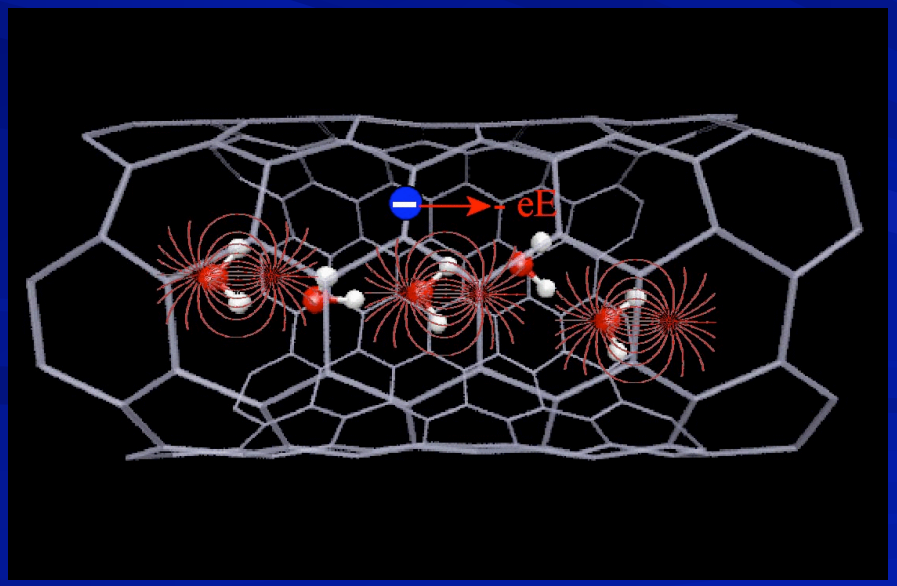
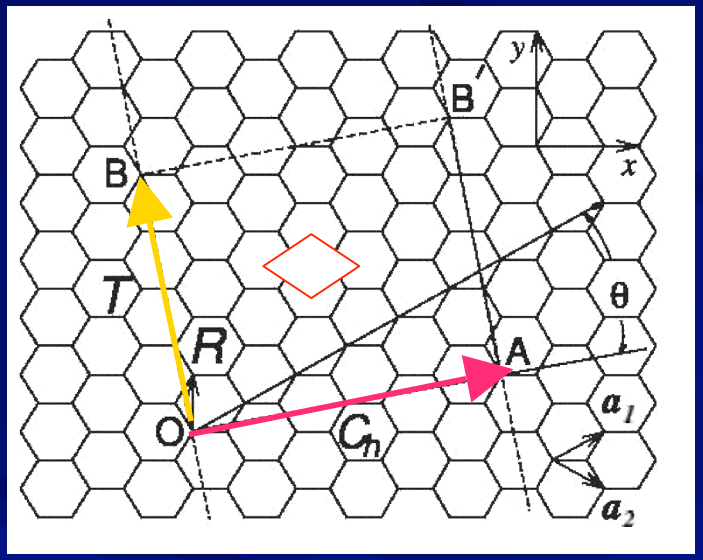
Electronic structure and dielectric behavior of finite-length single-walled armchair carbon nanotubes

Deyu Lu, Klaus Schulten
Yan Li, Slava Rotkin, Umberto Ravaioli
Beckman Institute, UIUC

