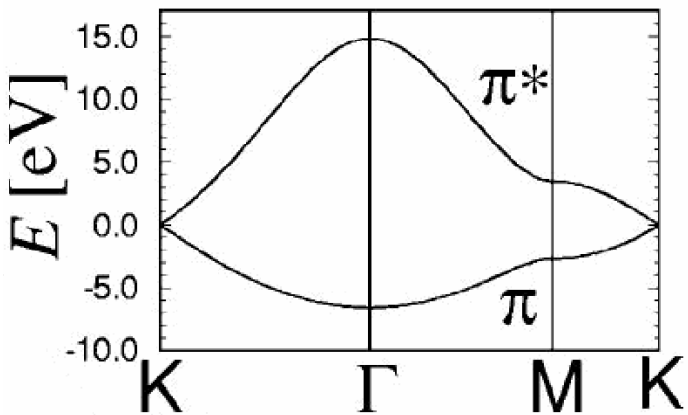
Unit cell
(real space)

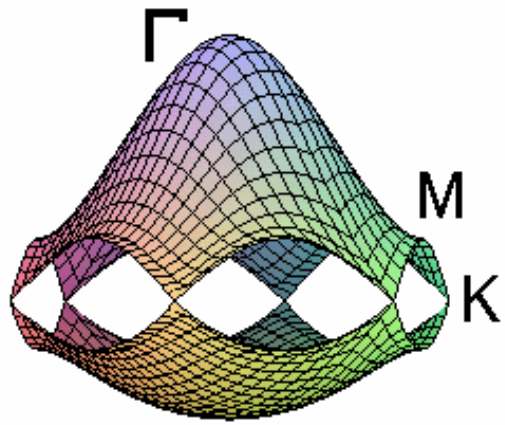


Brillouin zone
(k-space)



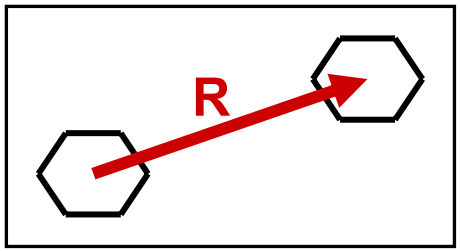
- Dispersion of the graphite π band near E_F
  - Graphite is zero-gap semiconductor
  - Fermi point is **K**

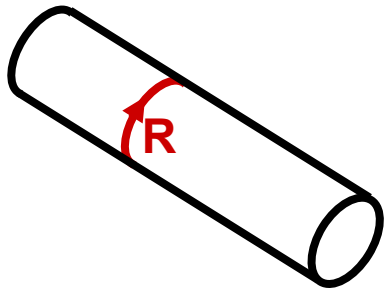


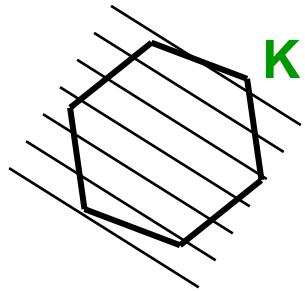


Metallicity depends on chiral vector

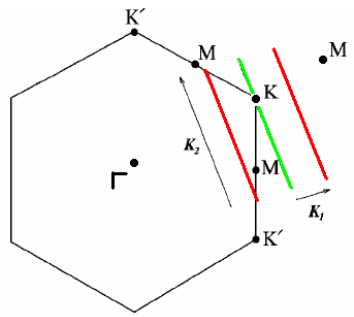
- Electronic structure changes caused by momentum quantization along lines in the Brillouin zone

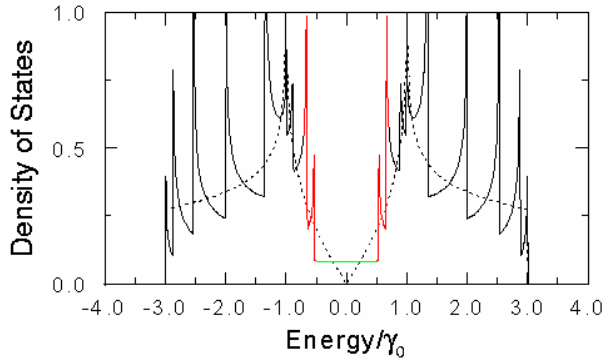






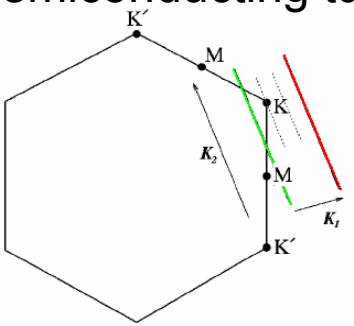
  - Metallic tubes contain K point on quantization lines

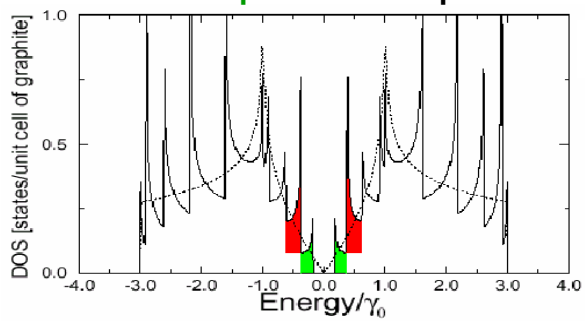




(n,m)=(9,0)

  - Semiconducting tubes do not contain K point on quantization lines





(n,m)=(10,0)

Bravais lattice points: $\mathbf{r} = \mathbf{R} = n\mathbf{a}_1 + m\mathbf{a}_2$

$\psi(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} = e^{i\varphi}$ Bloch theorem

Basis points: $\mathbf{r'} = \mathbf{R} + \tau = (n+\frac{1}{3})\mathbf{a}_1 + (m+\frac{1}{3})\mathbf{a}_2$

$\psi(\mathbf{r'}) = e^{i\mathbf{k}\cdot\mathbf{r'}} = e^{i\varphi'}$

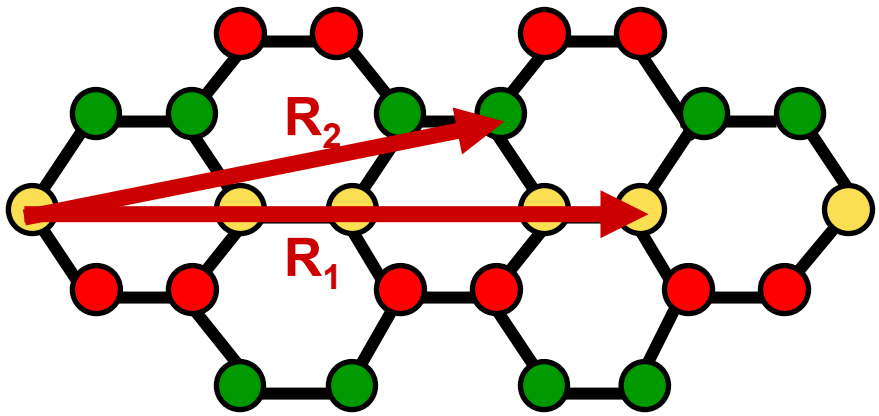
Consider carrier with momentum K:

$\varphi = \mathbf{K}\cdot\mathbf{r} = \frac{1}{3}(\mathbf{b}_2-\mathbf{b}_1)\cdot(n\mathbf{a}_1+m\mathbf{a}_2) = \frac{1}{3}(-2\pi n+2\pi m) = 2\pi/3\,(m-n)$

$\varphi' = \mathbf{K}\cdot\mathbf{r'} = \frac{1}{3}(\mathbf{b}_2-\mathbf{b}_1)\cdot[(n+\frac{1}{3})\mathbf{a}_1+(m+\frac{1}{3})\mathbf{a}_2] = \frac{1}{3}[-2\pi\,(n+\frac{1}{3}) + 2\pi(m+\frac{1}{3})] = 2\pi/3(m-n)$

Possible phases: 0°, +120°, -120°

Bravais lattice point and basis point have same phase



Bravais lattice

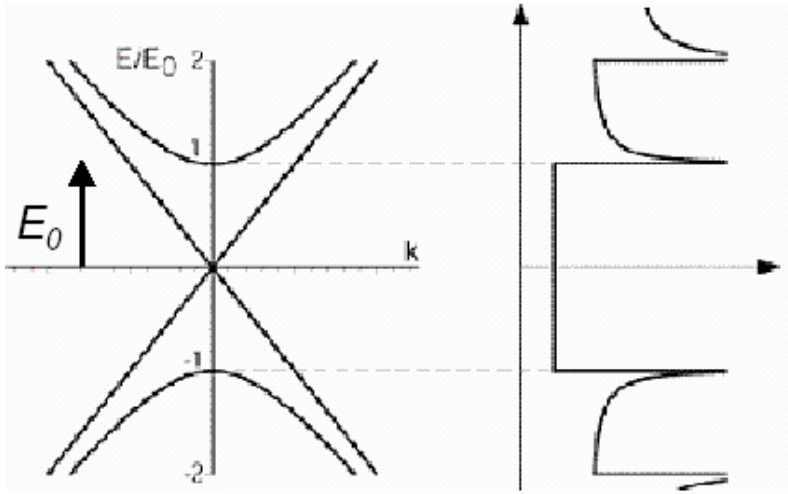
$\mathbf{R}_1$ yields conducting nanotube: **K** is allowed eigenstate

$\mathbf{R}_2$ yields insulating nanotube: **K** is not an allowed eigenstate
(i.e. electrons with Fermi momentum are not allowed)

Band structure and density of states

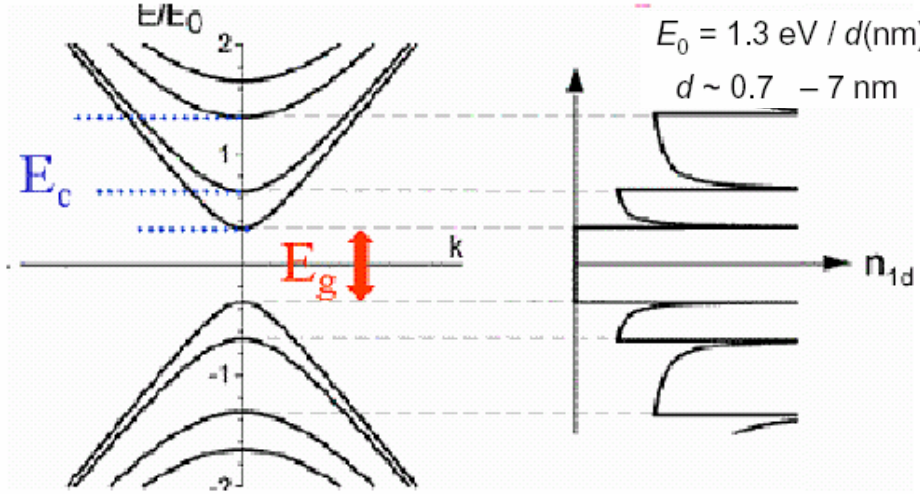
Type I. Metallic tubes

$M-N = 0$ $E_g=0$

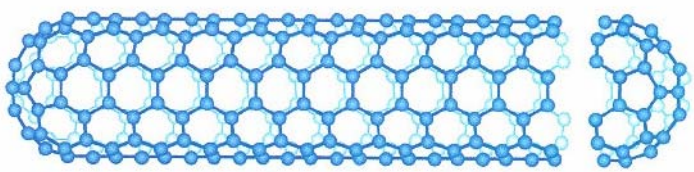


Type II. Wide-gap semiconducting tubes

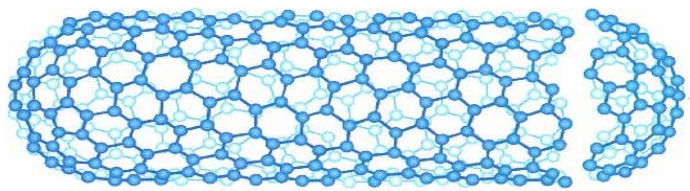
$M-N <> 3p$ $E_g = 2/3\ E_0$



E_g ~ 0.5-1 eV



(m,n) = (5,5)



