Optoelectronic Properties of Carbon Nanostructures

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Oak Ridge National Laboratory

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Computational Materials Physics

Computational Materials Physics
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Naval Research Laboratory
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- Daniel Gunlycke

Optoelectronic Properties of Carbon Nanostructures

- Research issues and goals
- Approach: quasi-one-dimensional nanostructures
  - Use of helical symmetry
  - Use of first-principles band structure methods for helical polymers
- Current research projects
  - ✓ Polymers for photovoltaic bulk heterojunctions
  - ✓ Graphene nanoribbons
  - ✓ Silicon/inorganic nanowires
  - ✓ Double-walled carbon nanotubes
- Research plans
  - TDDFT for quasi-1D systems
  - Transport in electroactive polymers

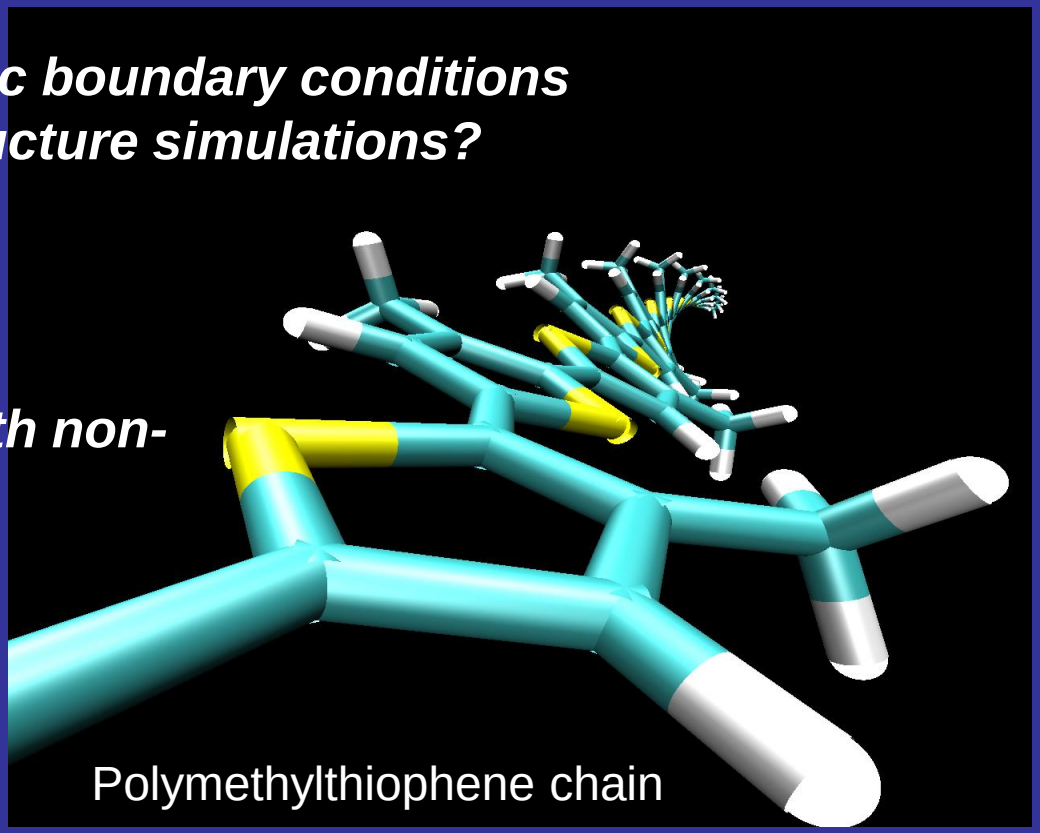
Optoelectronic Properties of Carbon Nanostructures

Research Issues and Goals

Computational modeling of quasi-one-dimensional nanostructures.

How do we use periodic boundary conditions effectively for nanostructure simulations?

How do we treat carbon nanostructures such as electroactive polymers with non-translational periodicity?



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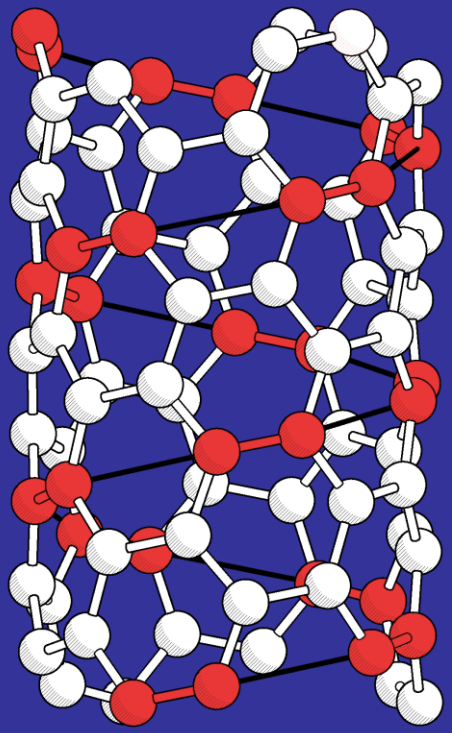
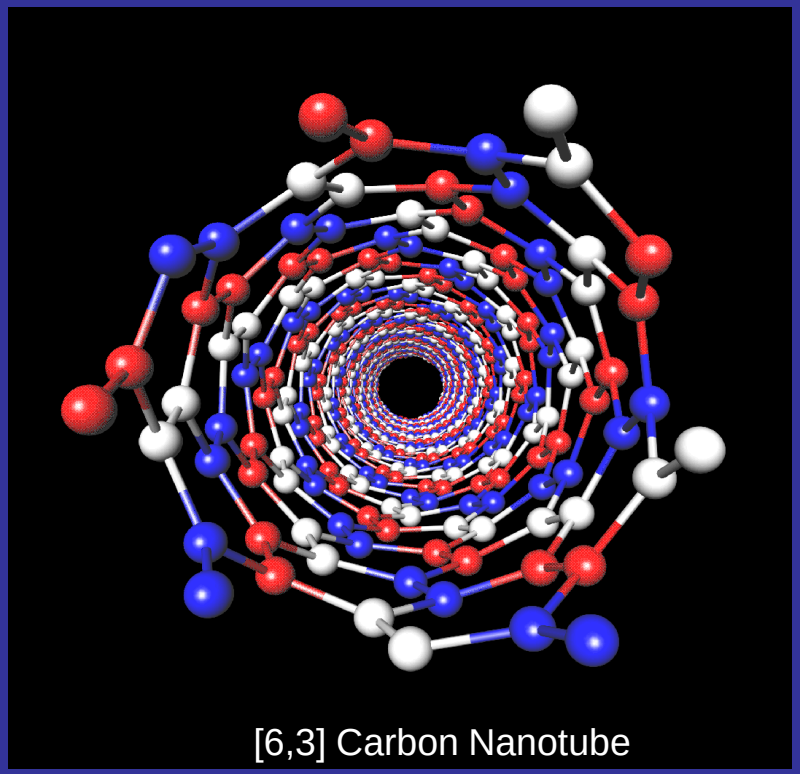
Helical Symmetry

All carbon nanotubes have helical symmetry.
Methods developed to treat polymers apply.
Helical symmetries are essential to comprehensive calculations.





Band Structure of Helical Polymers

Use helical symmetry of polymer backbone

$$\mathcal{S}(h,\phi)\,\mathbf{r} \equiv \begin{pmatrix} x\cos\phi - y\sin\phi \\ x\sin\phi + y\cos\phi \\ z+h \end{pmatrix}$$

One-electron Bloch functions constructed from linear combinations of Gaussian-type functions (real spherical harmonics)

$$\psi_i(\mathbf{r};\kappa) = \sum_j c_{ji}(\kappa)\,\varphi_j(\mathbf{r};\kappa)$$

$$\varphi_j(\mathbf{r};\kappa) = \sum_m e^{-i\kappa m}\,\mathcal{S}^m\,\chi_j(\mathbf{r})$$

$$\rho(\mathbf{r}) = \sum_{i,k} n_i(k)\,\psi_i^*(\mathbf{r};k)\,\psi_i(\mathbf{r};k)$$

Computational needs scale with number of basis functions in unit cell to third power. 10-20 functions usually needed per heavy atom.

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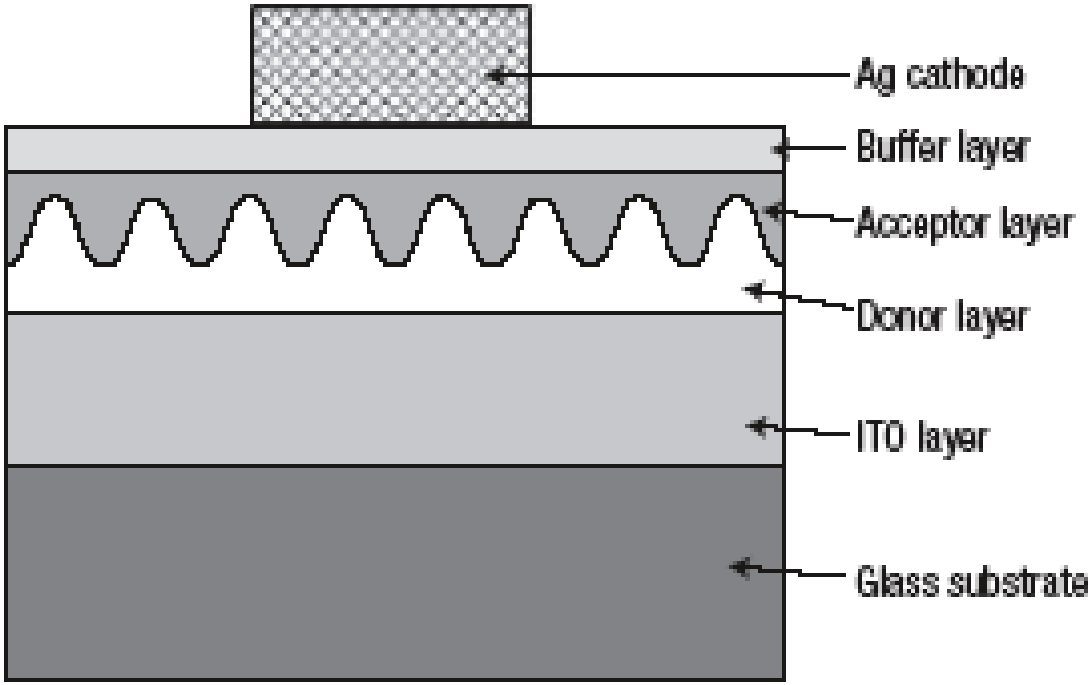
Bulk Heterojunction Photovoltaics

•Need both good donor and acceptor materials, with appropriate hole and electron mobilities

•Polymer-based bulk heterojunctions are cheap to make, but still have relatively low efficiencies

•Few electroactive polymers have good electron mobilities

•Need rapid separation of electron-hole pair to prevent recombination



SWNTs have good electron mobilities

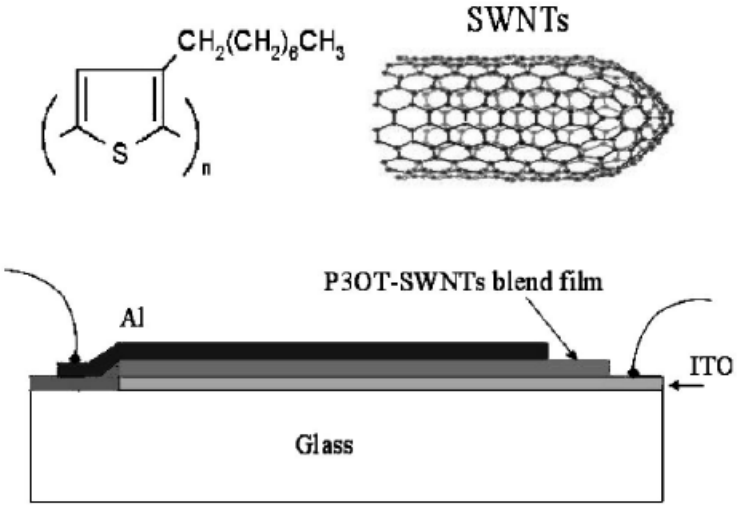


FIG. 1. Chemical structures of P3OT, SWNTs and device architecture of the photovoltaic cells.