8/10/2004



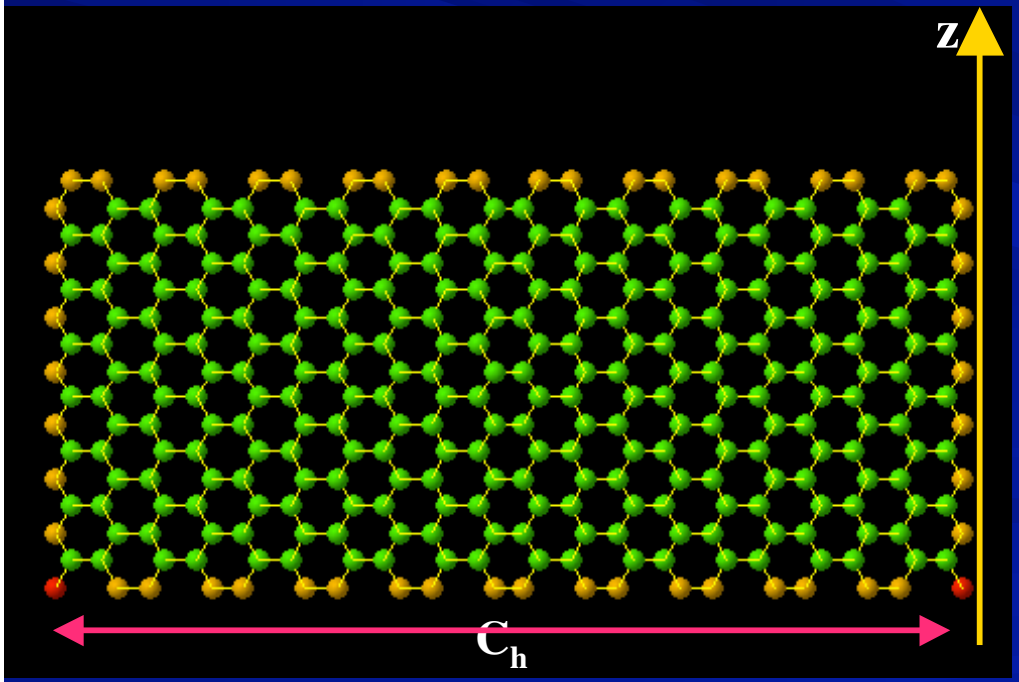
Carbon Nanotube



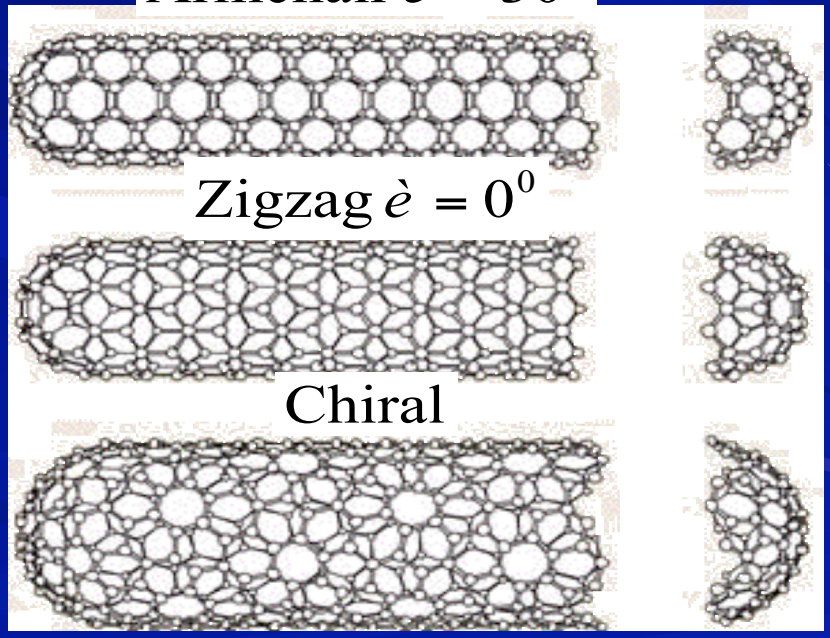
Rolling up a (10,10) nanotube

$$\vec{C}_h = n\vec{a}_1 + m\vec{a}_2 \text{ or } (n,m)$$

$$\begin{cases} \text{metallic}: & \text{mod}(n-m,3) = 0 \\ \text{semiconducting}: & \text{mod}(n-m,3) = 1 \text{ or } 2 \end{cases}$$