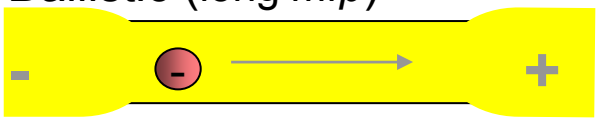
(m,n) = (10,5)

In reality, also Type III: Small-gap semiconducting tubes (zigzag metals)

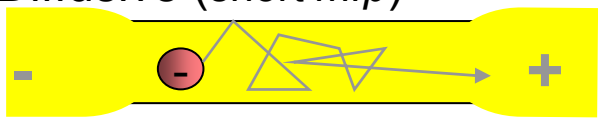
Ballistic and diffusive conduction

- Carbon nanotubes exhibit ***ballistic*** or ***diffusive*** transport

Ballistic (long *mfp*)

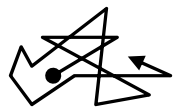


Diffusive (short *mfp*)



mfp: electron mean free path

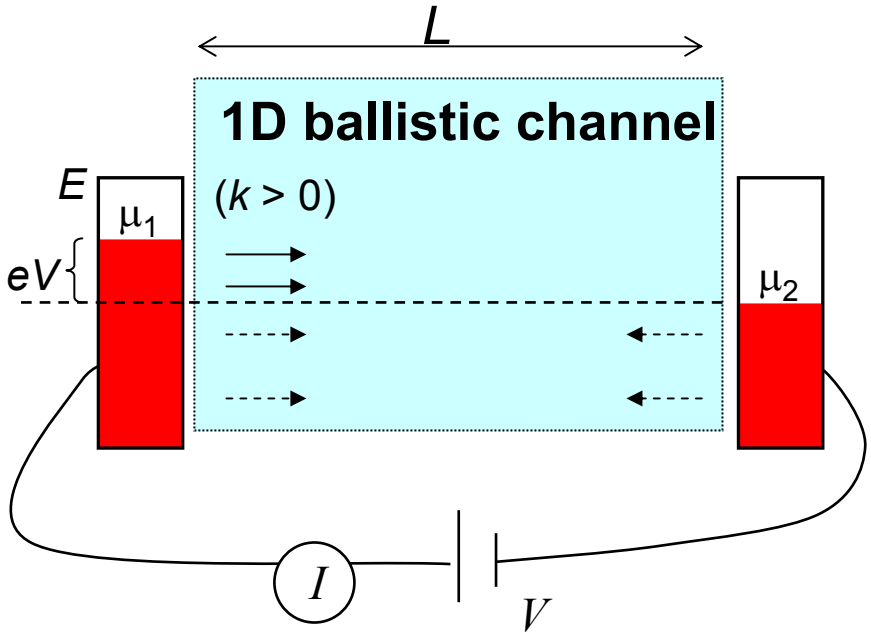
- **Ballistic transport**, $L << L_m, L_\phi$
  - no scattering, only geometry (eg. QPC)
  - when $\lambda_F \sim L$: quantized conductance $G \sim e^2/h$
- **Diffusive**, $L > L_m$
  - scattering, reduced transmission



- **Localization**, $L_m << L_\phi << L$
  - $R \sim \exp(L)$ due to quantum interference at low T
- **Classical** (incoherent), $L_\phi, L_m << L$
  - ohmic resistors T

- **Length Scales:** λ_F Fermi wavelength (only electrons close to Fermi level contribute)
  L_m momentum relaxation length (static scatterers)
  L_Φ phase relaxation length (fluctuating scatterers)
  L sample length

Ballistic conductance in nanowires is quantized



- Contacts: 'Ideal reservoirs'
- Chemical potential μ ~ E_F (Fermi level)
- Channel: 1D, ballistic
  (transport without scattering)

- 1D density of states per unit length:

$$g_{1D}(E) = \frac{2}{h}\sqrt{\frac{2m}{E}} = \frac{2}{hv(E)}$$

velocity — 1D density — spin — $k > 0$

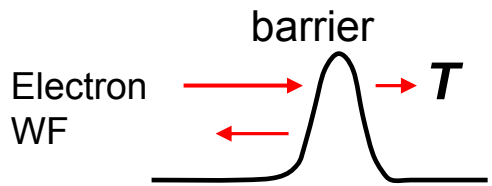
$$I = \int_{\mu_1}^{\mu_2} ev(E)\left(2\frac{1}{2}g_{1D}(E)\right)\mathrm{d}E = \int_{\mu_1}^{\mu_2} ev(E)\left(\frac{2}{hv(E)}\right)\mathrm{d}E = \frac{2e}{h}(\mu_2-\mu_1) = \frac{2e}{h}(eV)$$

$$G = I/V = \frac{2e^2}{h}$$

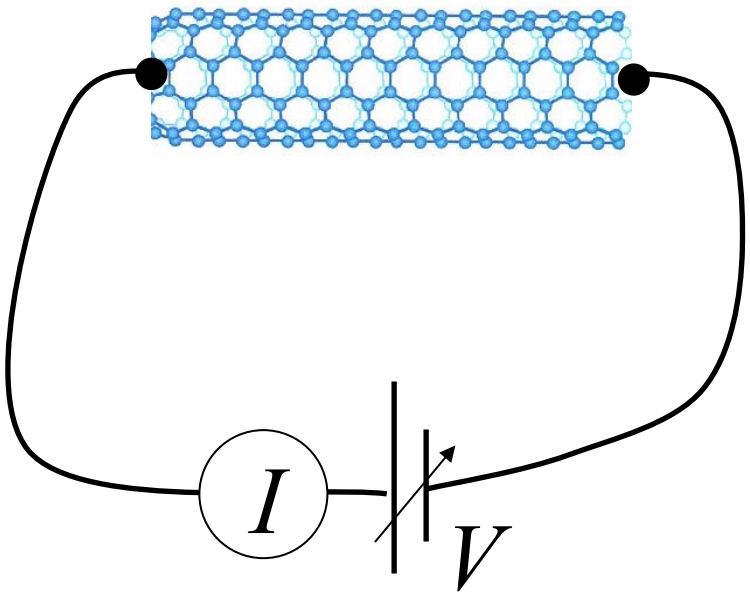
Conductance is fixed, regardless of length *L;*
(no well defined conductivity σ)

$$G(E_F) = \frac{2e^2}{h}\sum_n T_n(E_F)$$

Landauer formula for N transmission channels



Ballistic conductance of a metallic single-wall nanotube



With perfect contacts:

$$G = \textit{current} / \textit{voltage}$$

$$= 2*2e^2/h$$

(two subbands in NT)

Quantum of resistance:

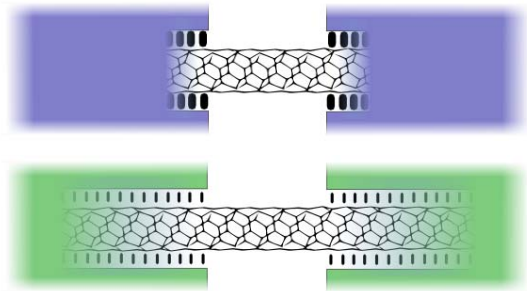
$h/e^2 = 25$ kOhm

Beware of contacts!

- **Which metal-nanotube contacts optimize charge injection?**

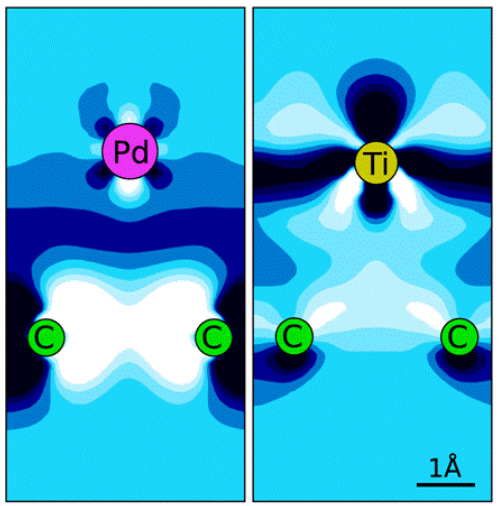
•Short, strong contact?

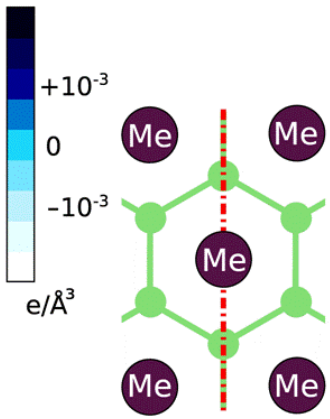
•Long, weak contact?

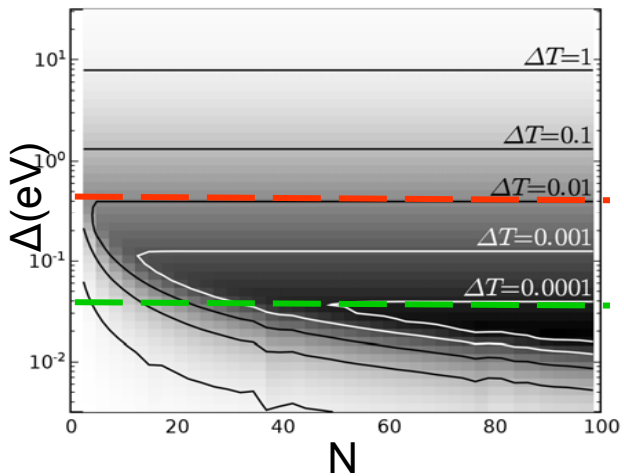


N. Nemec, D. Tomanek, G. Cuniberti, Phys. Rev. Lett. **96,** 076802 (2006)

- **Charge injection at the Pd/nanotube and Ti/nanotube interface:**







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- Introduction
  - **Nanocarbon pioneers**
  - **What is so special about carbon nanotubes?**
- Theoretical tools
  - **Computational tools**
  - **State of the art of computer simulations**
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- Mechanical properties
  - **Graphitic sp^2 versus diamond sp^3 bonding**
  - **High Young's modulus**
- Chemical and thermal resilience, and thermal conductivity
  - **Chemical resilience**
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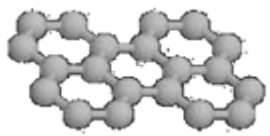
  - **Thermal contraction**
- Summary and Conclusions

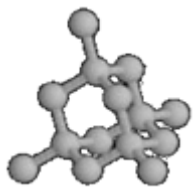
Mechanical properties

Graphitic sp^2 versus diamond sp^3 bonding

- Graphitic *sp*^{2} bonded structures are stiffer than *sp*^{3} bonded diamond



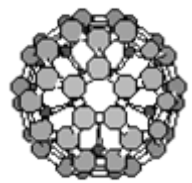
sp^2



sp^3

$$\frac{\text{Binding Energy}}{3} > \frac{\text{Binding Energy}}{4}$$

$$sp^2 > sp^3$$



High Young's modulus

- **Prediction:**

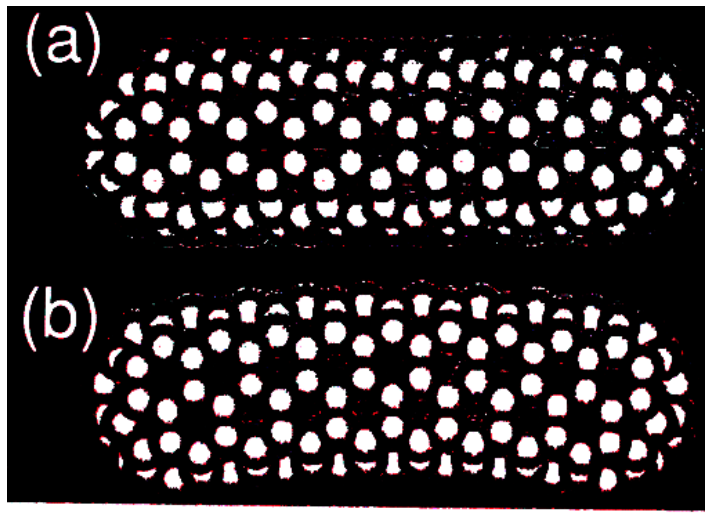
  [G. Overney, W. Zhong, and D. Tomanek: Structural Rigidity and Low Frequency Vibrational Modes of Long Carbon Tubules, Z. Phys. D 27, 93-96 (1993)]