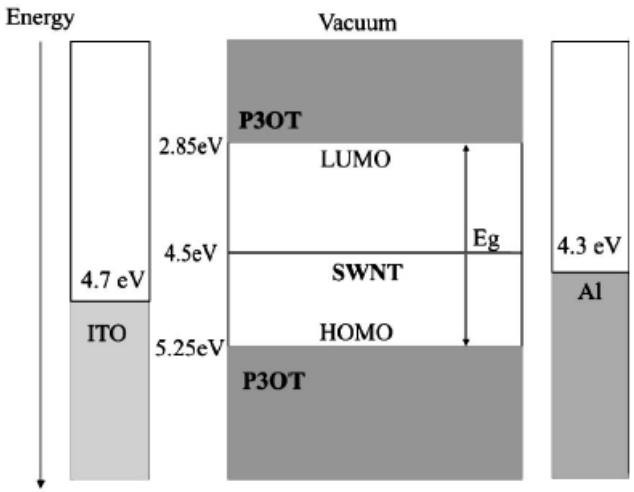
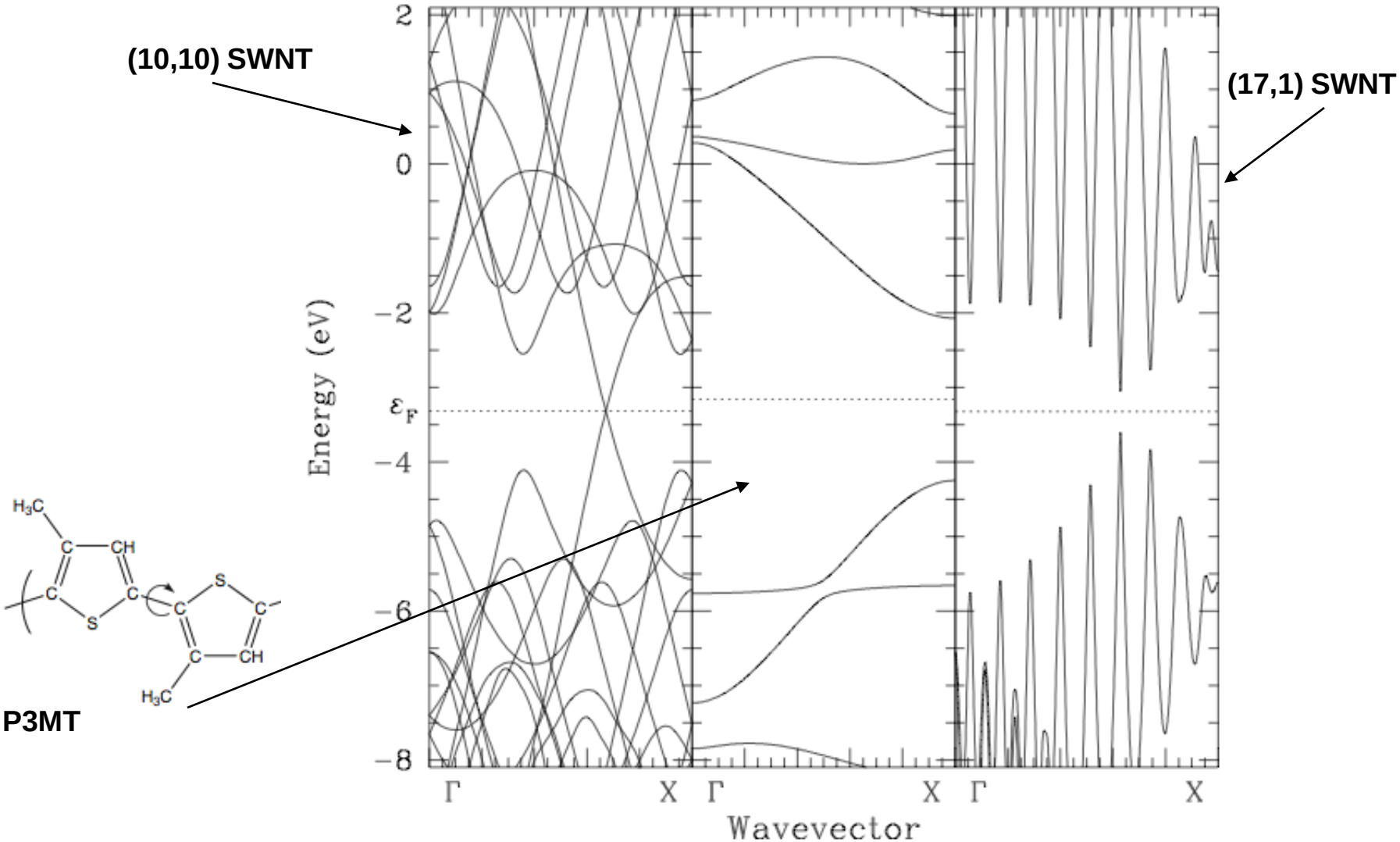


FIG. 7. Potential energy diagrams relative to vacuum level, where LUMO and HOMO are, respectively, the Lumo and Homo of the P3OT.

Kymakis & Amaratunga, APL 80, 113 (2002)



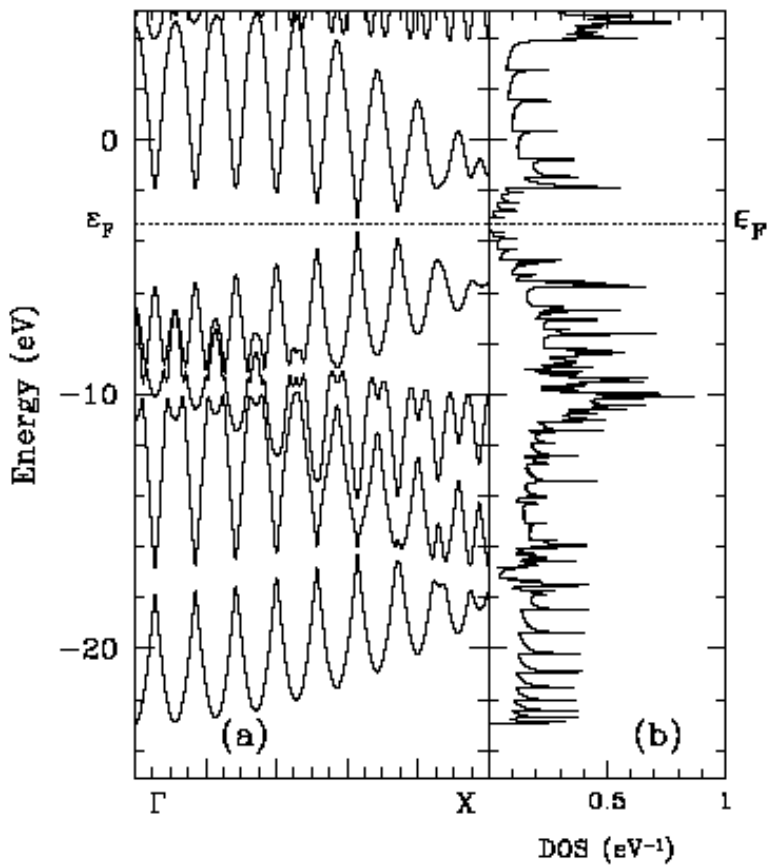
Will electron transport be through metallic or semiconducting SWNTs?

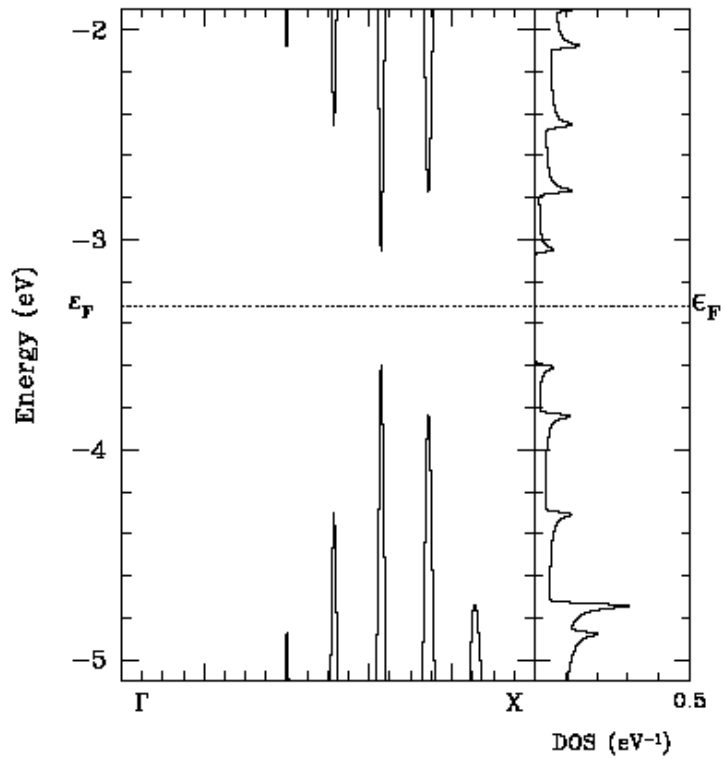
How will backbone dihedral angle disorder change transport properties?