Armchair $\grave{e} = 30^0$

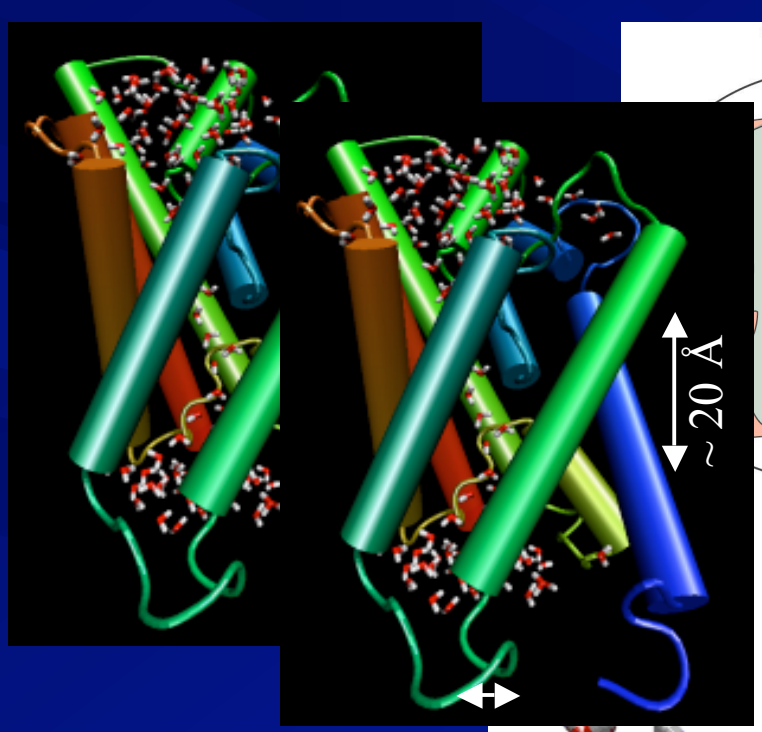


Zigzag $\grave{e} = 0^0$

Chiral

By Shigeo Maruyama, University of Tokyo, Japan

Nanotube & molecular channels



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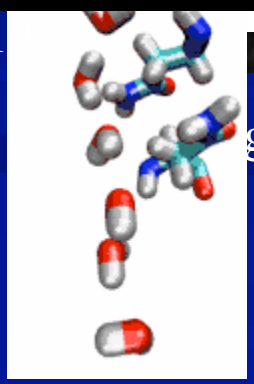
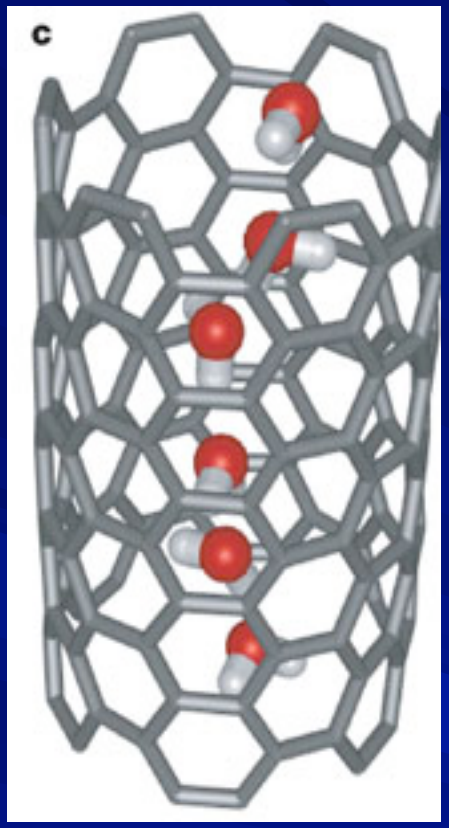