  Y≈5 TPa

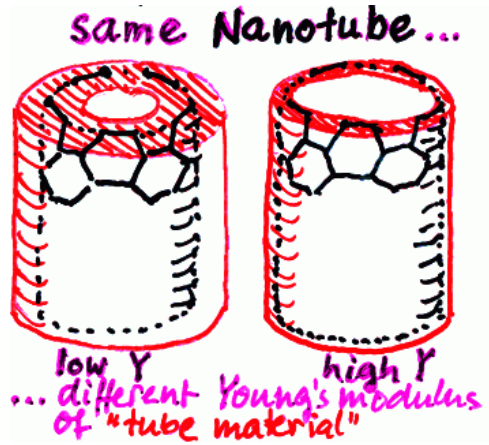
- **Observation:**

  [M.M.J. Treacy, T.W. Ebbesen, and J.M. Gibson, Exceptionally high Young's modulus observed for individual carbon nanotubes, Nature 381, 678 (1996)]

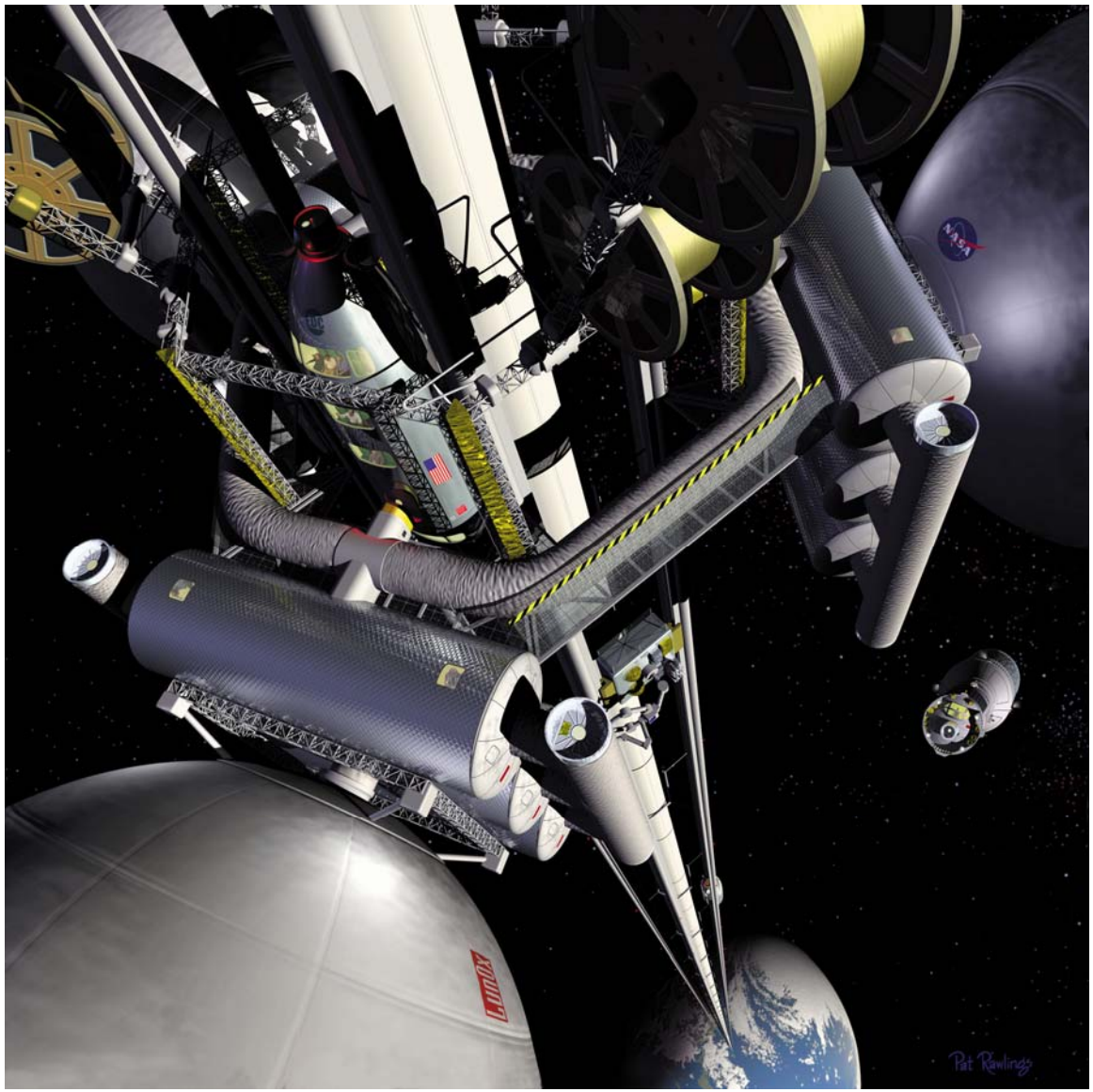
  Y≈4 TPa



"Young's modulus" of nanotubes



Tough, light-weight nanotubes are crucial for the “2020” Space Elevator Concept



Strain energy estimates

- Continuum elasticity theory ignores precise atomic positions

- Strain in deformed sp^2 bonded graphene sheet is given by:
  - flexural rigidity: D=1.41 eV
  - Poisson's ratio: α=0.165
  - (Reference System: Planar Graphene Sheet)

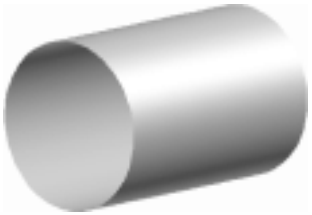
Energy of fullerenes, nanotubes, scrolls

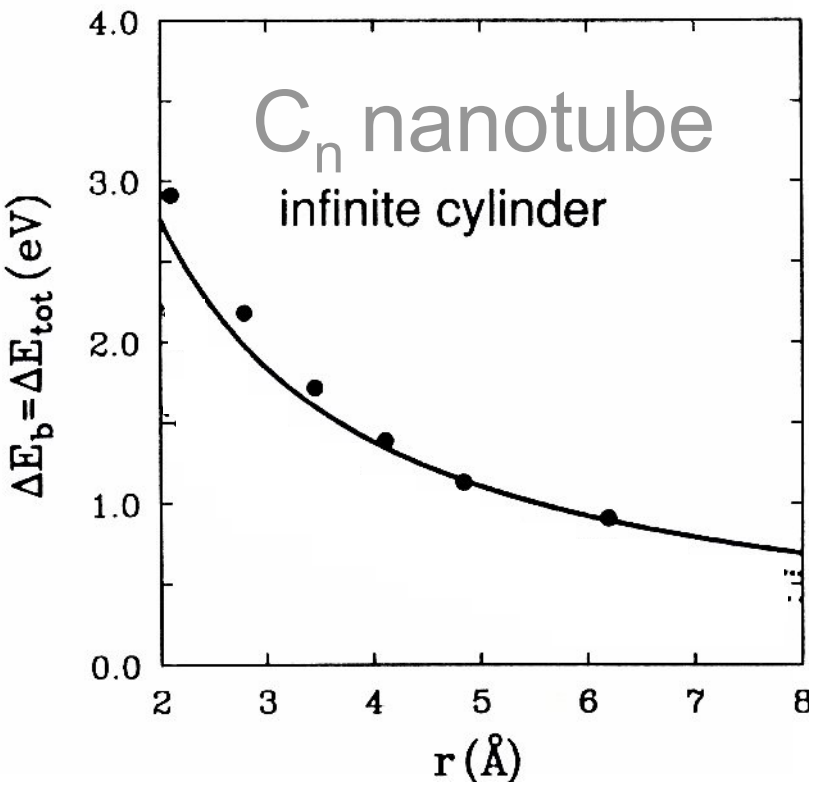
Cylinder: $\Delta E_s = \pi DL/R = \varepsilon_{cyl} L/R$

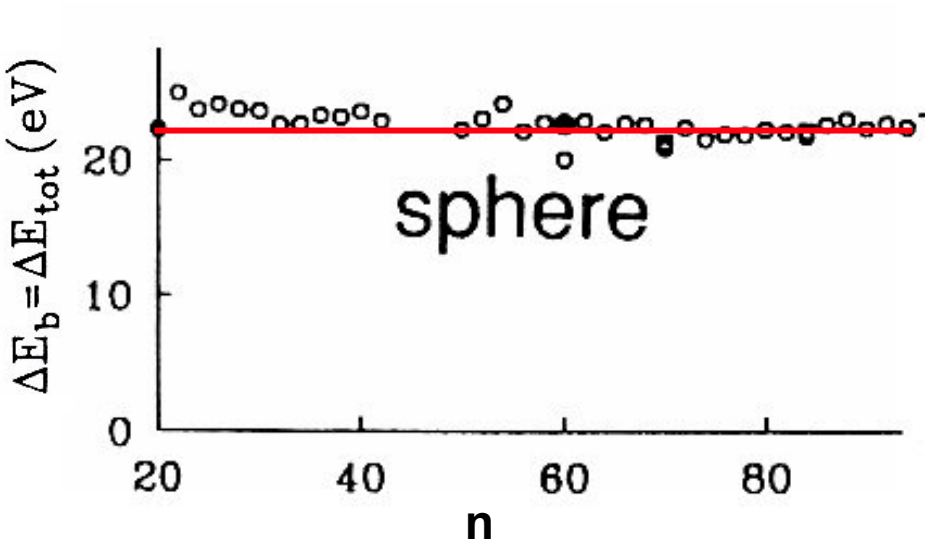
(ε_{cyl}= 4.43 eV, R=radius, L=axial length)

Sphere: $\Delta E_s = 4\pi D(\alpha + 1) = 20.6\text{eV}$

Reliability of the continuum description





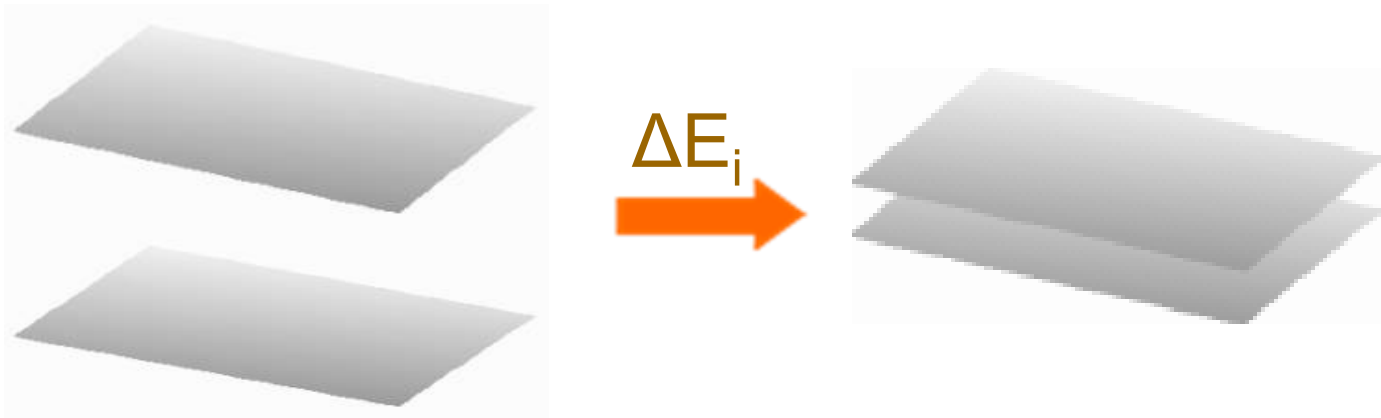


D. Tománek, W. Zhong, and E. Krastev, Phys. Rev. B 48, 15461 (1993)

Additional terms in finite-size and multi-wall systems

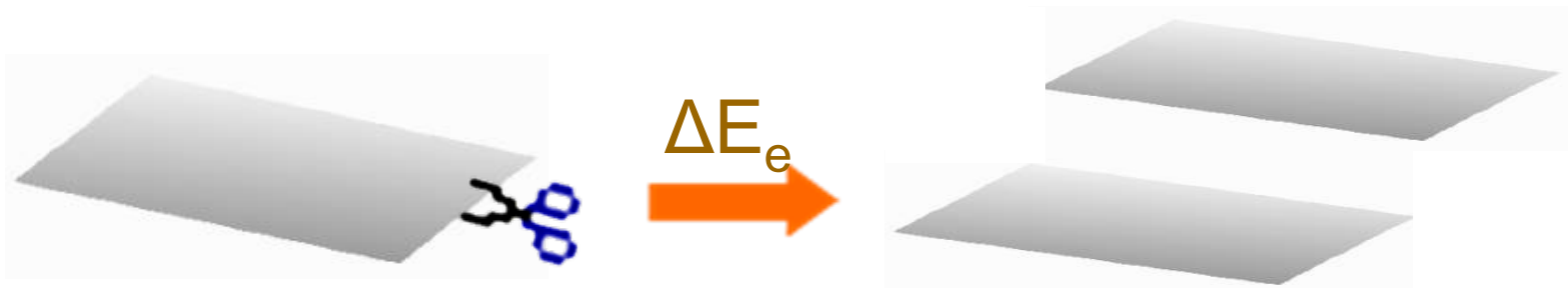
Interlayer Interaction:

$$\Delta E_i = \varepsilon_{vdw} A \quad (\varepsilon_{vdw} = 2.48\,{}^{eV}/_{nm^2},\quad A = \text{area})$$

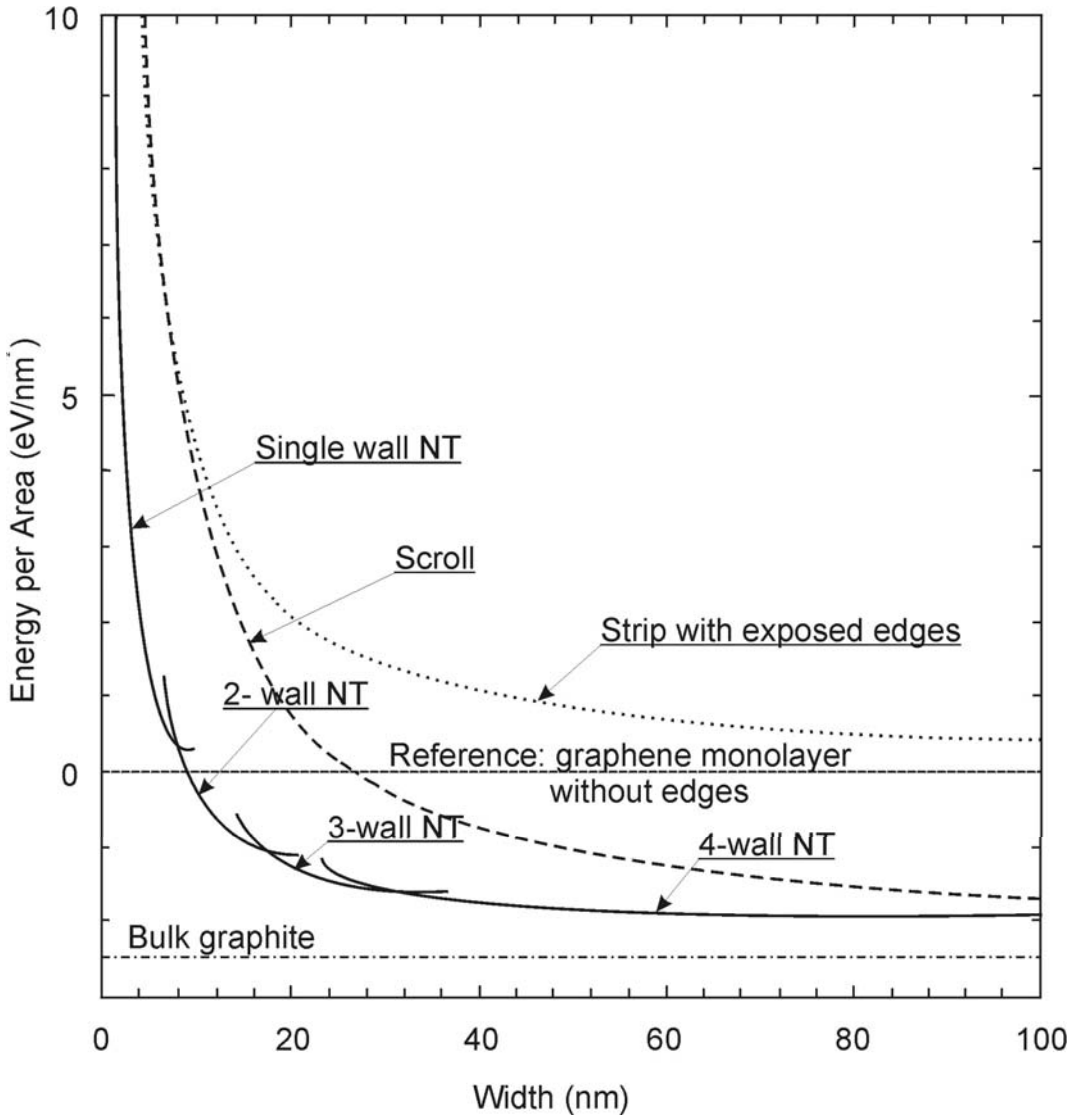


Exposed Edge:

$$\Delta E_e = \varepsilon_e L \quad \left(\varepsilon_e = 21\,{}^{eV}/_{nm}\right)$$



Strain energy of scrolls and nanotubes



- Strain energy described by Continuum Elasticity Theory
- Energy corresponds to optimum geometry
- Multiwall nanotubes are always more stable than scrolls

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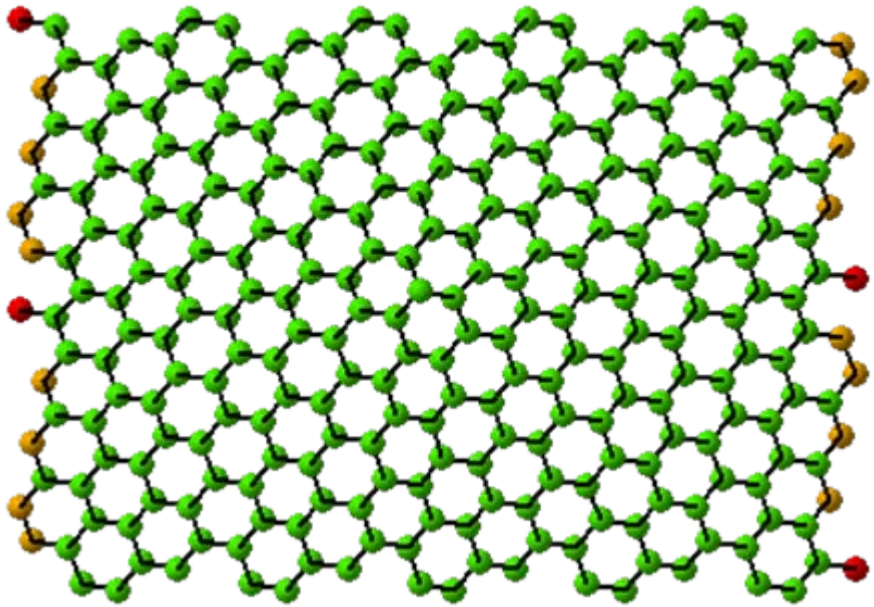
Chemical and thermal resilience, and thermal conductivity

Chemical resilience

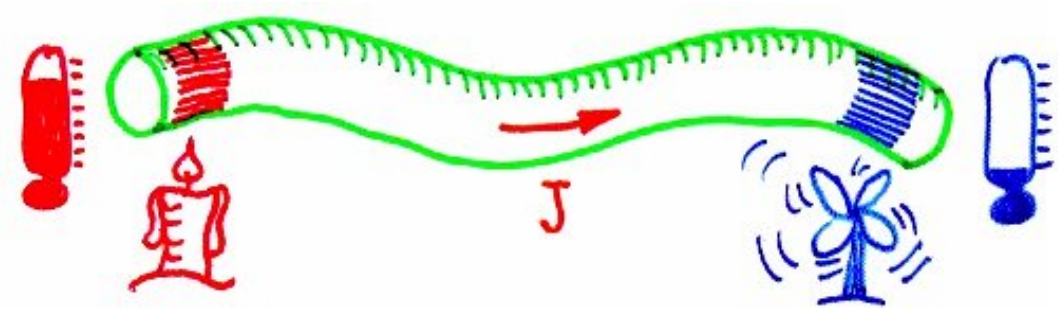
- Carbon nanotubes are chemically unreactive, similar to graphite



Thermal stability

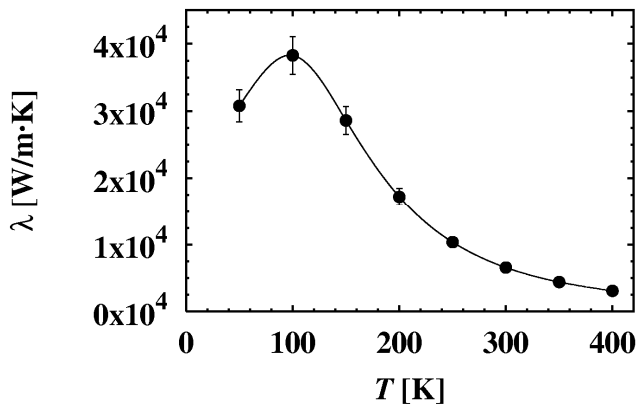
- Melting temperature of carbon nanotubes is similar to that of graphite, $T_M \approx 4000$ K

High Thermal Conductivity



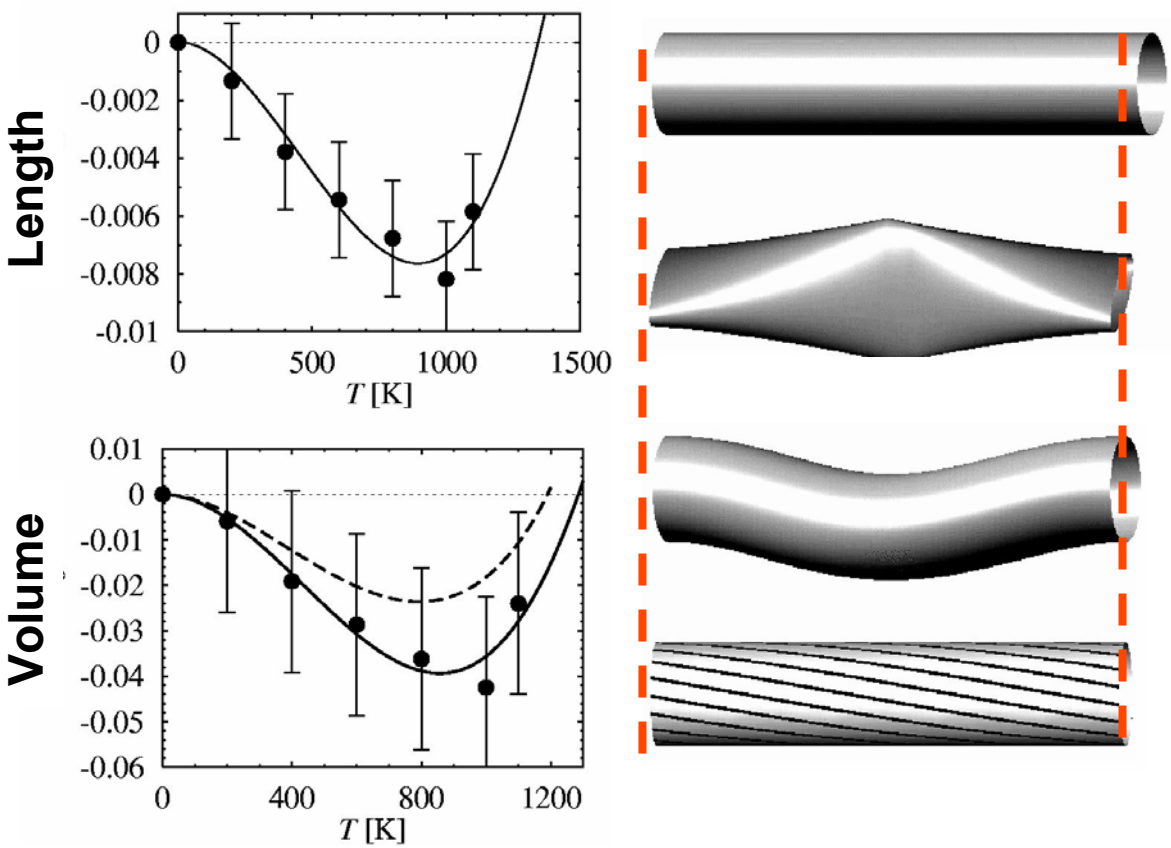
[Savas Berber, Young-Kyun Kwon, and David Tománek, Phys. Rev. Lett. 84, 4613 (2000)]