Computational Materials Physics

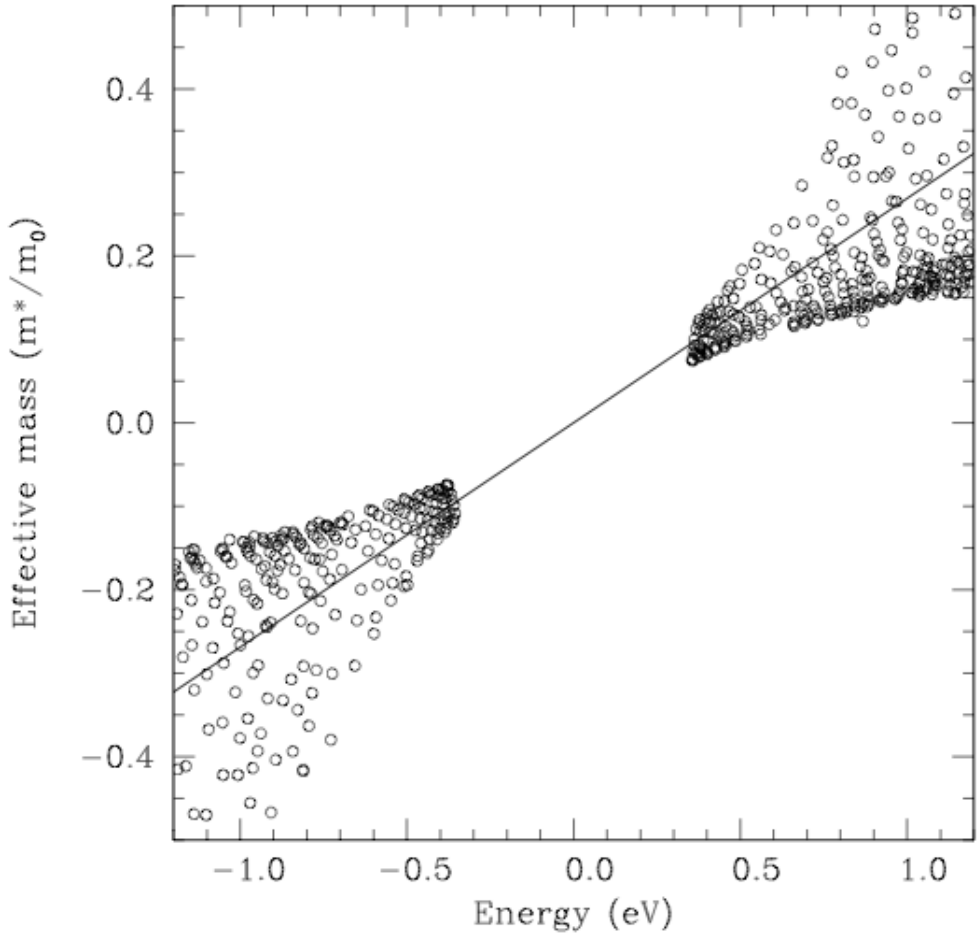
SWNT effective mass proportional to distance from Fermi level

$$m^* = \frac{4\hbar^2 \varepsilon_m}{3V_{pp\pi} a^2} = \frac{4}{3}\frac{\hbar^2}{a^2}\left(\frac{\varepsilon_m}{V_{pp\pi}}\right)$$





T. Jayasekera, M. S. Monigold, S. L. Elizondo, and J.W. Mintmire, Int. J. Quantum Chem. **107**, 3120 (2007).



Calculated effective masses of electron (positive values) and hole (negative values) carriers for several SWNTs at van Hove singularities near the Fermi level for band extrema other than those nearest the Fermi level. The solid line shows the effective mass of charge carriers in the SWNTs as calculated from GSM using $V_{pp\pi}$ = -2.7 eV.

Calculated Effective Mass in Carbon Nanotubes and Polythiophene Polymer

We have calculated the effective mass of the electrons and holes in the polymers at the van Hove singularity closest to the Fermi level and tabulated them with the equivalent values calculated in several carbon nanotubes. Negative values for effective masses represent hole effective masses.

Material	E_v (eV)	m^*_h / m_0	E_c (eV)	m^*_e / m_0
(13 x 6) CNT	-0.29	-0.09	0.29	0.09
(17 x 1) CNT	-0.27	-0.08	0.27	0.08
(17 x 12) CNT	-0.19	-0.10	0.19	0.10
P3MT (147.5)	-1.09	-0.30	1.09	0.42

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Graphene Nanostrips

Why now?

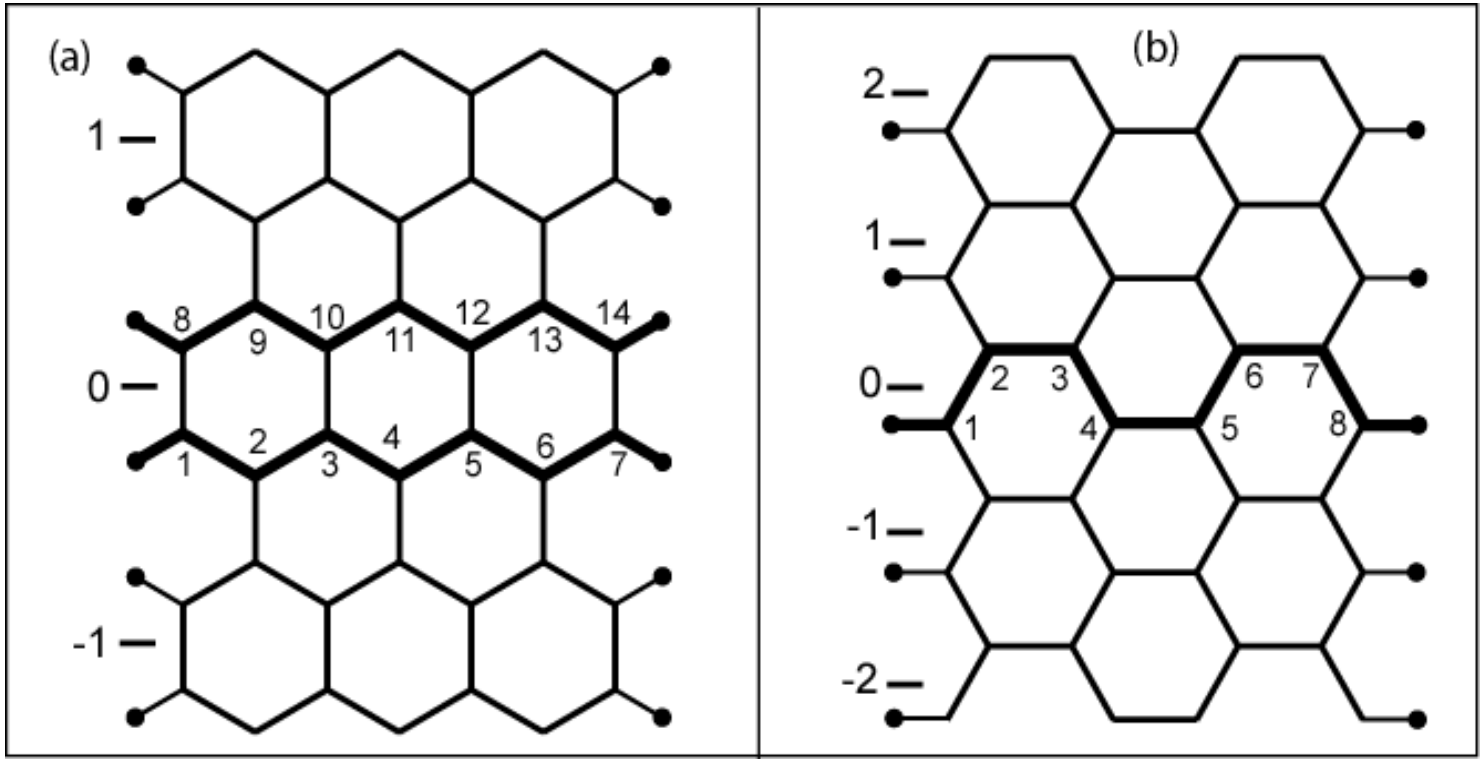
Recently macroscopic single sheets of graphite known as graphene were isolated and found stable, highly crystalline, and chemically inert at ambient conditions. Novoselov, K. S., *et al. PNAS* (USA) **2005**, *102*, 10451.

This advance has stimulated increasing interest in graphene nanostrips (GNSs) partly because they could combine the advantages of high-resolution lithography with nanotube-like electronic properties to achieve large-scale integration of ballistic devices. Berger, C; *et al.*, *J. Phys. Chem. B* **2004**, *108*, 19912.

Novoselov, K. S., et al. *Nature* **2005**, *438*, 197.
Zhang, Y.; *et al*., *Nature* **2005**, *438*, 201.
Berger, C.; *et al*., *Science* **2006**, *312*, 1191.

Graphene Nanostrips (GNSs)
(Graphene Nanoribbons)

Fujita, M. *et al*. *J. Phys. Soc. Jpn.* 1996, *65*, 1920.