gre

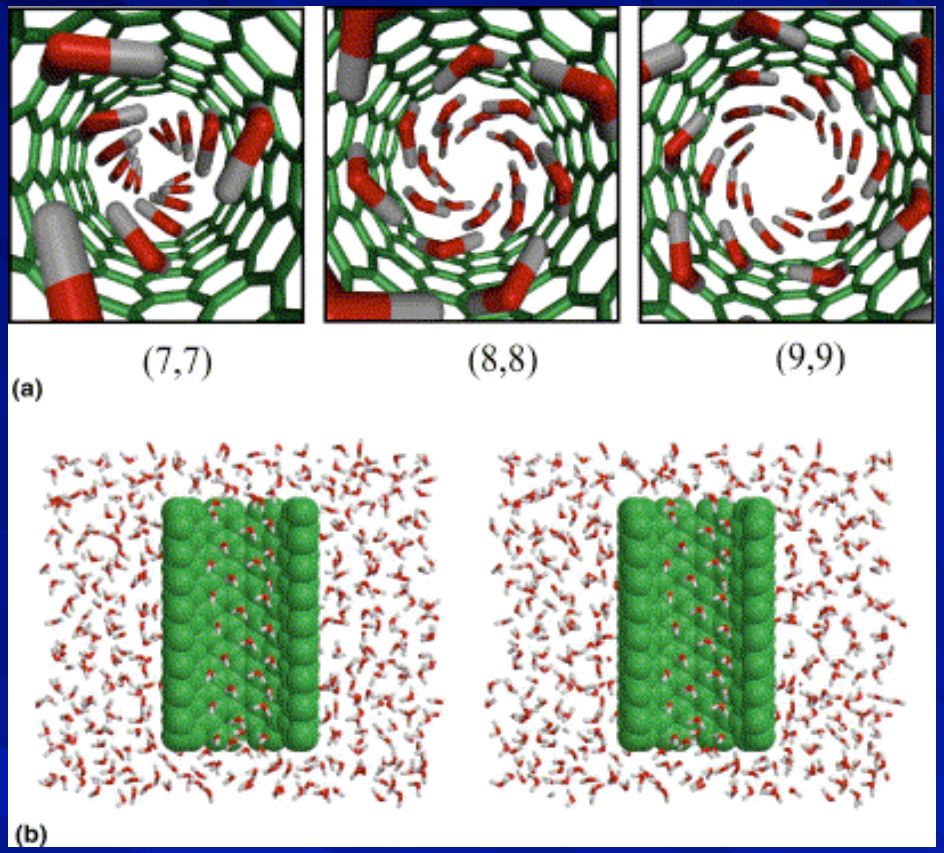
Roderick

8 Å

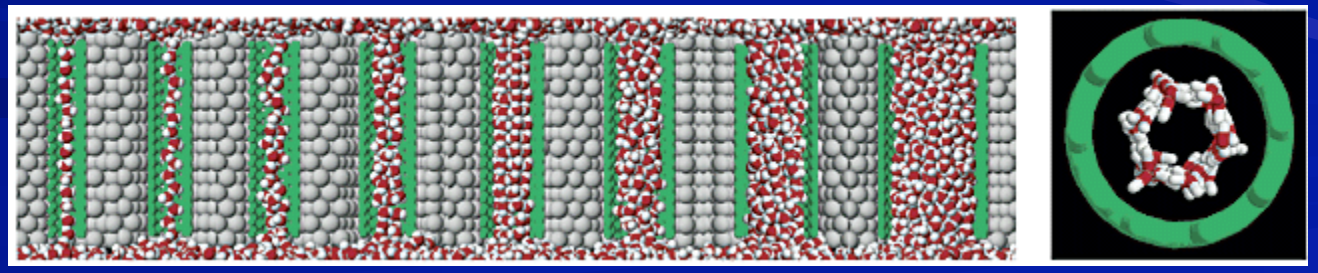
Nano-water



Hummer *et al.,* 2001

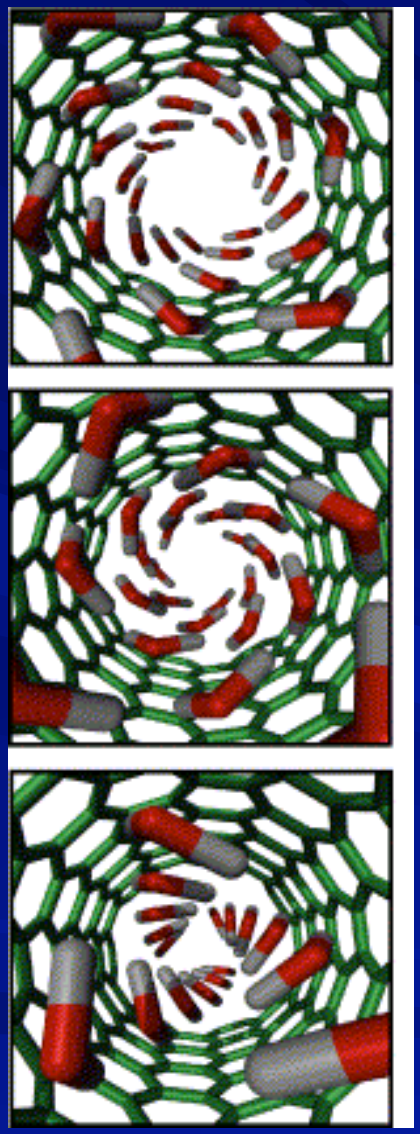


Noon *et al.,* 2002



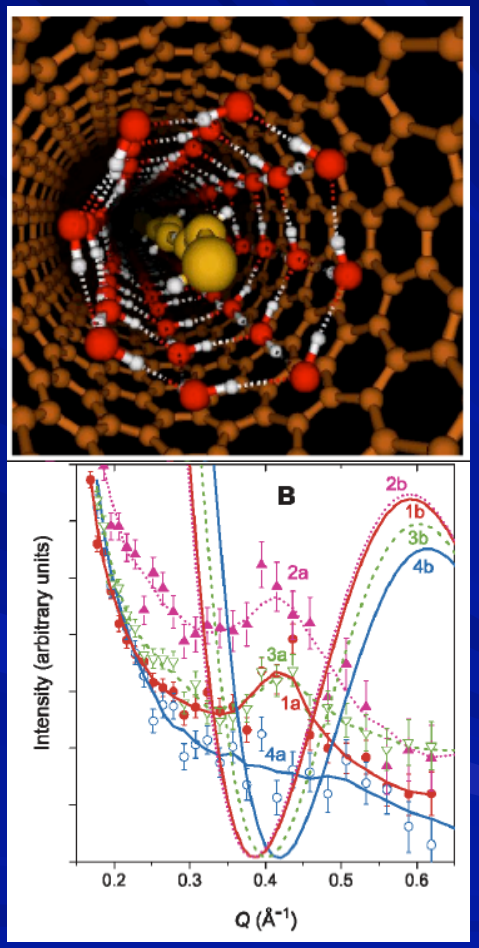
Mashl *et al.,* 2003

Nano-water



Noon *et al.*, 2002

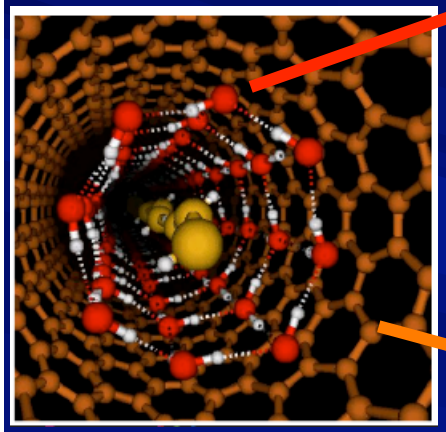
simulation



Kolesnikov *et al.*, 2004

Experiment + simulation

Motivation: Model nano-water system
A polarizable model



Kolesnikov *et al., PRL*, 2004

Water (ions,polymers)