- NanoNanotubes may help solve the heat problem in nanoelectronics:
  - Efficient conductors of electrons and heat
  - Record Heat Conductivity:
    - Diamond (isotopically pure): 3320 W/m/K
    - Nanotubes: 6,600 W/m/K (theory, SWNT)
      >3,000 W/m/K (experiment, MWNT)
      (room temperature values)
    - Origin: combination of large phonon mean free path, speed of sound, hard optical phonon modes



Temperature dependence of the thermal conductivity λ for a (10,10) carbon nanotube for temperatures below 400 K

Thermal contraction



Savas Berber, Young-Kyun Kwon, and David Tománek, Phys. Rev. Lett. 92, 015901 (2004)

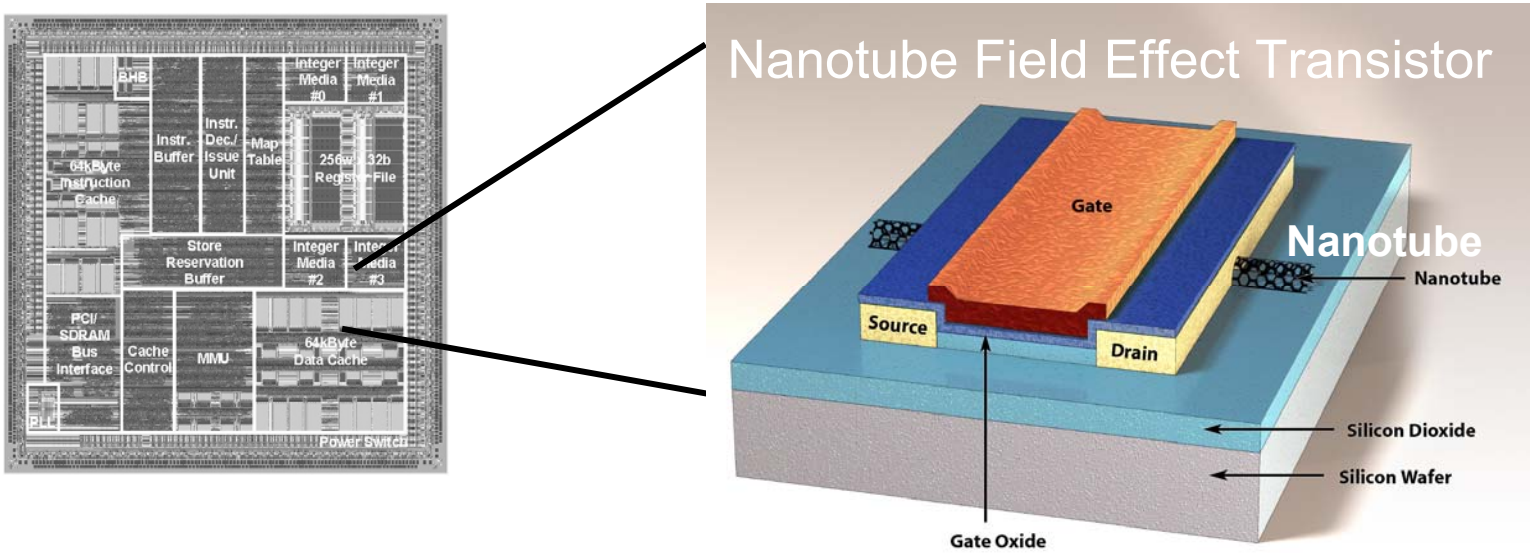
See also Comment and Reply: Phys. Rev. Lett. 94, 209702 (2005)

- Nanotubes contract rather than expand
- Physical origin: length contraction due to a gain in configurational and vibrational entropy

Outline

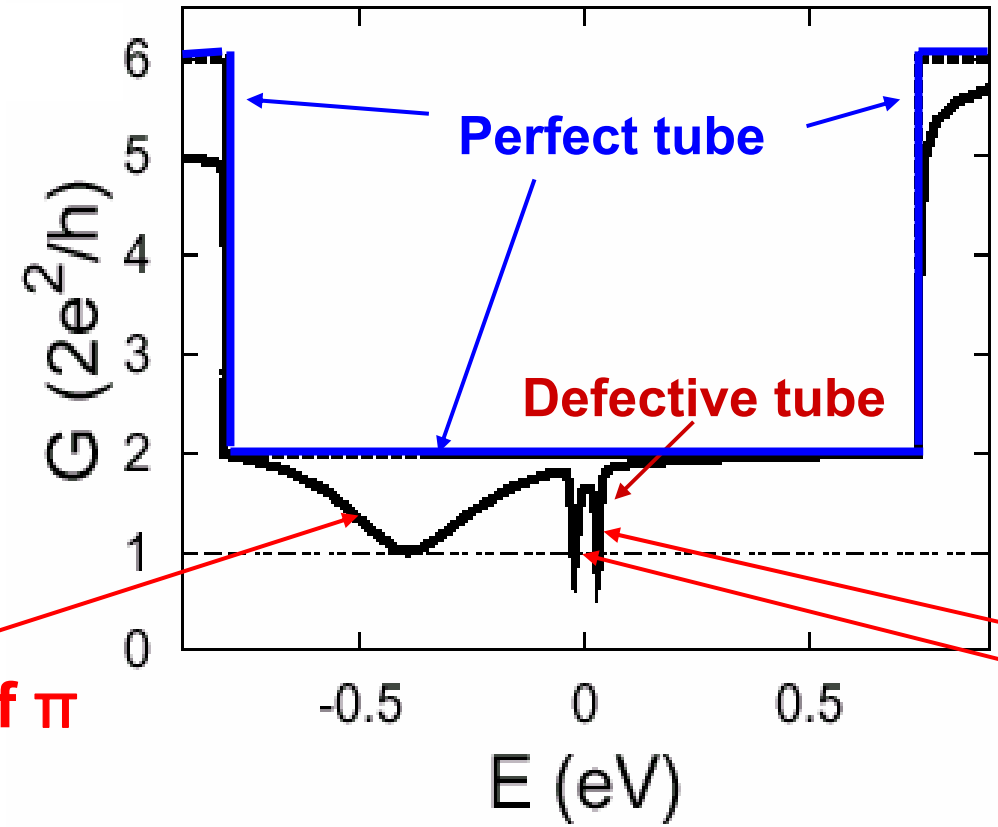
- ….
- ….
- Limitations of nanotube devices
  - **How stable are defective tubes?**
  - **Deoxidation of defective nanotubes**
- Acknowledgments and the real end

Limitations of nanotube devices



- What limits the speed of nanotube-based electronics?
- How to best contact a carbon nanotube?
- How to inter-connect carbon nanostructures?
- Are nanotube devices as sensitive to defects as Si-LSI circuits?
- Can defects heal themselves?
- Are there ways to selectively remove defects?

Quantum conductance of a (10,10) nanotube with a single vacancy



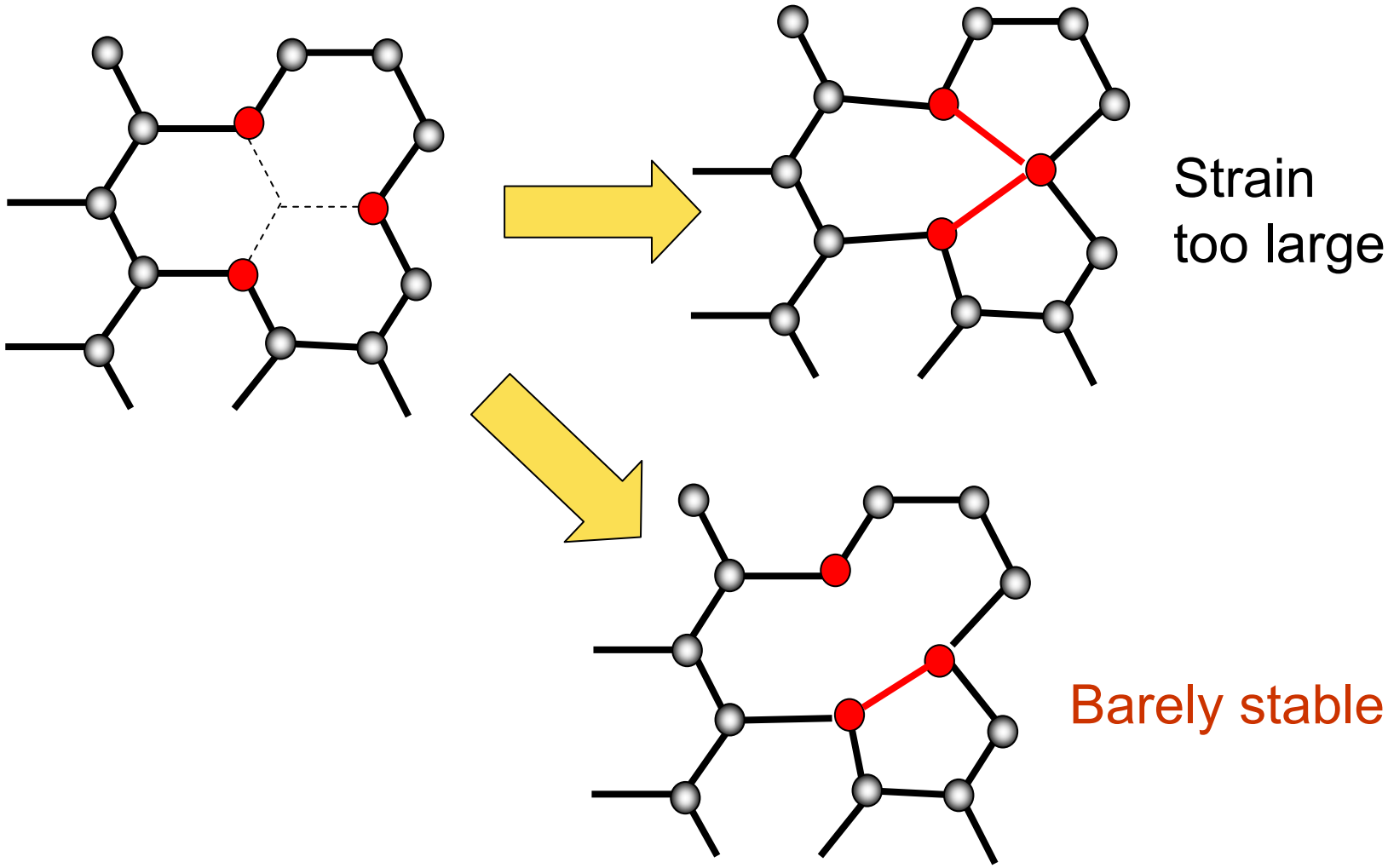
Choi, Ihm, Louie, Cohen, PRL (2000)