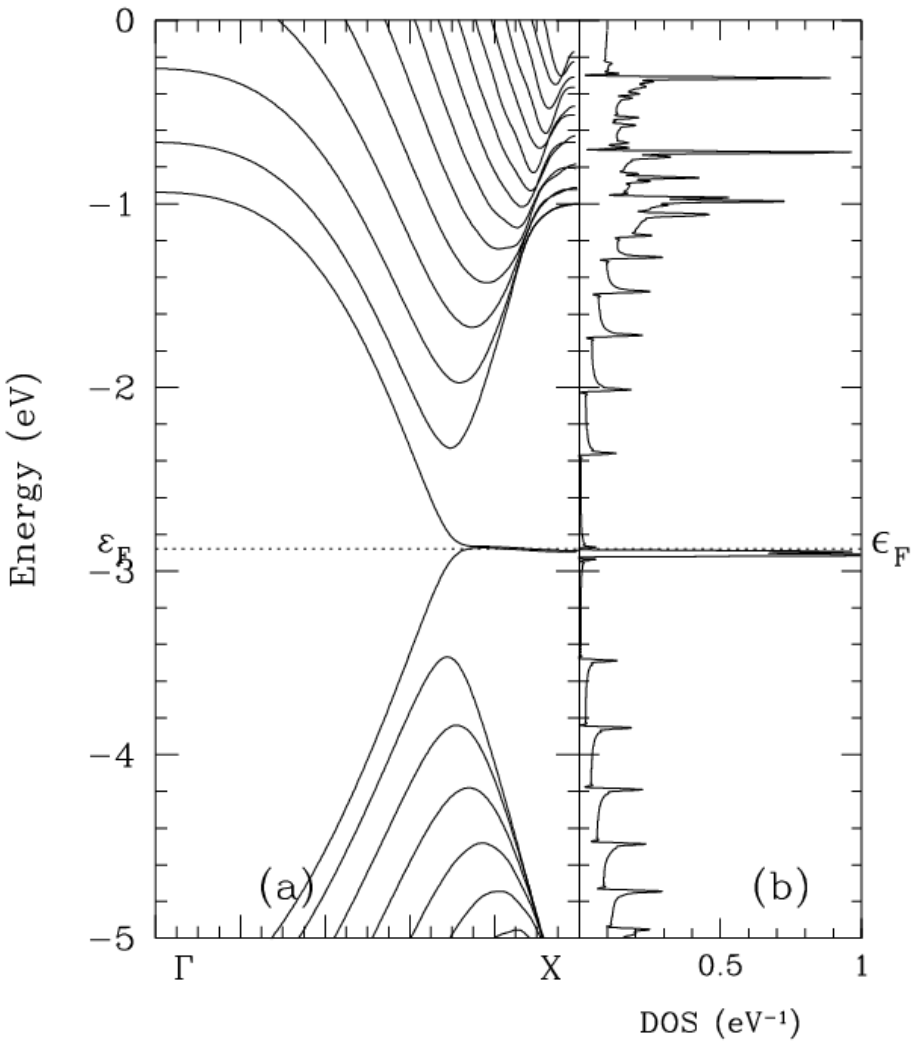
Armchair-edge GNS

Zigzag-edge GNS

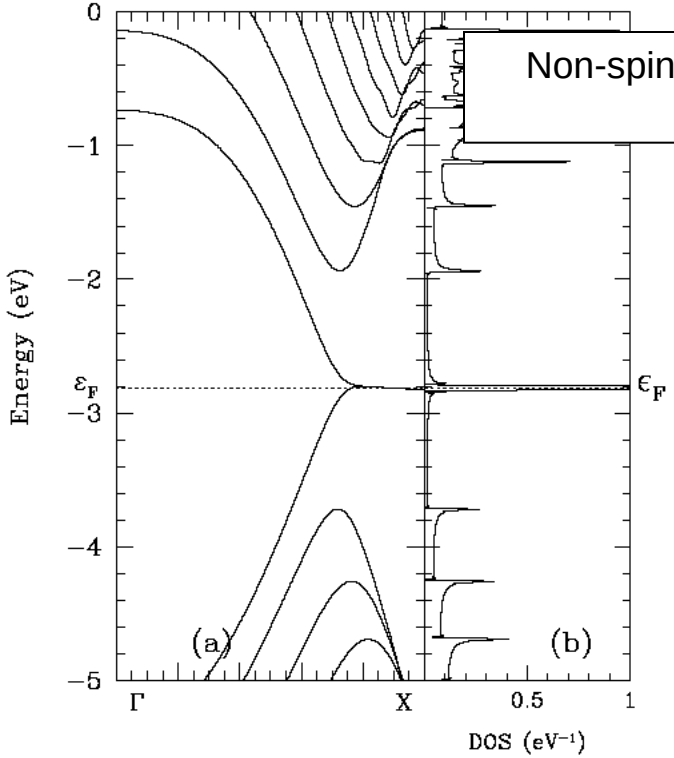
Ferromagnetic States in Zigzag Edge Graphite Nanostrips

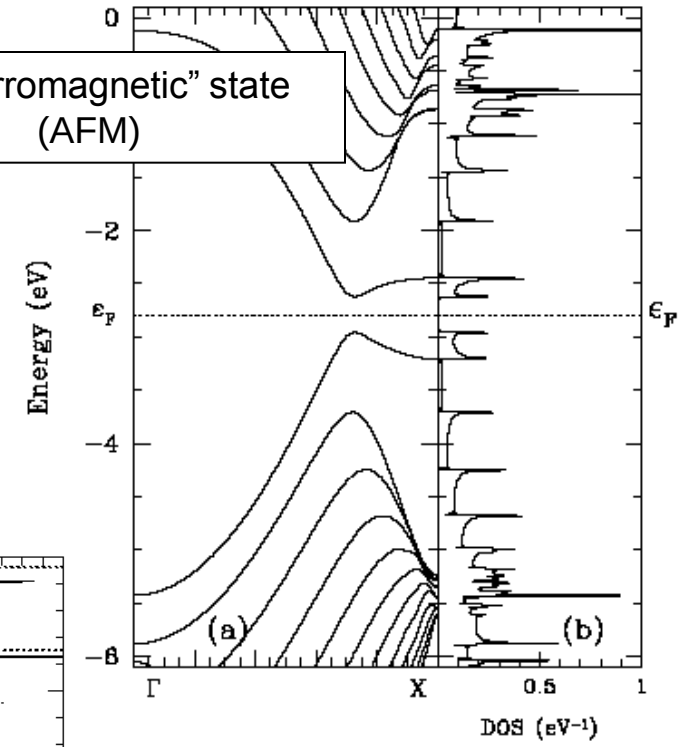
First-principles band structure simulations on zigzag edge graphene strips with finite width and infinite length show spin-polarized edge states.

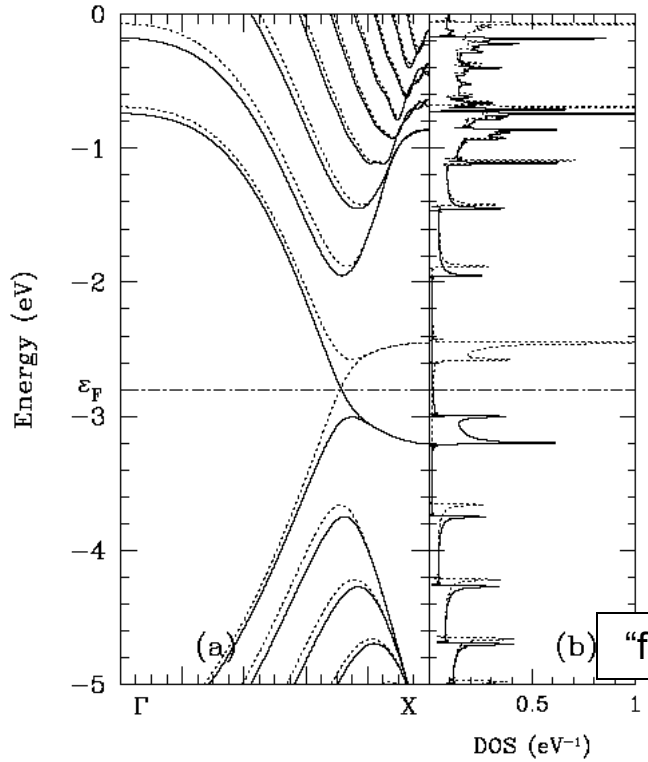
Figure to the left depicts band structure for non-spin-polarized (closed shell) band structure results for strip width corresponding to N=10.



Y.-W. Son, M. L. Cohen, and S. G. Louie, Nature (London) 444, 347 (2006).







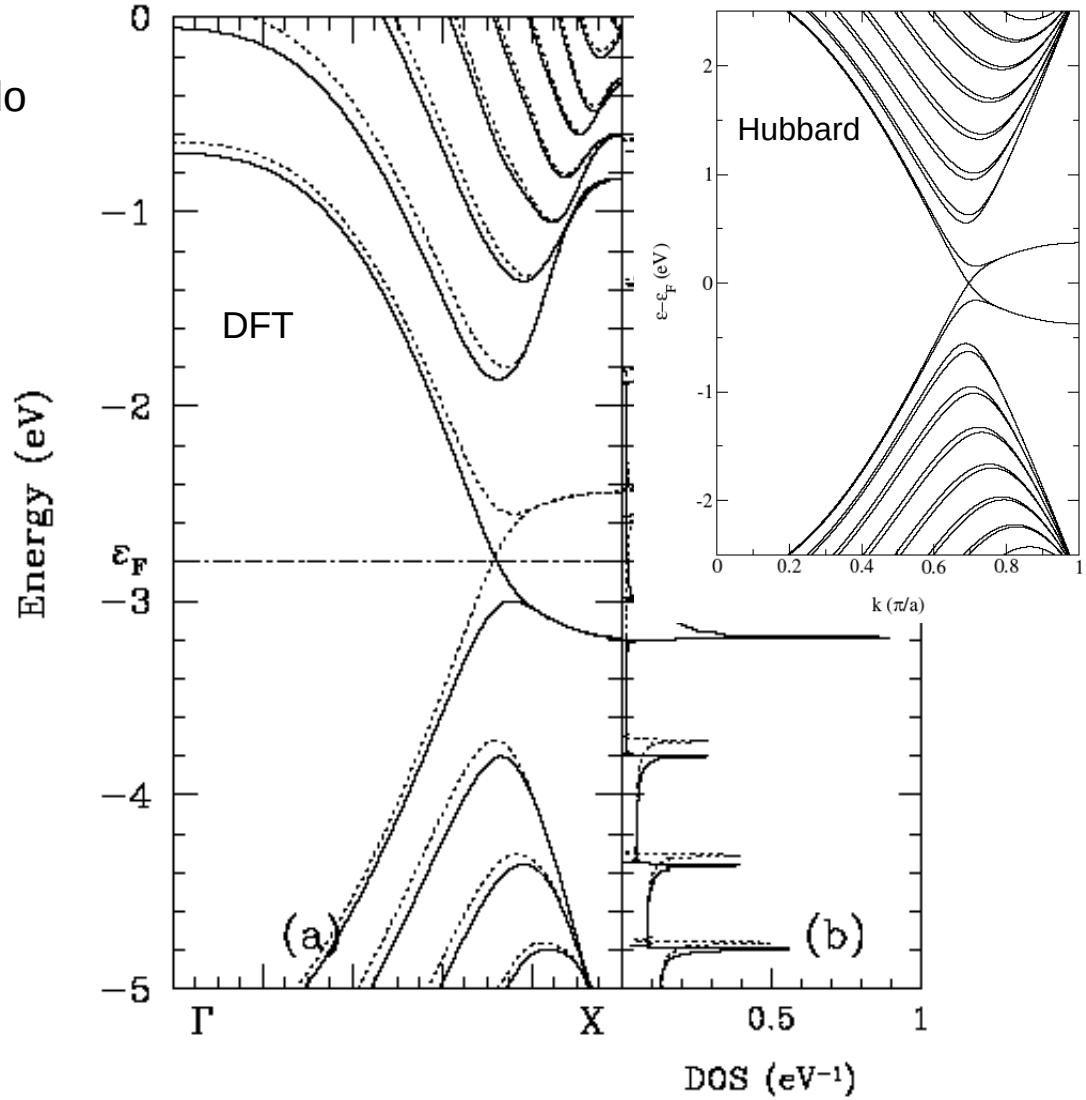
"ferromagnetic" state (AFM)

Ferromagnetic States in Zigzag Edge Graphite Nanostrips

What type of ferromagnetic states do we get in the zigzag GNS?

Localization at edge leads to spin polarization, with DFT and Hubbard mean field results very similar. Figures show spin-polarized, ferrimagnetic band structure results for zigzag-edge graphene strip. Right-hand figure depicts results using Hubbard Hamiltonian model, and left-hand results depict first-principles results.

Excellent agreement between first-principles and Hubbard results was observed.