VdW interaction

Electronic interaction

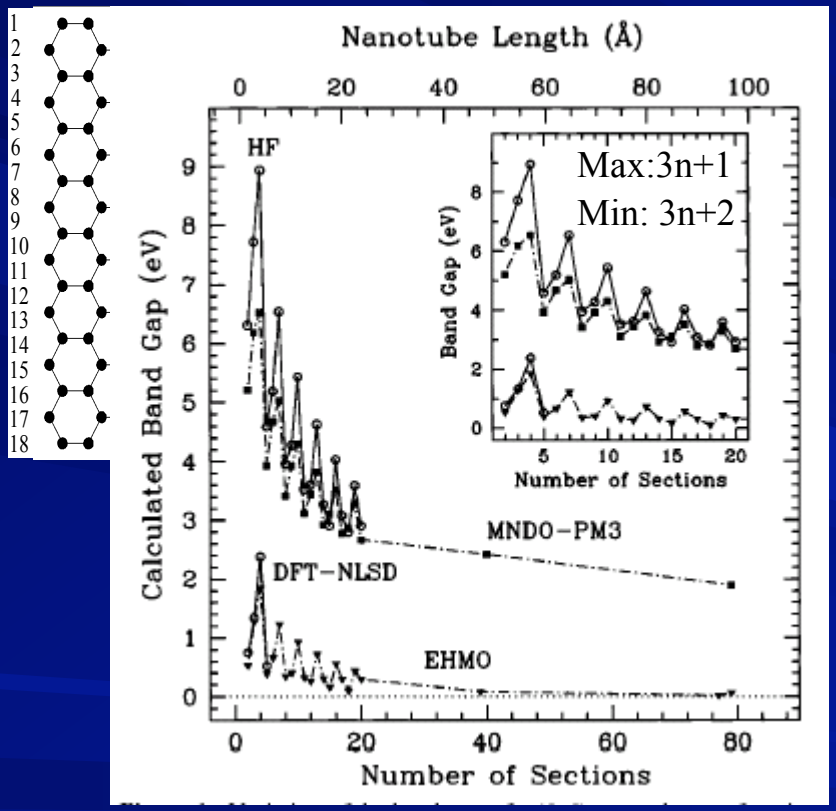
Polarizable CNT

CNT does not only serve as a nm-size pore. The polarization effect of CNT may also modify the channel transport dynamics.

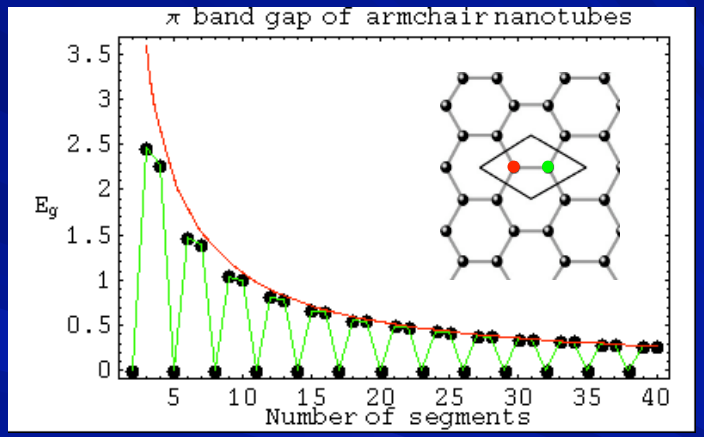
- Classic molecular dynamics: non-polarized CNT
- *ab initio* method: e.g. CPMD polarizable, but slow
- Develop a fast MD method including polarization
  - CNT polarization: Tight-binding model
  - Atomic motion: Classic force field

Band gap of finite armchair CNT

(6,6) armchair



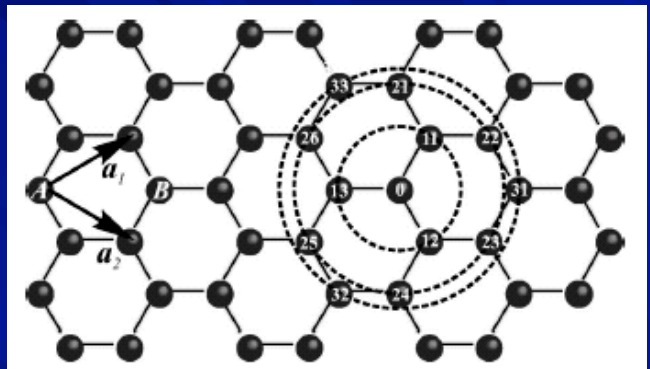
Particle in the box:



Rochefort, et al., *J. Phys. Chem. B*, 103:641-646, 1999.

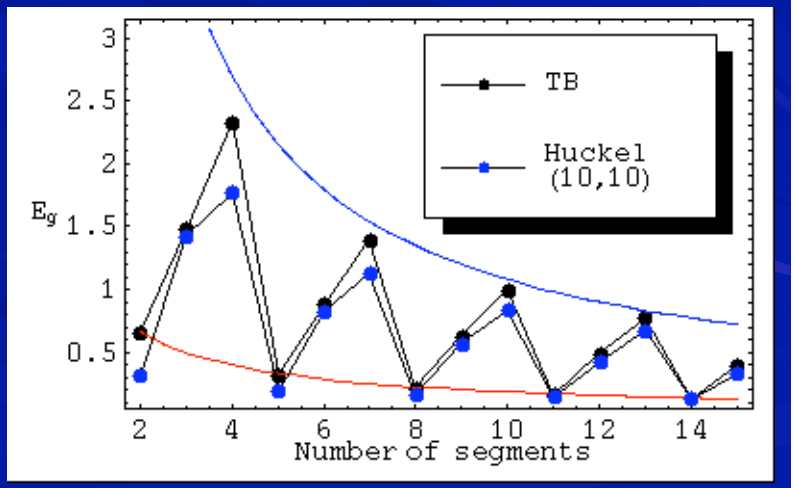
Electronic properties of finite armchair CNT