Missing network of π electrons

Dangling bonds: σ electrons

Individual defects significantly degrade conductance of a nanotube

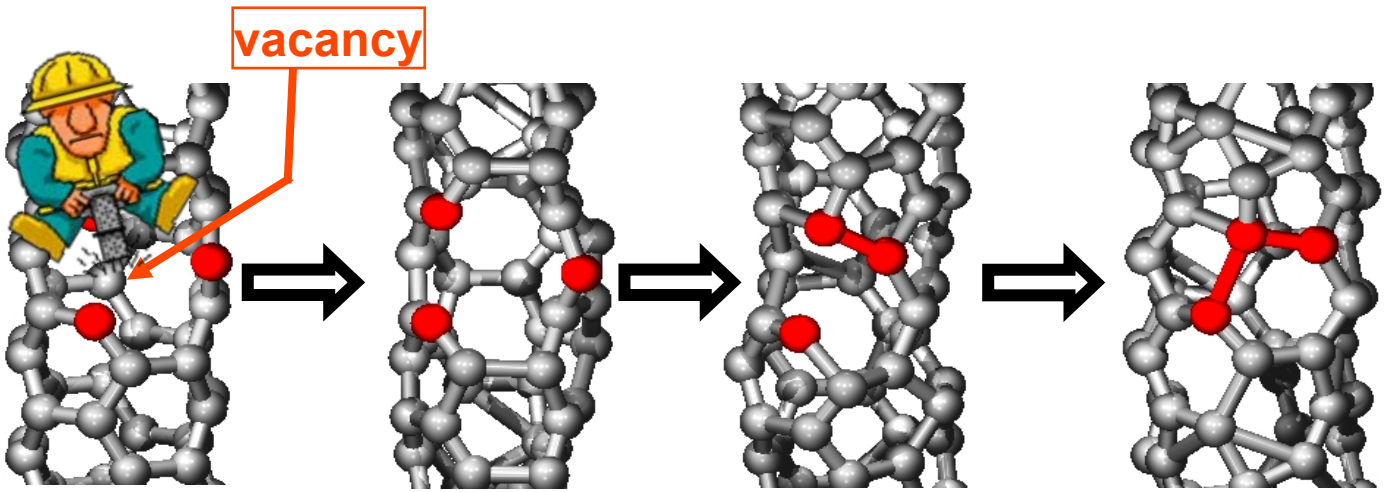
Equilibrium structure near a monovacancy in sp^2 carbon

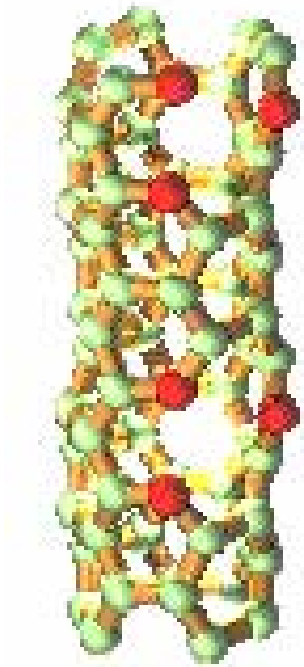


How stable are defective tubes?

Stability of defective tubes at high temperatures

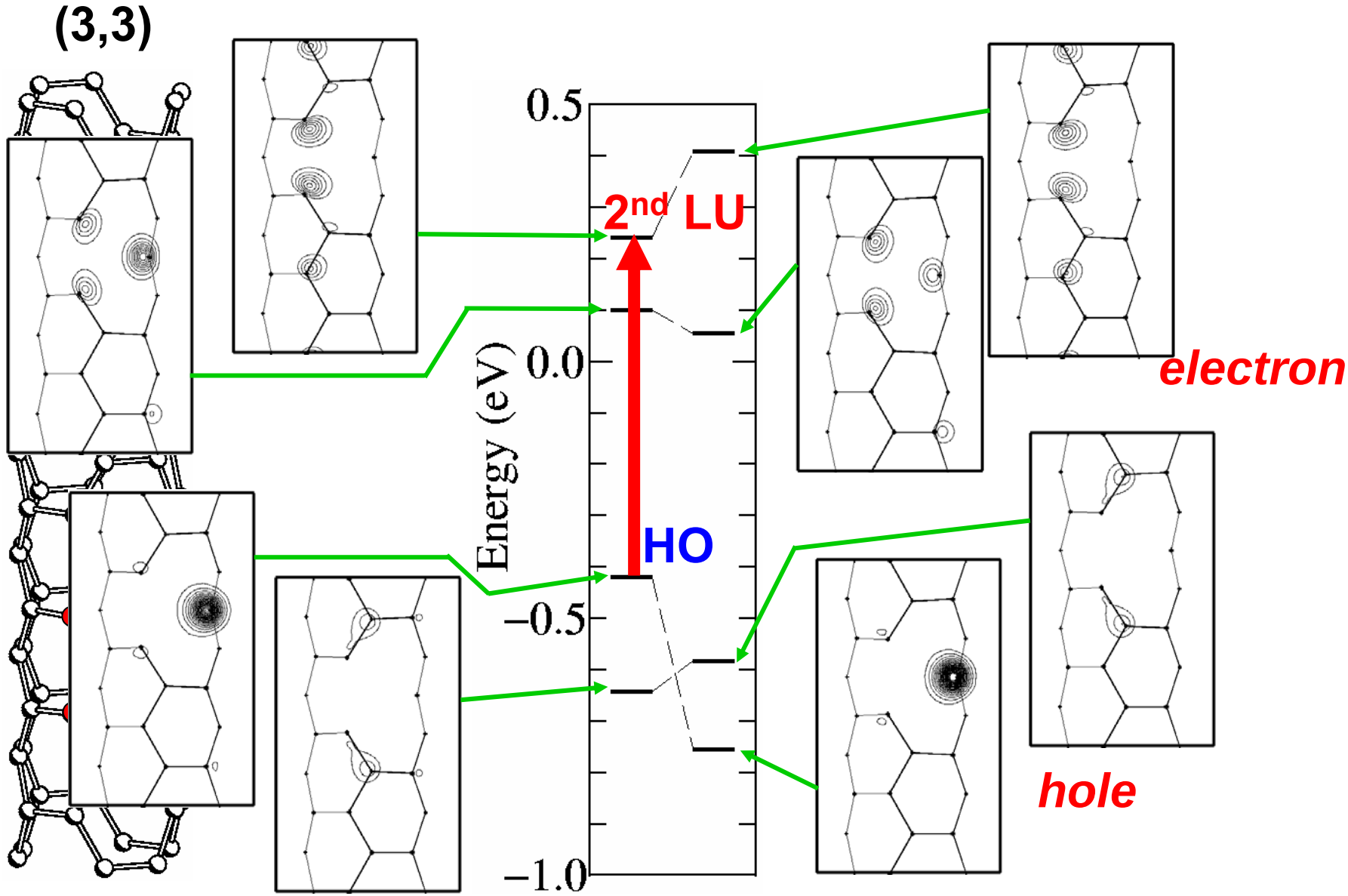
- Danger of pre-melting near vacancies?



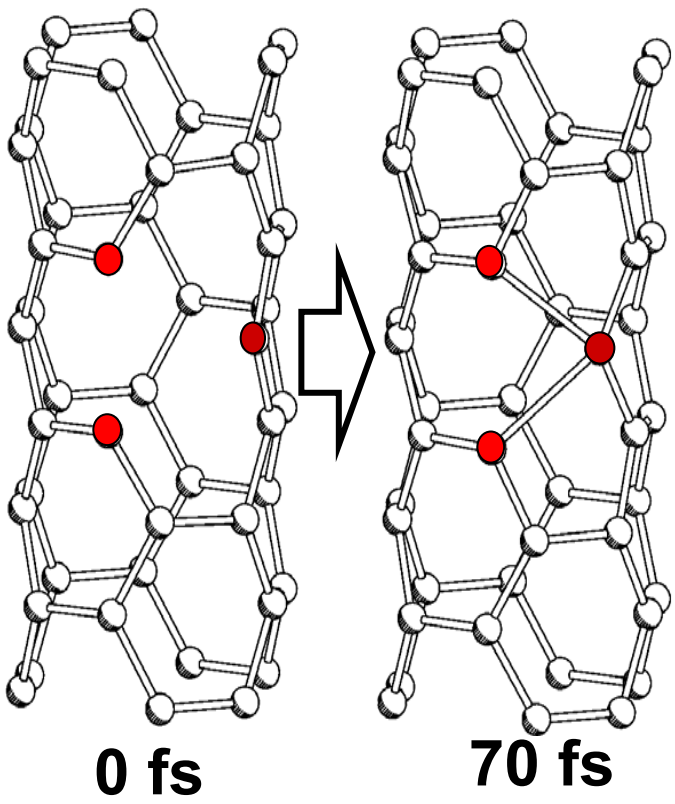


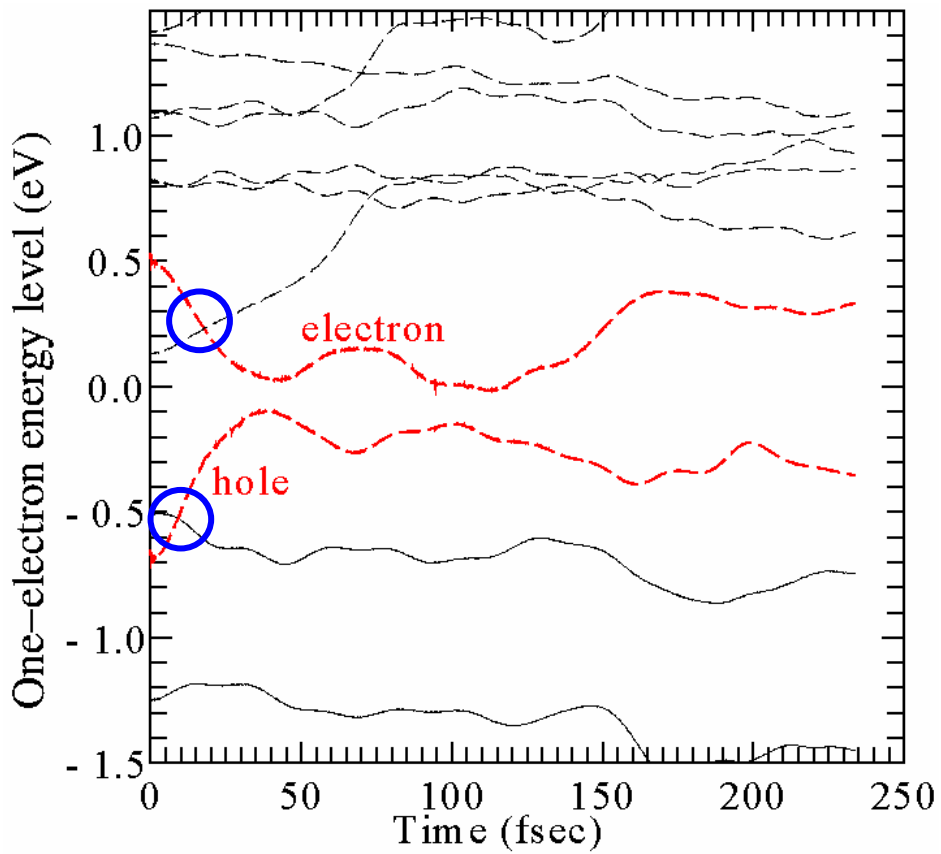
- Nanotube remains intact until 4,000 K
- Self-healing behavior:
  Formation of new bond helps recover
  - structural stiffness
  - conductance

Optical excitation (ΔE=0.9 eV)