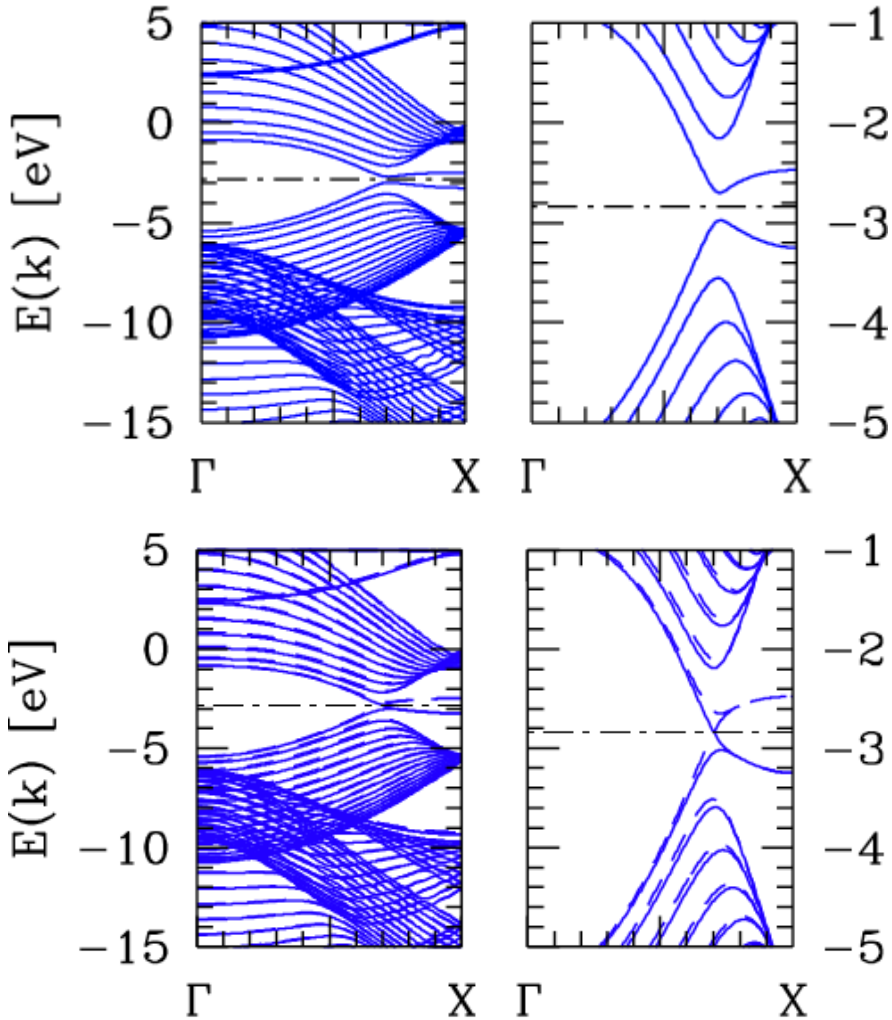
Computational Materials Physics

Effects of Edge Chemistry on the Electronic Structure of Zigzag-Edge Nanostrips

H-terminated
Spin-polarized (anti)

H-terminated
Spin-polarized (symm)

APL 91, 112108 (2007)



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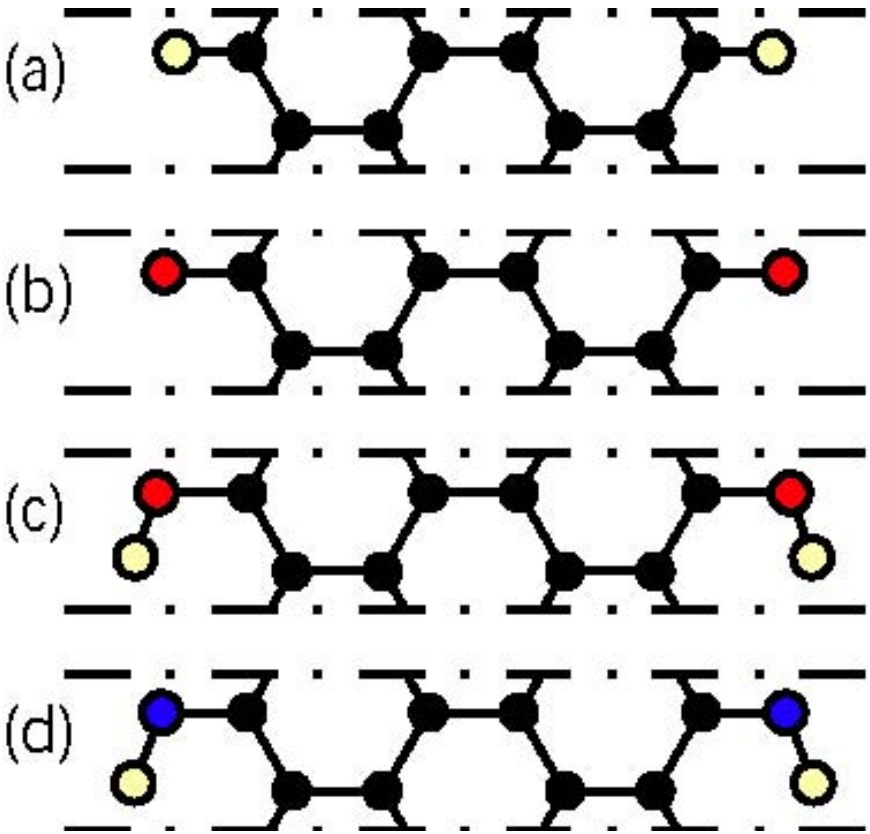


H	d_{CH}	1.11 Å
O	d_{CO}	1.30 Å
Hydroxyl (OH)	d_{CO}	1.40 Å
	d_{OH}	1.07 Å
	θ_{COH}	109°
Imine (NH)	d_{CN}	1.34 Å
	d_{NH}	1.19 Å
	θ_{CNH}	111°

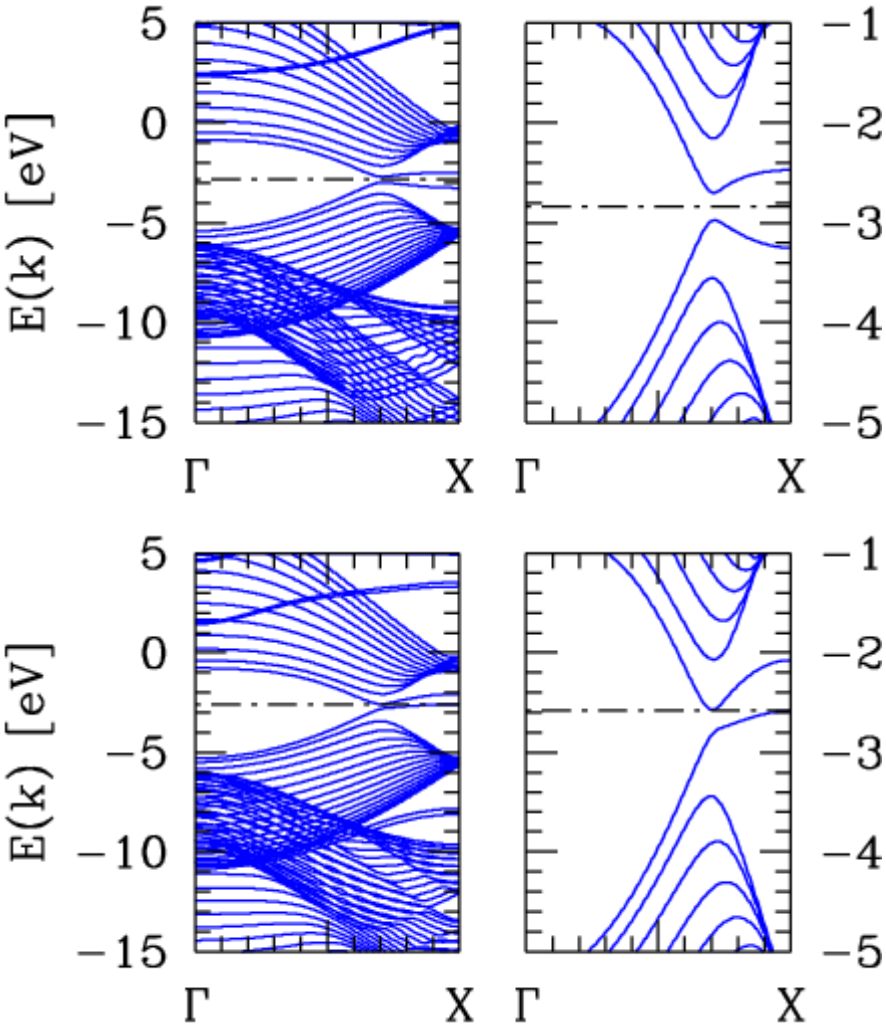
Gunlycke, Li, Mintmire, White, APL 91, 112108 (2007)

Effects of Edge Chemistry on the Electronic Structure of Zigzag-Edge Nanostrips

H-terminated
Spin-polarized

OH-terminated
Spin-polarized

APL 91, 112108 (2007)



Computational Materials Physics

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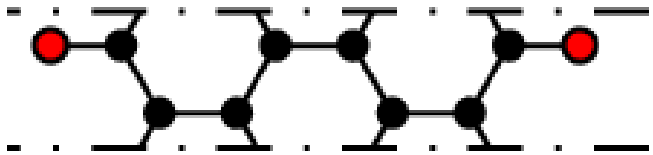
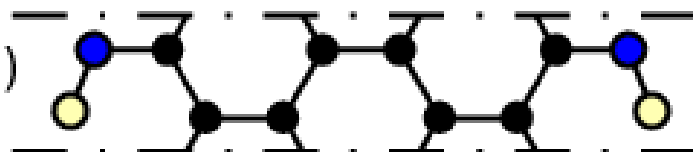
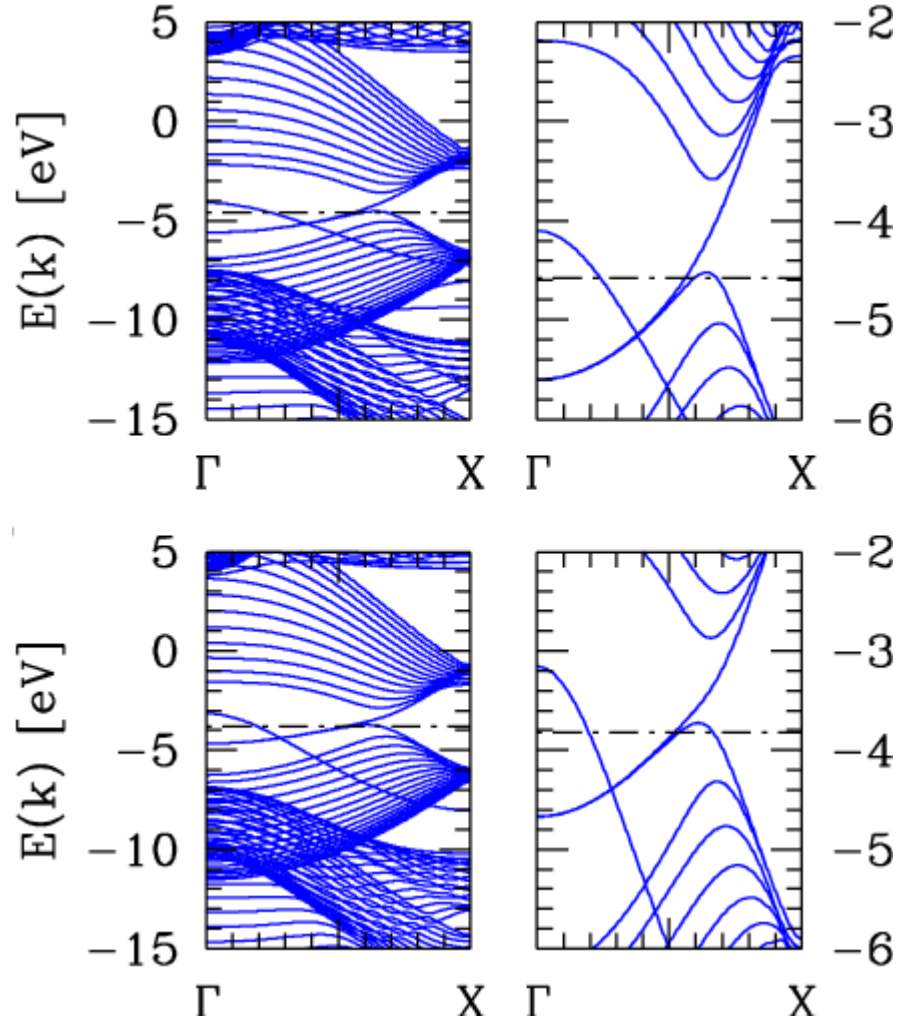