- Frontier wave functions are from π-orbitals
- 3rd n.n. hopping integral need to be included to break the A-B degeneracy at 3n+2
- The 3rd n.n. TB calculation is able to generate the same band gap pattern as *ab* initio results
- Curvature effect is not large for HOMO/LUMO gap
- The frontier orbitals from the 3rd n.n. TB are identical with Huckel orbitals (n>7)

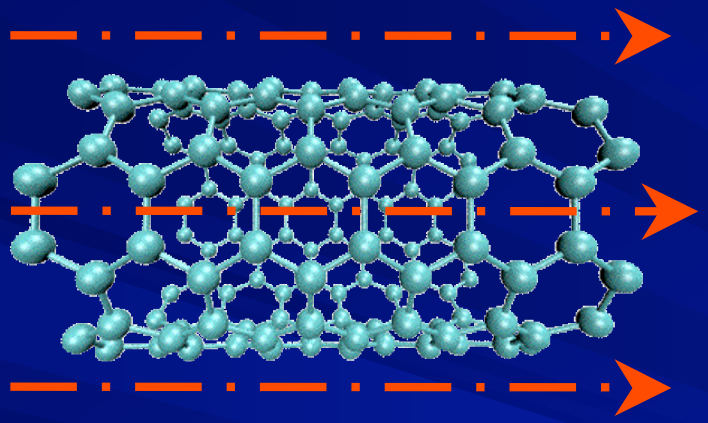


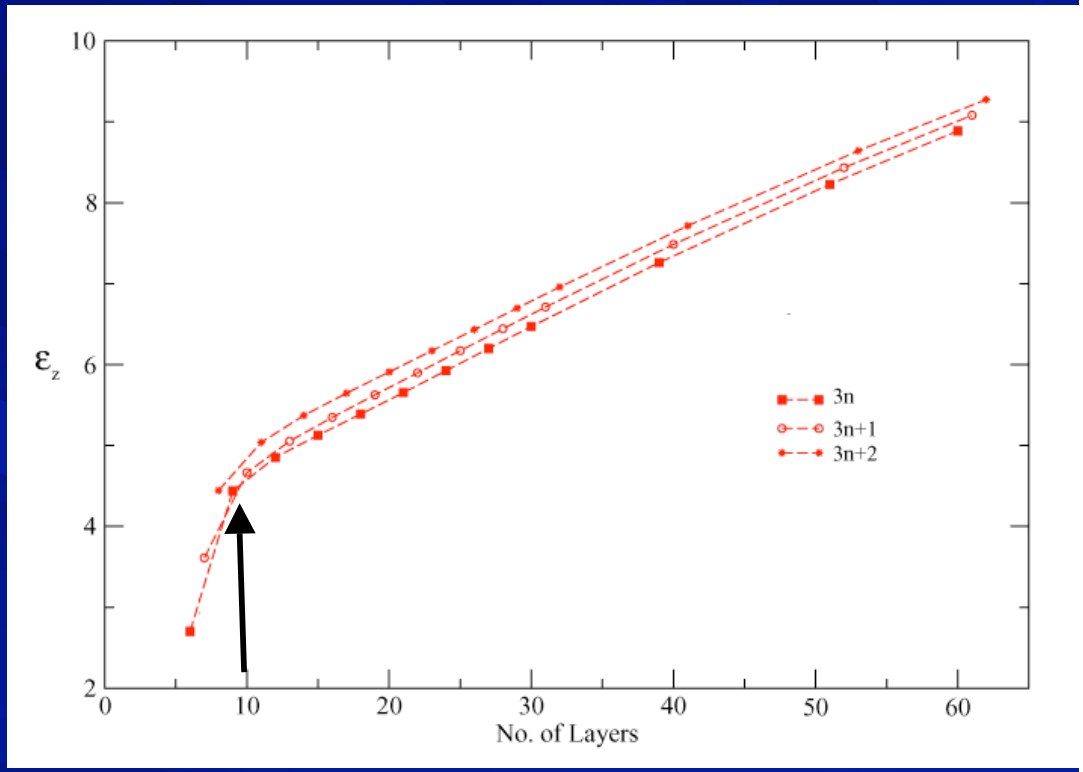
$\gamma_1 = -2.97$ eV, $\gamma_2 = -0.073$ eV, $\gamma_3 = -0.33$ eV