Time evolution of the electronic states

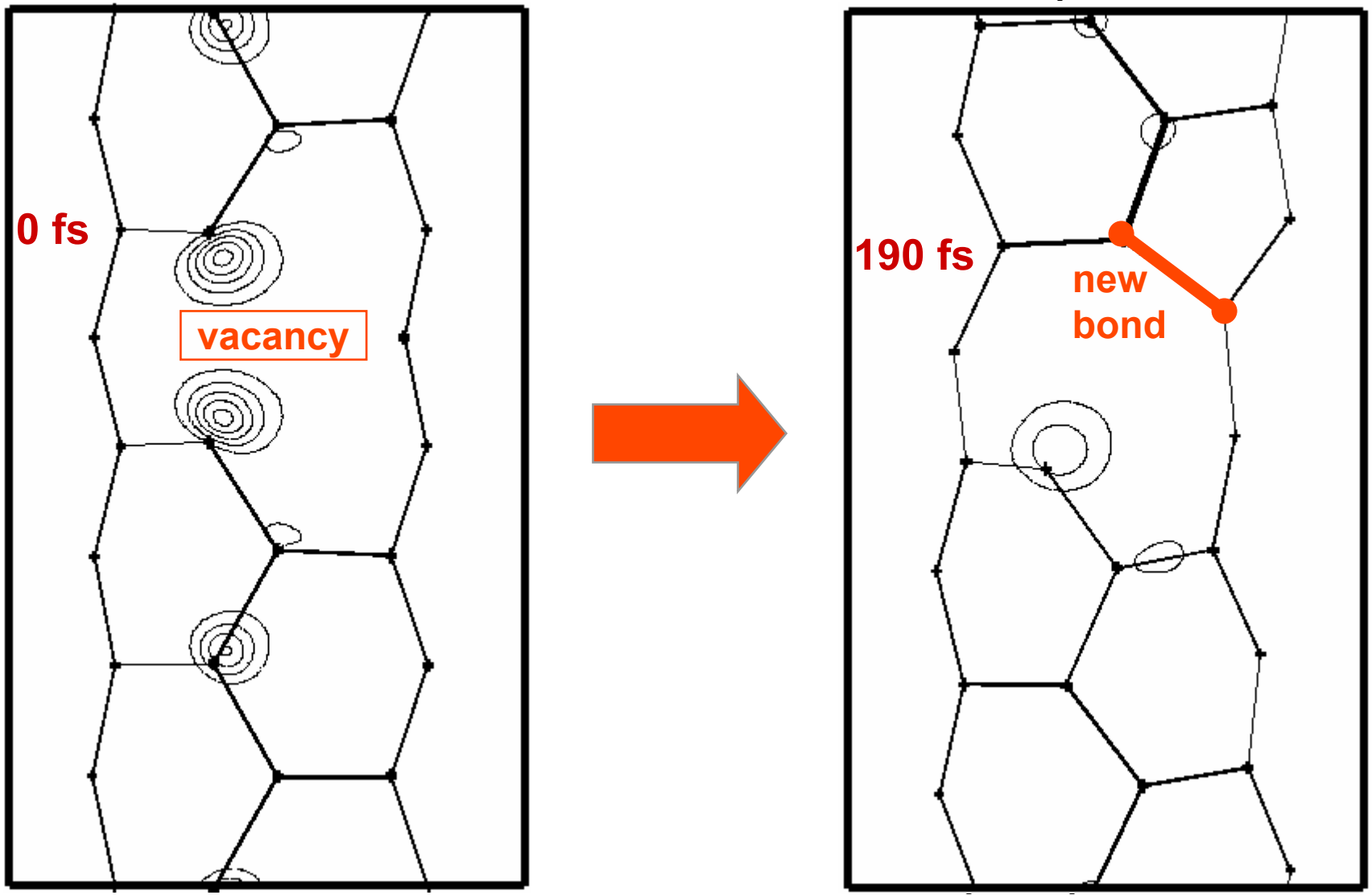




$\Psi_n(t+\Delta t)=\exp(-i/h\, H\Delta t)\,\Psi_n(t)$

- Very long-lived excitation
- Correct PES is followed in case of level alternation

Structural changes under illumination

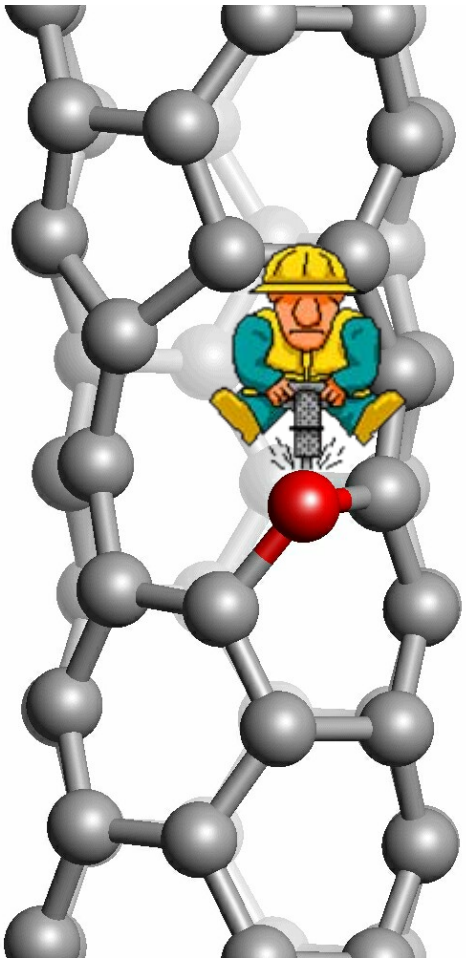


♦Self-healing due to new bond formation

Y. Miyamoto, S. Berber, M. Yoon, A. Rubio, D. Tománek, Can Photo Excitations Heal Defects in Carbon Nanotubes? Chem. Phys. Lett. 392, 209–213 (2004)

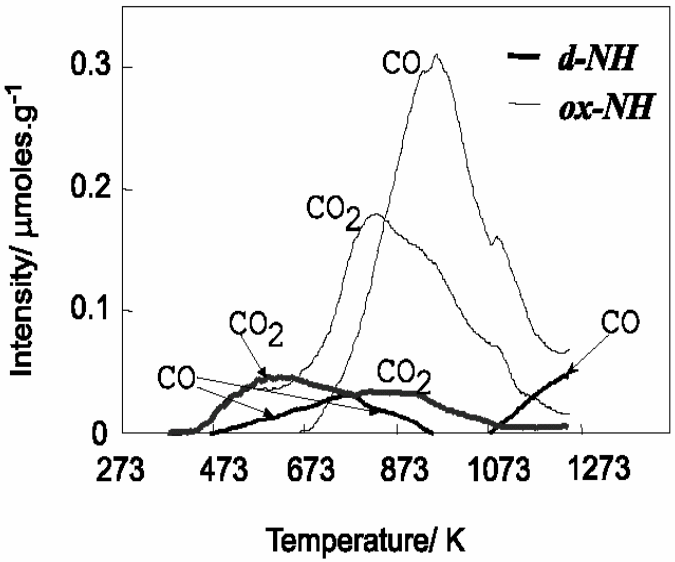
Deoxidation of defective nanotubes

How to deoxidize?

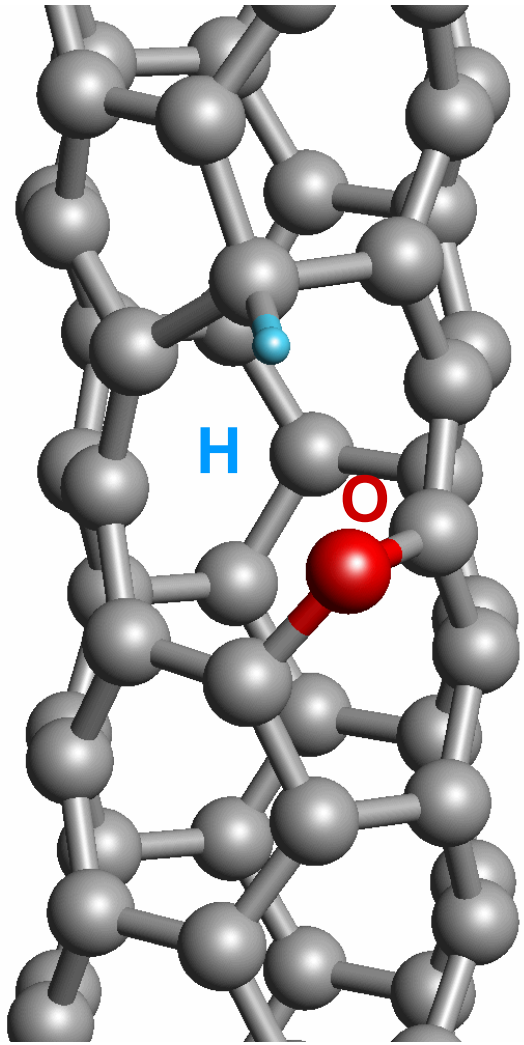


▪By heat treatment?

⇒No: Larger damage to nanotube



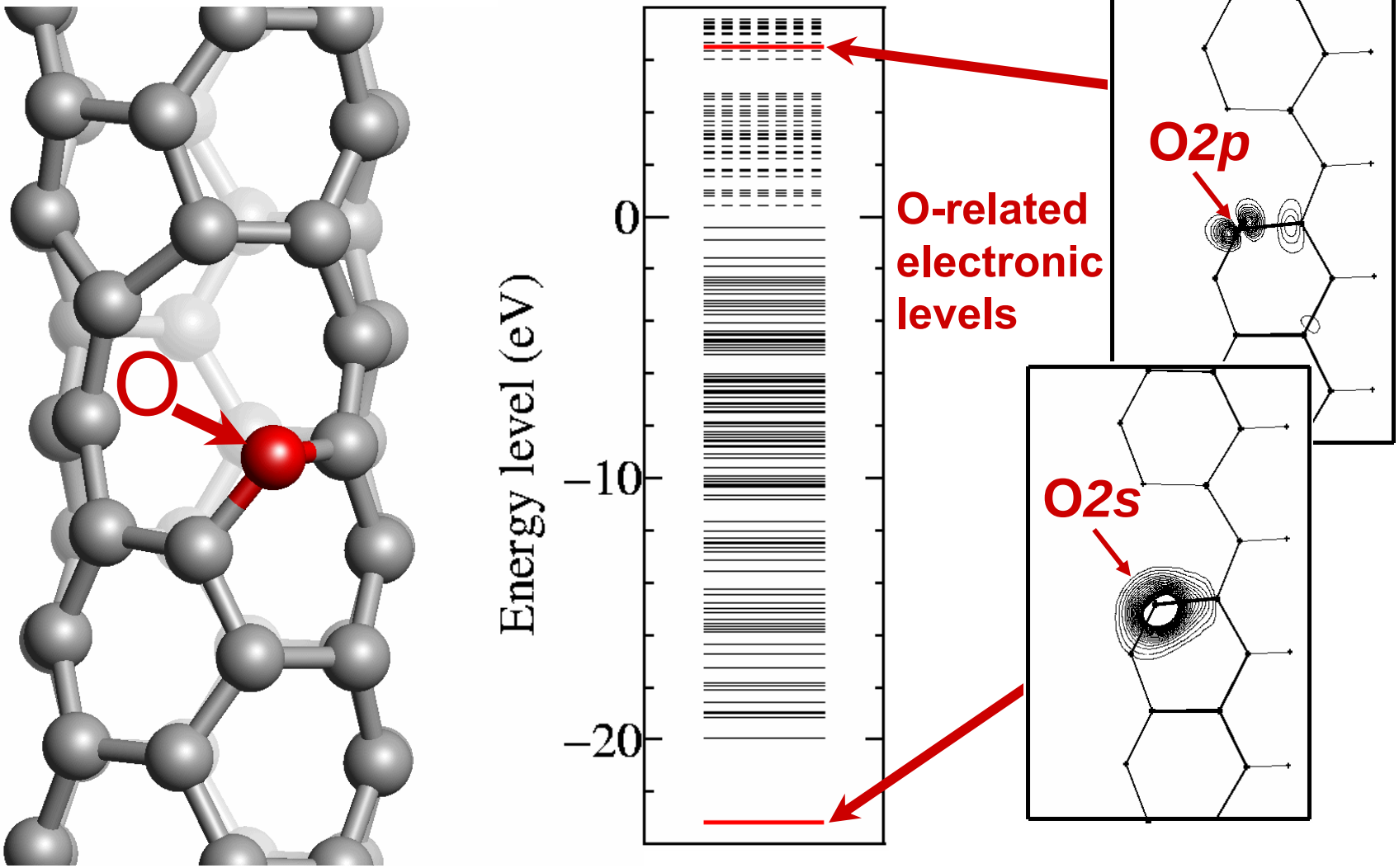
▪By chemical treatment with H?