O-terminated
Spin-unpolarized

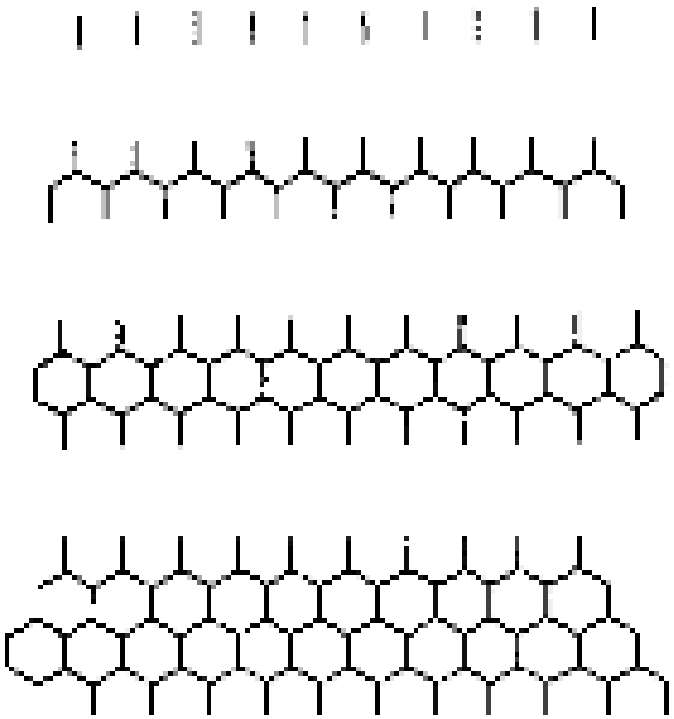


NH-terminated
Spin-unpolarized

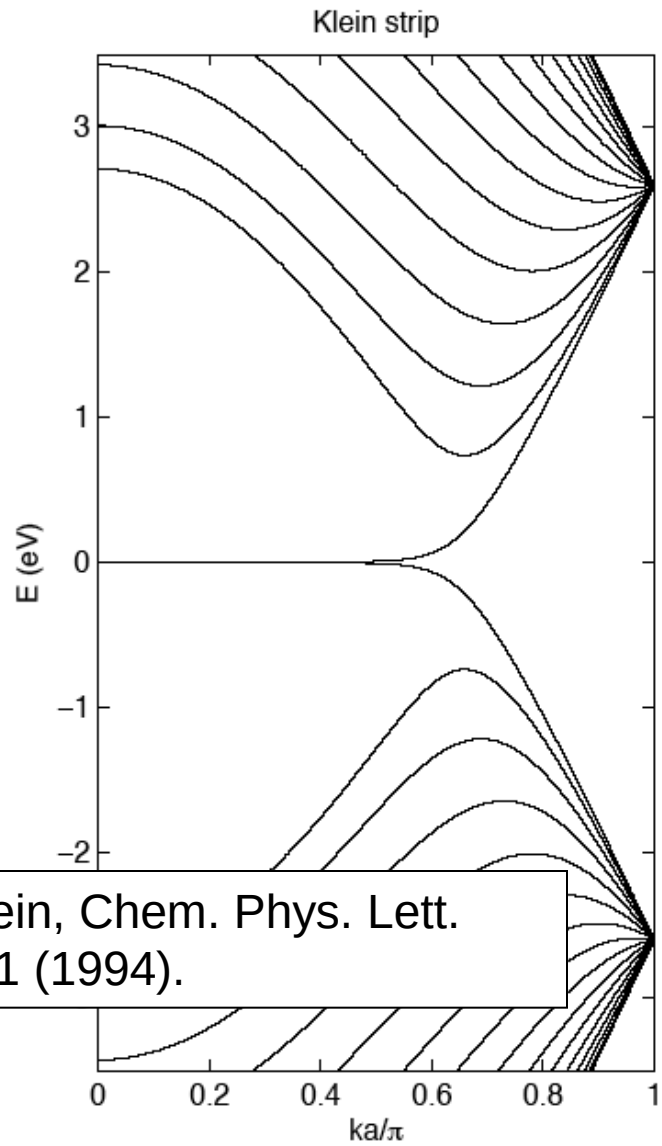


APL 91, 112108 (2007)

Computational Materials Physics



D. J. Klein, “Graphitic polymer strips with edge states”, Chem.Phys. Lett. 217, 261 (1994).



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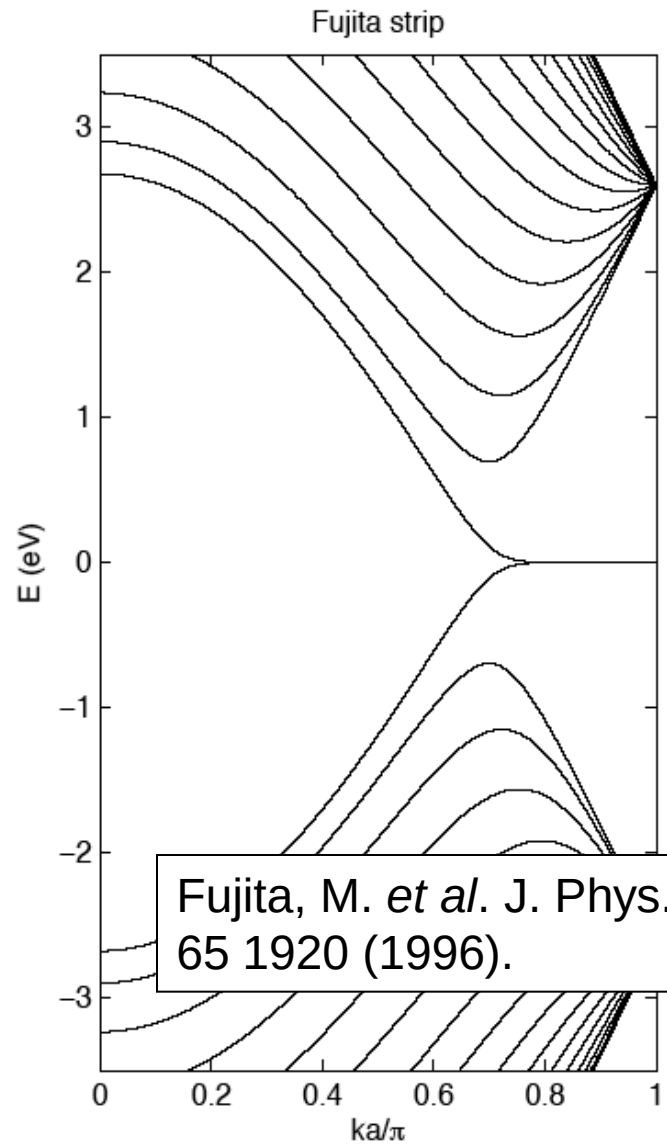
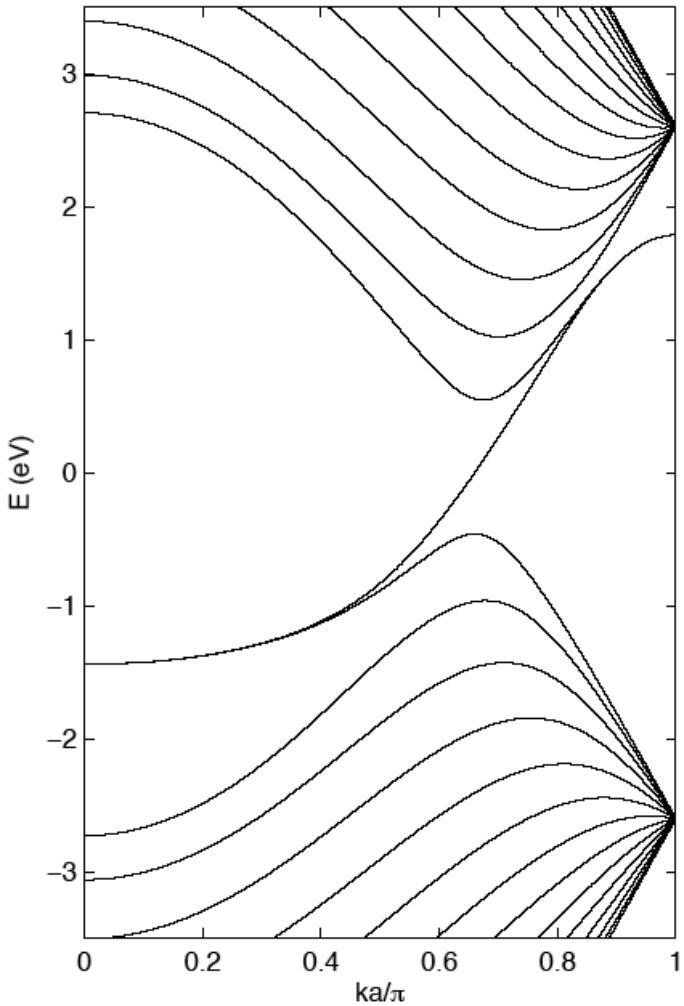
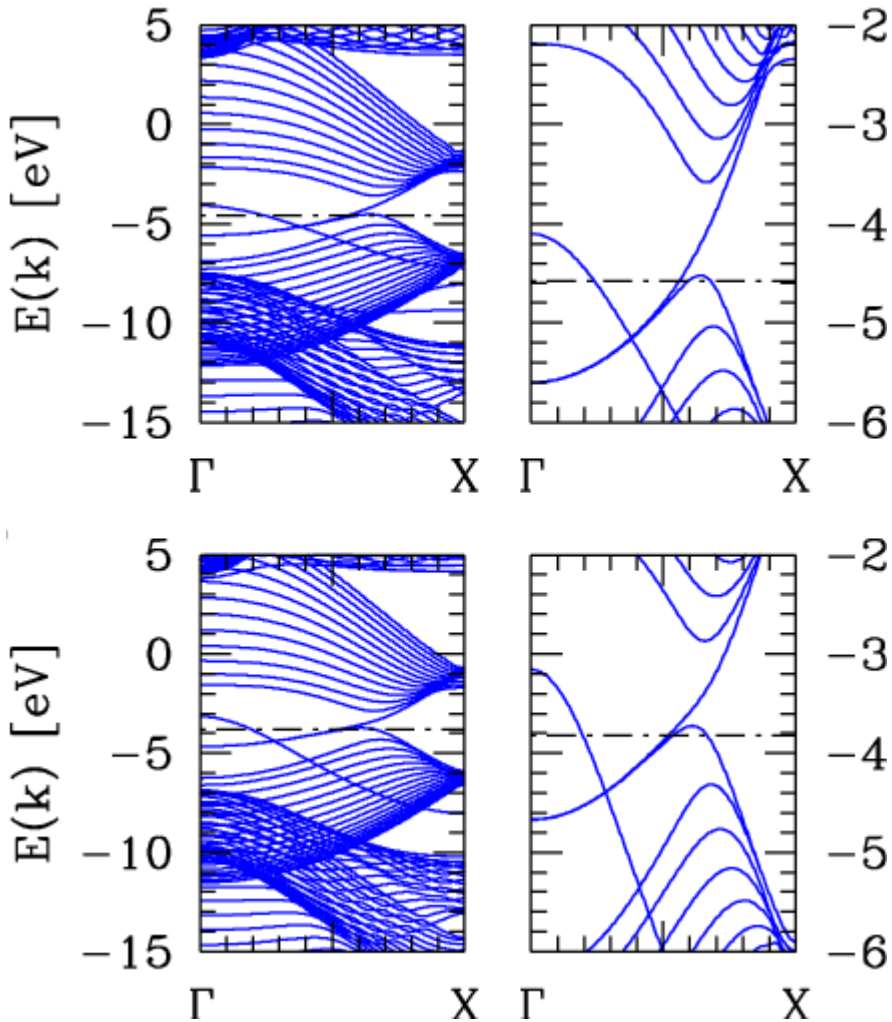