S. Reich, *et al.*, *PRB*,66,035412,2002.



Axial Screening

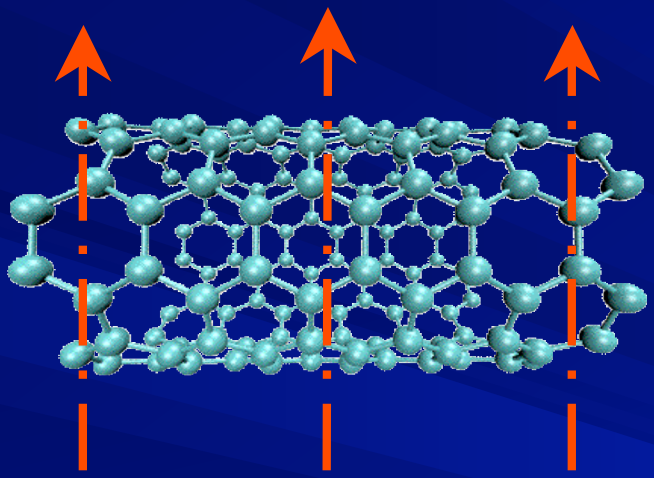


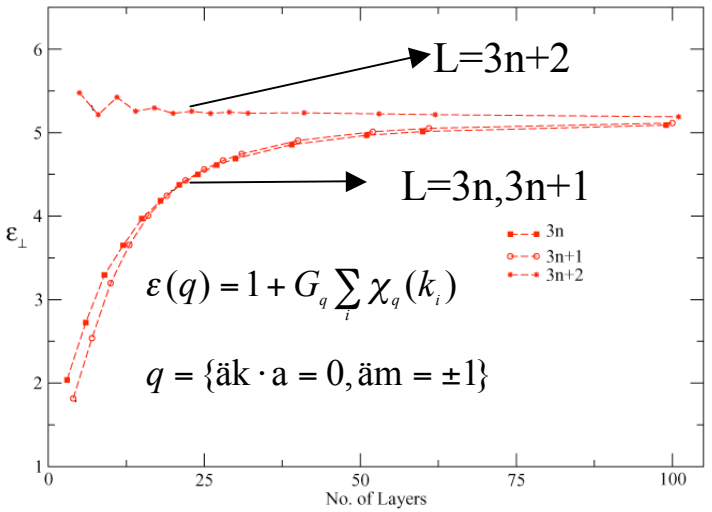


- Infinite long CNT:
  external field is well screened
- Finite length CNT:
  expect the screening effect becomes weaker
- Define:

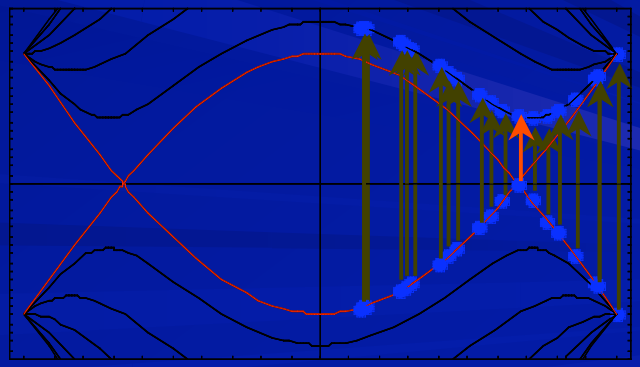
$$\varepsilon_{\parallel} = \left. \frac{V^{ext}}{V^{tot}} \right|_{mid}$$