Yoshiyuki Miyamoto, Noboru Jinbo, Hisashi Nakamura, Angel Rubio, and David Tománek, Photosurgical Deoxidation of Nanotubes, Phys. Rev. B 70, 233408 (2004).

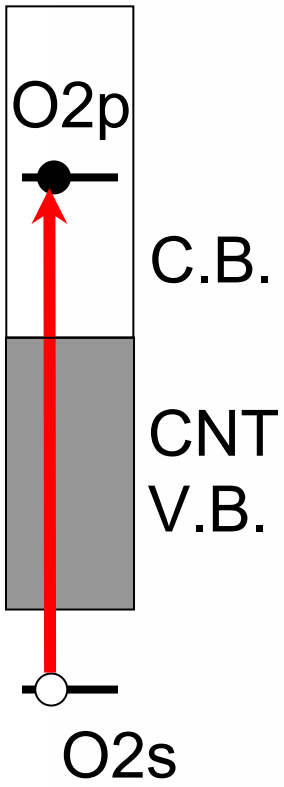
Alternative to thermal and chemical treatment

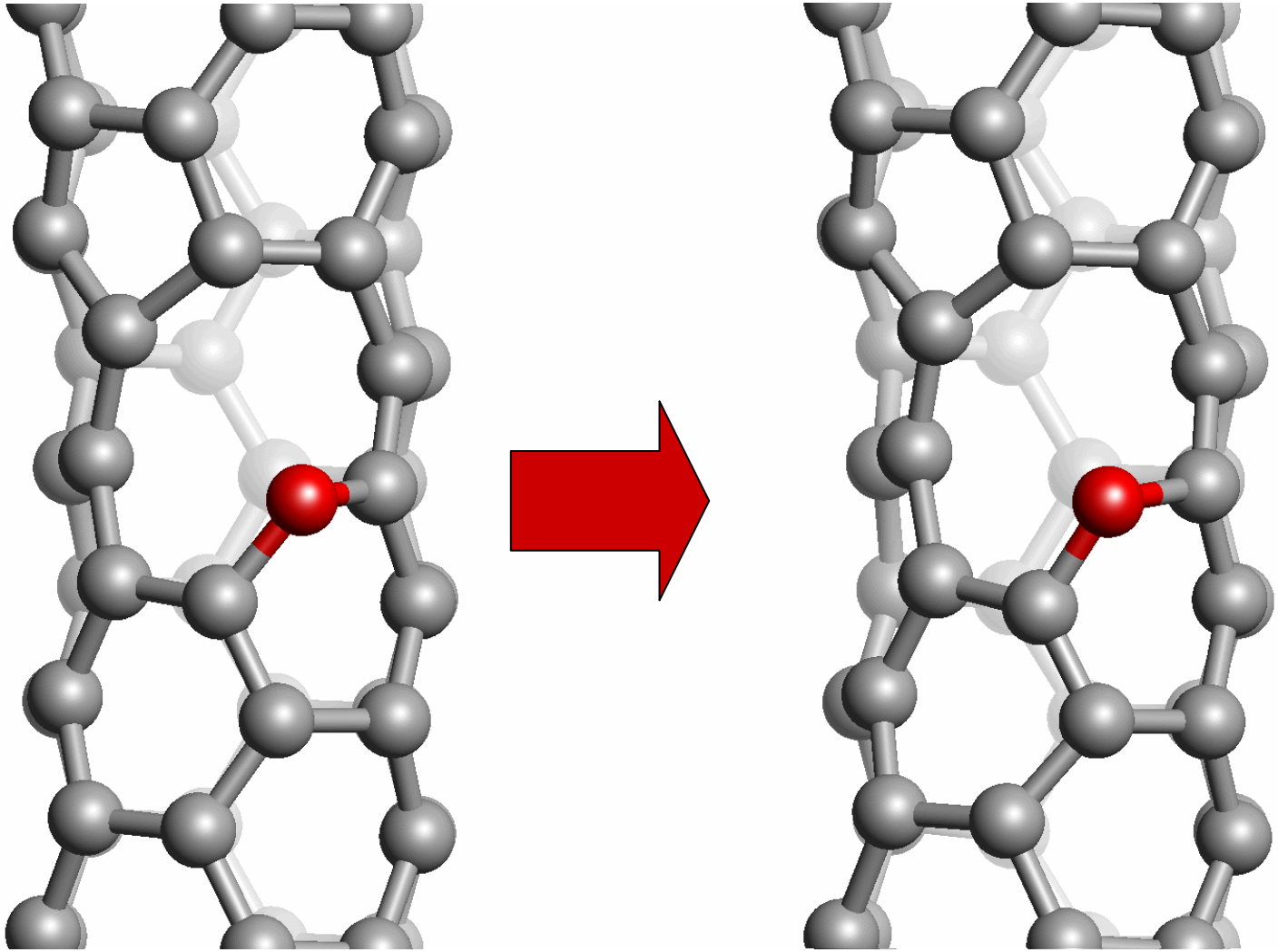
Electronic excitations!



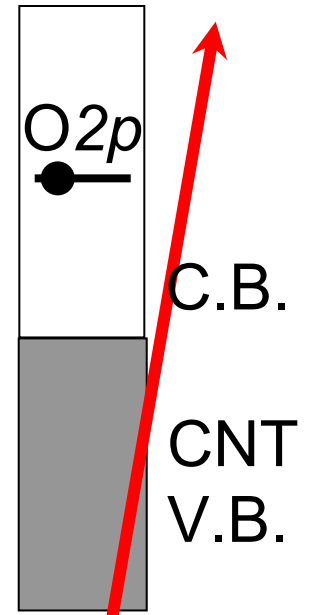
O2*s* → O2*p excitation (33 eV)*

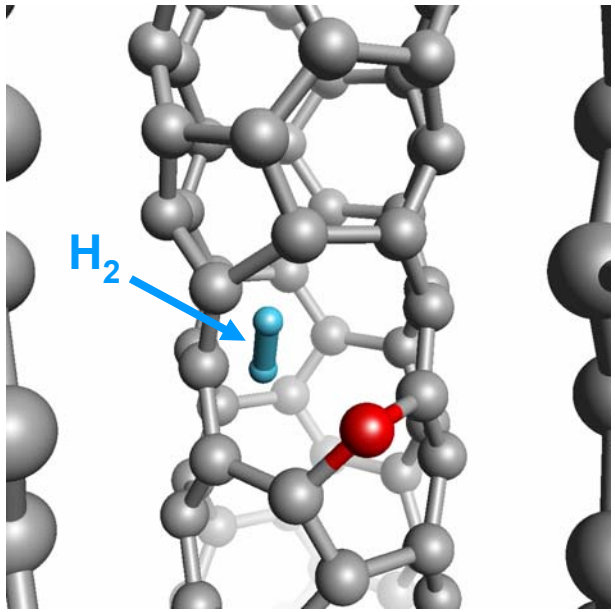
hopeless

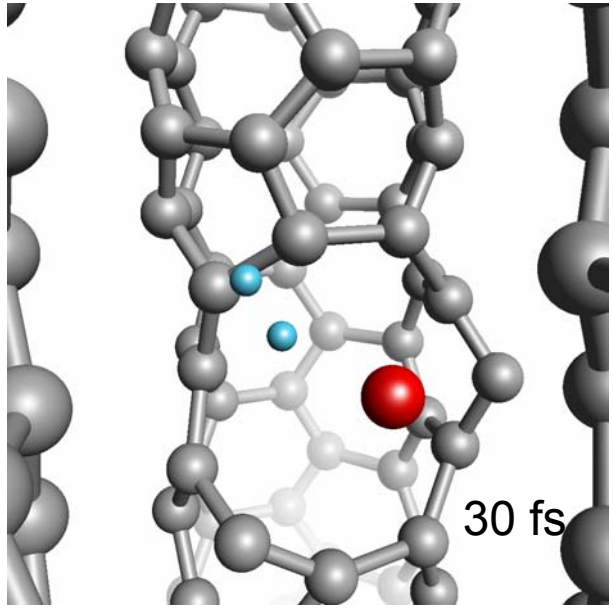


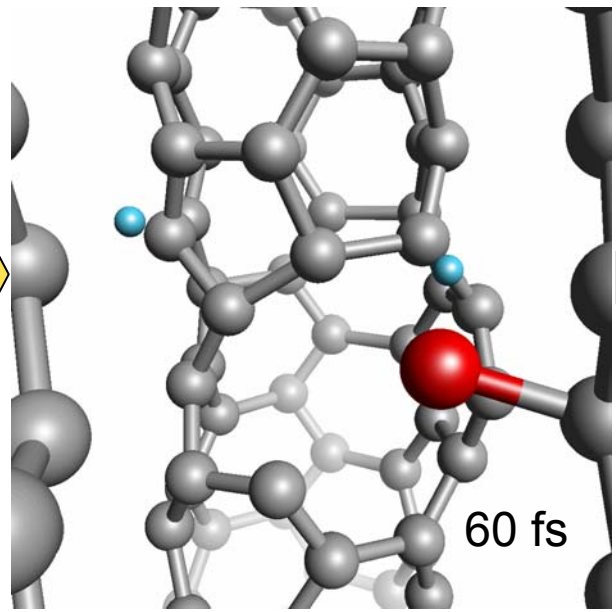


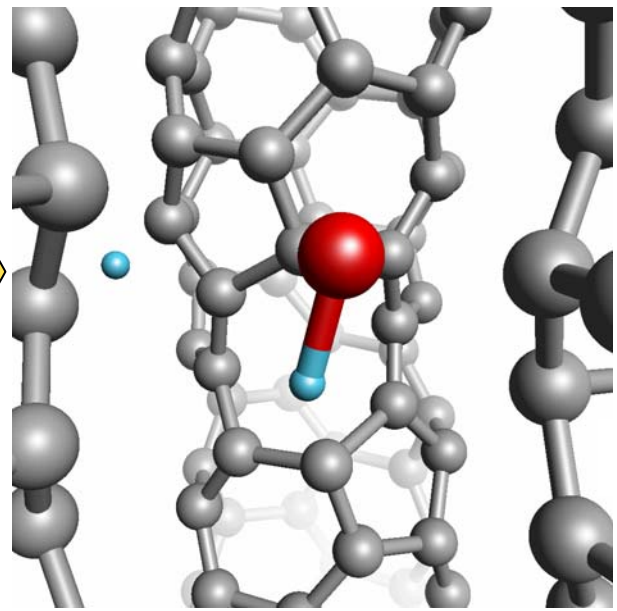
Auger decay following the O1s → 2p excitation (~520 eV)











♦Deoxidation by photo-surgery

Acknowledgements

Savas Berber,	*University of Tsukuba, Japan*
Young-Kyun Kwon,	*University of Massachusetts, Lowell*
Yoshiyuki Miyamoto,	*N.E.C. Tsukuba, Japan*
Hisashi Nakamura,	*RIST Tokyo*
Angel Rubio,	*University of Pais Vasco, Spain*

Special thanks for electronic structure viewgraphs:

Jesper Nygård	*University of Copenhagen*

Financial Support:

NSF-NSEC
NSF-NIRT

JAMSTEC-ESC (Japan)
RIST (Japan)