Fujita, M. *et al*. J. Phys. Soc. Jpn. 65 1920 (1996).



=O terminated



=NH terminated

Computational Materials Physics

Chemical Substituent Effects on Zigzag-Edge Graphene Nanoribbons

- Different chemical edge-substituents produce dramatic variations in electron states near Fermi level.
- H and OH terminated zigzag edge strips have spin-polarized ground states, =O and =NH terminated strips have non-spin-polarized ground states.
- High-lying substituent states can participate in both pi and sigma band orbitals near the Fermi level.

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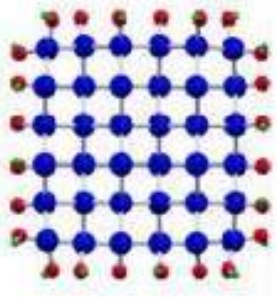
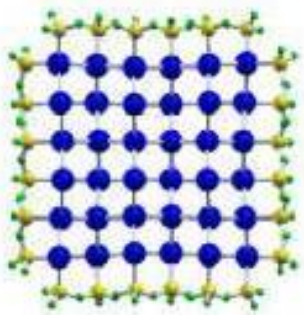
Silicon Nanowires Studied

<100>-aligned SiNWs, 1.39 nm diameter, different passivations

OH

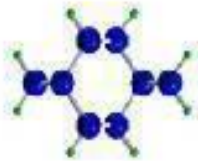


CH_3

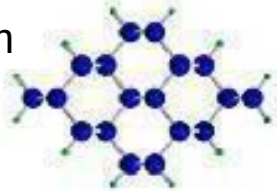


<110>-aligned SiNWs of differing diameters

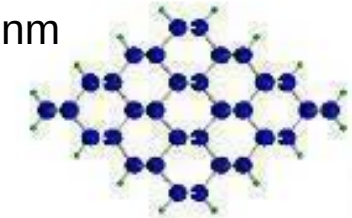
0.73 nm



1.09 nm



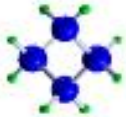
1.46 nm



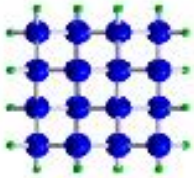
{111} faces

<100>-aligned SiNWs of differing diameters

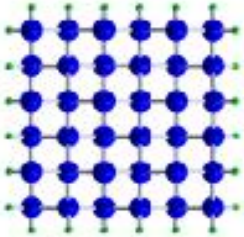
0.43 nm



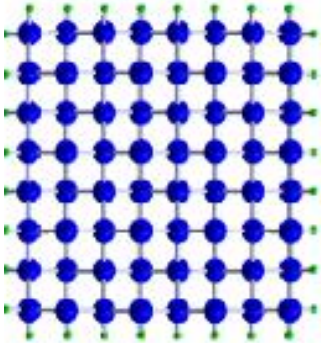
0.87 nm



1.30 nm



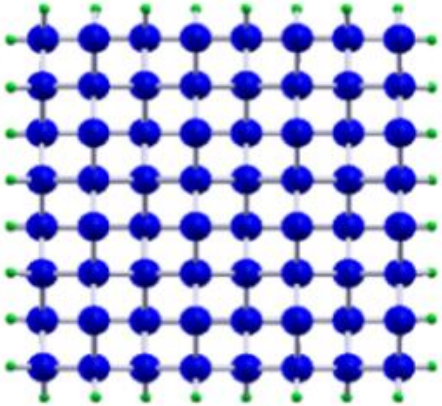
1.73 nm

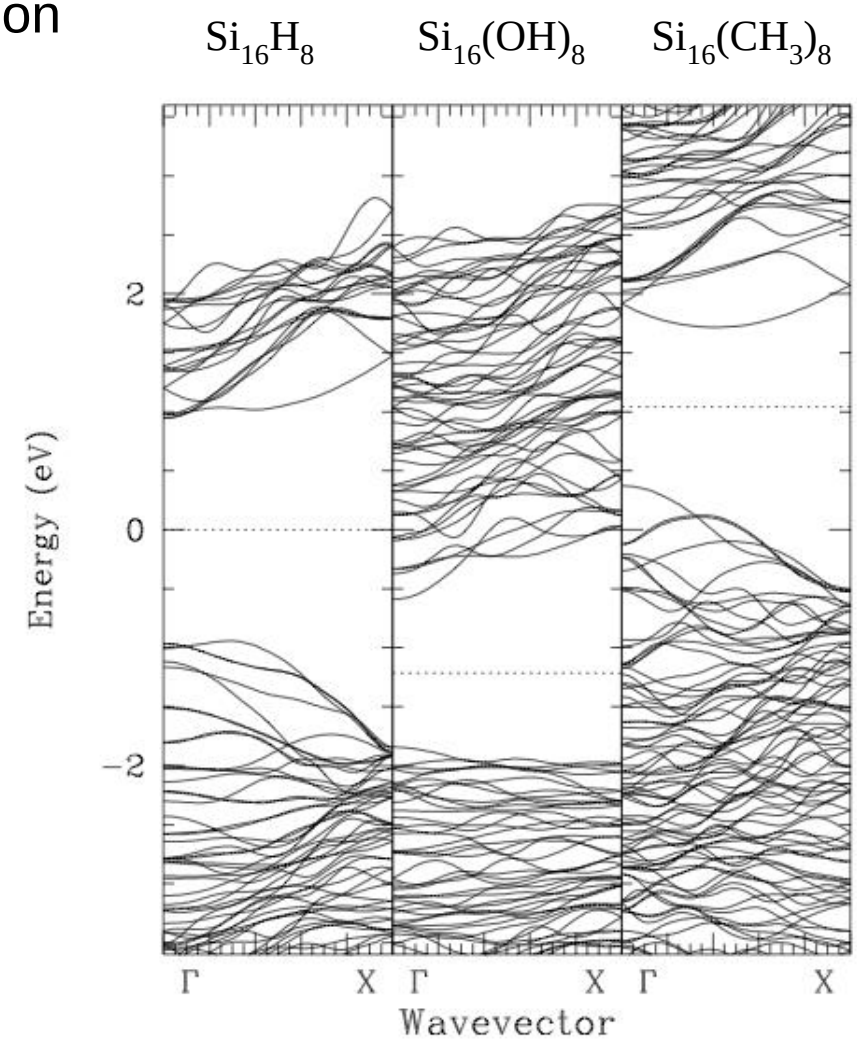


{110} faces

Band structure versus passivation for <100>-aligned SiNWs

- CH_3 passivation leads to indirect band gap.
- OH passivation results in smallest band gaps