Perpendicular screening



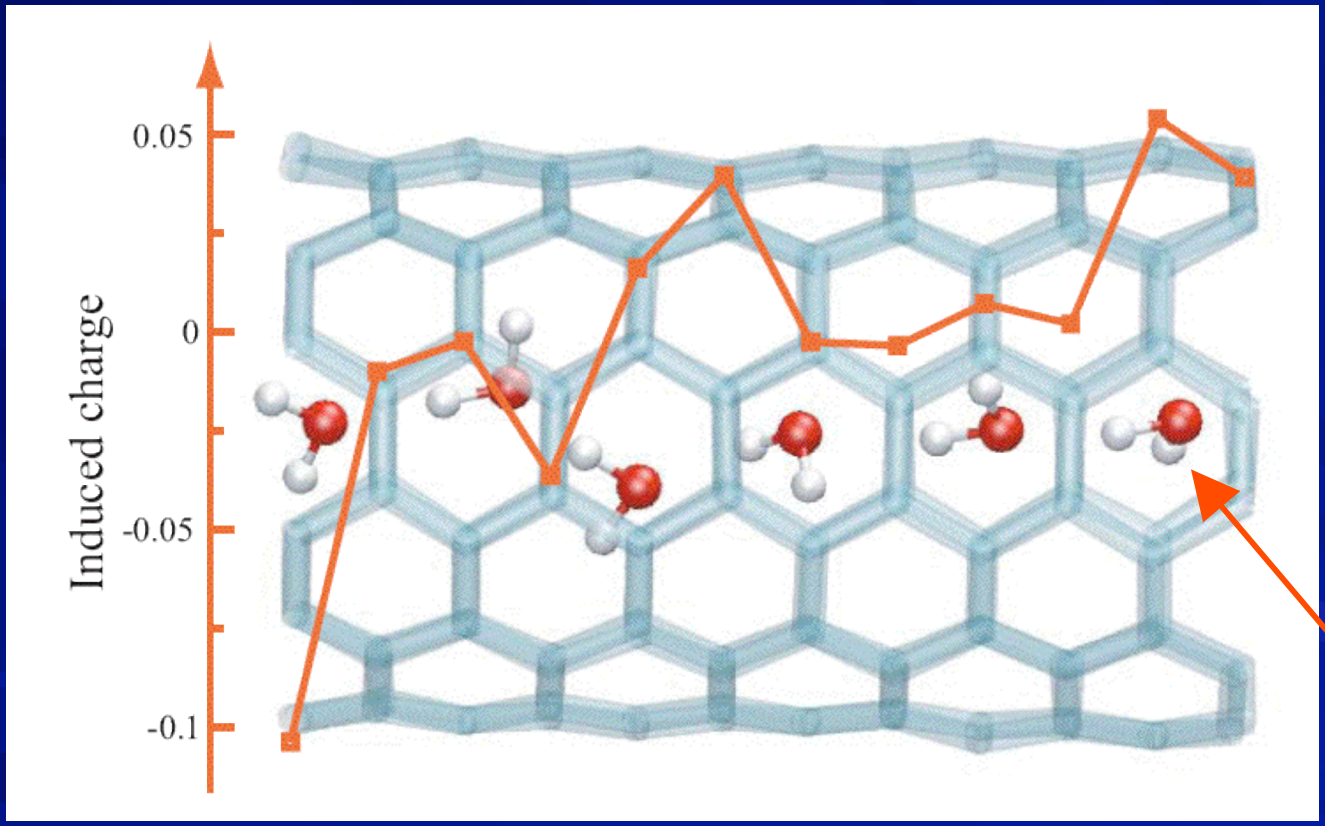


- $\varepsilon_\perp \sim 5$ for infinite long CNT
- For finite length CNT, the screening is the strongest in the middle.
- Define: $\varepsilon_\perp = \left. \frac{V^{ext}}{V^{tot}} \right|_{mid}$



Water chain in CNT channel

Induced charges along the axis of a (6,6)



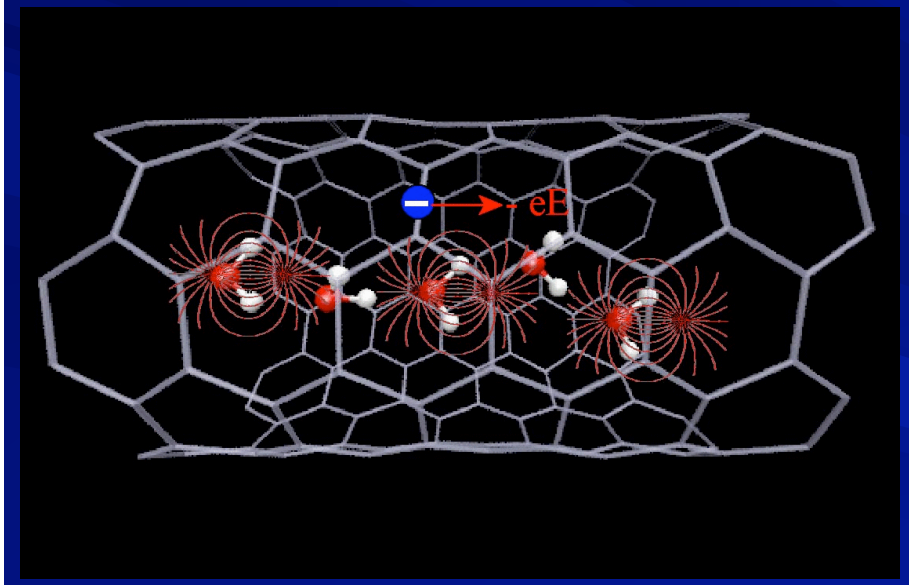
Partial charge

H: 0.417

O: -0.834

water profile from MD simulation

Water chain in CNT channel



dipole moments of a water-filled (6,6) CNT segment

H_2O wire length	μ_x	μ_y	μ_z	$\lvert \mu \rvert$
6 (no CNT)	2.13	-0.54	**-12.03**	**12.23**
	-0.49	-0.79	**16.07**	**16.09**
6 (with CNT)	0.43	-0.12	**-5.22**	**5.24**
	0.05	-0.15	**4.53**	**4.53**

ab initio calculation: D. J. Mann and M.D. Halls, *PRL*, 2003

Summary

- Electronic properties of finite length armchair CNT
  - HOMO/LUMO gap oscillation, frontier orbitals
  - Break A/B degeneracy by γ_3
- Factors affecting dielectric behavior
  - Tube length, cross-over of 1D and 0D
  - Different subclasses (l=3n,3n+1,3n+2)
- Induced charge distribution
  - Screening of water dipoles (1/2), large induced Coulomb energy
- **Implement the polarizable carbon nanotube model into MD**
  - **Molecular transport dynamics**
  - **Control channel by external field and functionalization**