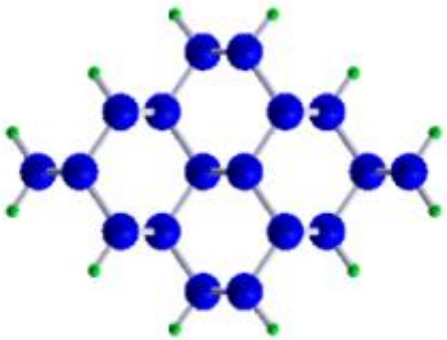


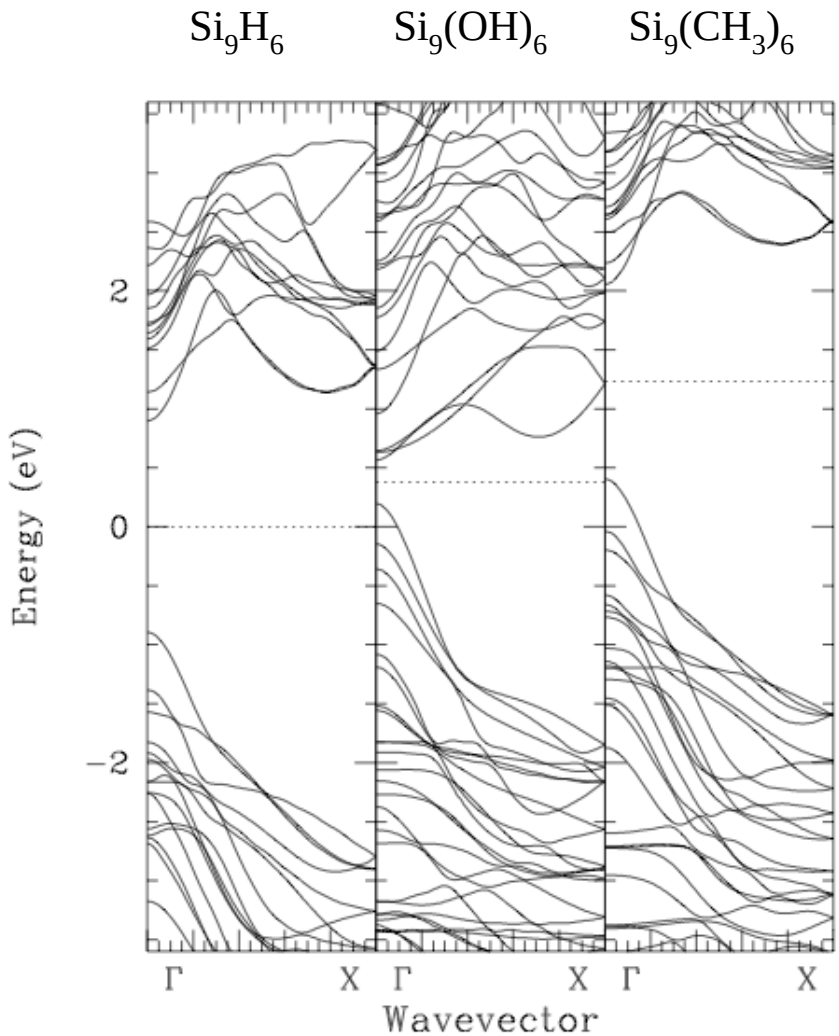


Band gap (eV)	1.89	1.25	1.35

Band structure versus passivation for <110>-aligned SiNWs

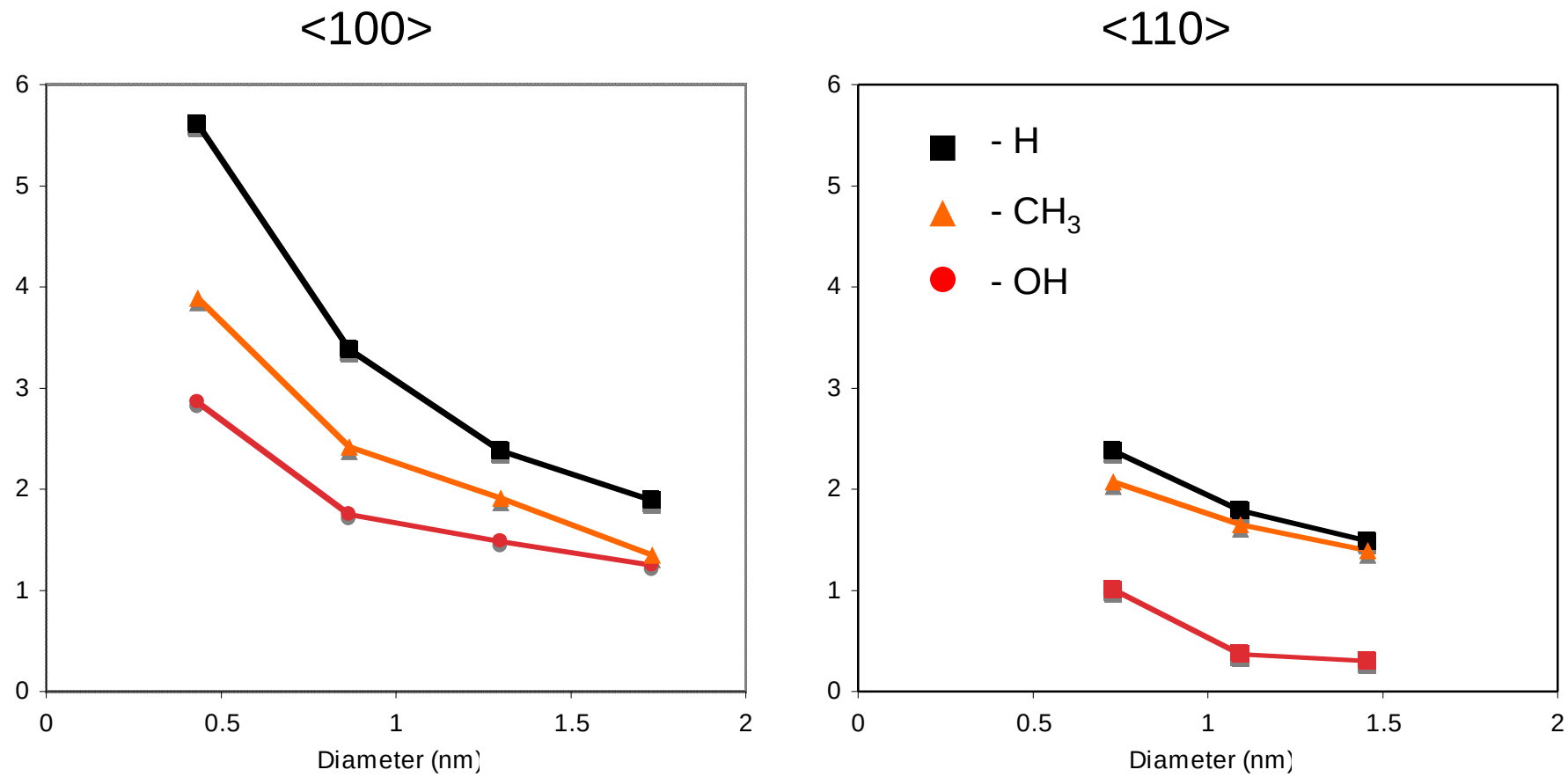
- CH_3 passivation leads to only small changes in bands near Fermi level.
- OH passivation results in much smaller band gaps



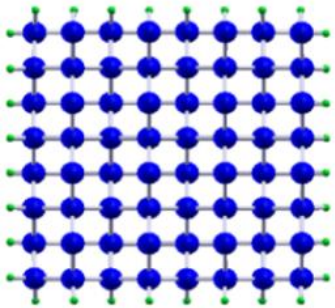


	Si_9H_6	$Si_9(OH)_6$	$Si_9(CH_3)_6$
Band gap (eV)	1.79	0.37	1.65

Band gap as a function of the wire diameter



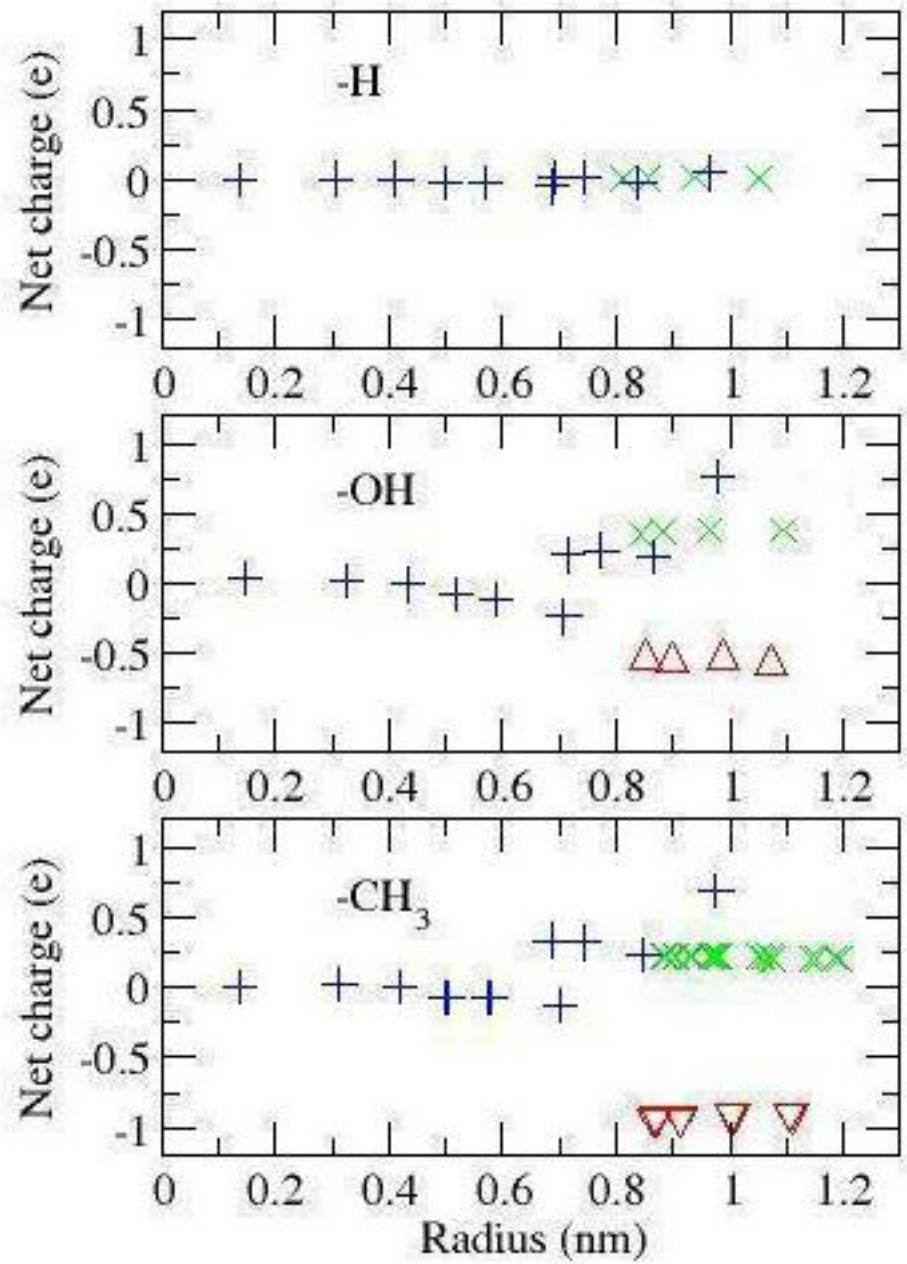
- Increasing quantum confinement increases band gaps
- Surface passivation reduces the band gap
- OH passivation greatly reduces the band gap



<100>-aligned SiNWs

Mulliken population analysis results as a function of radial distance from center of SiNW.

Both hydroxyl and methyl passivation lead to total positive charge on silicons near surface of nanowire.

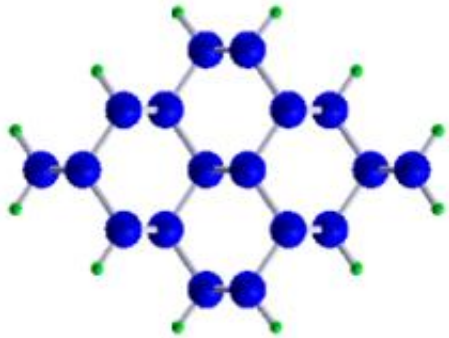


+ silicon

x hydrogen

△ oxygen

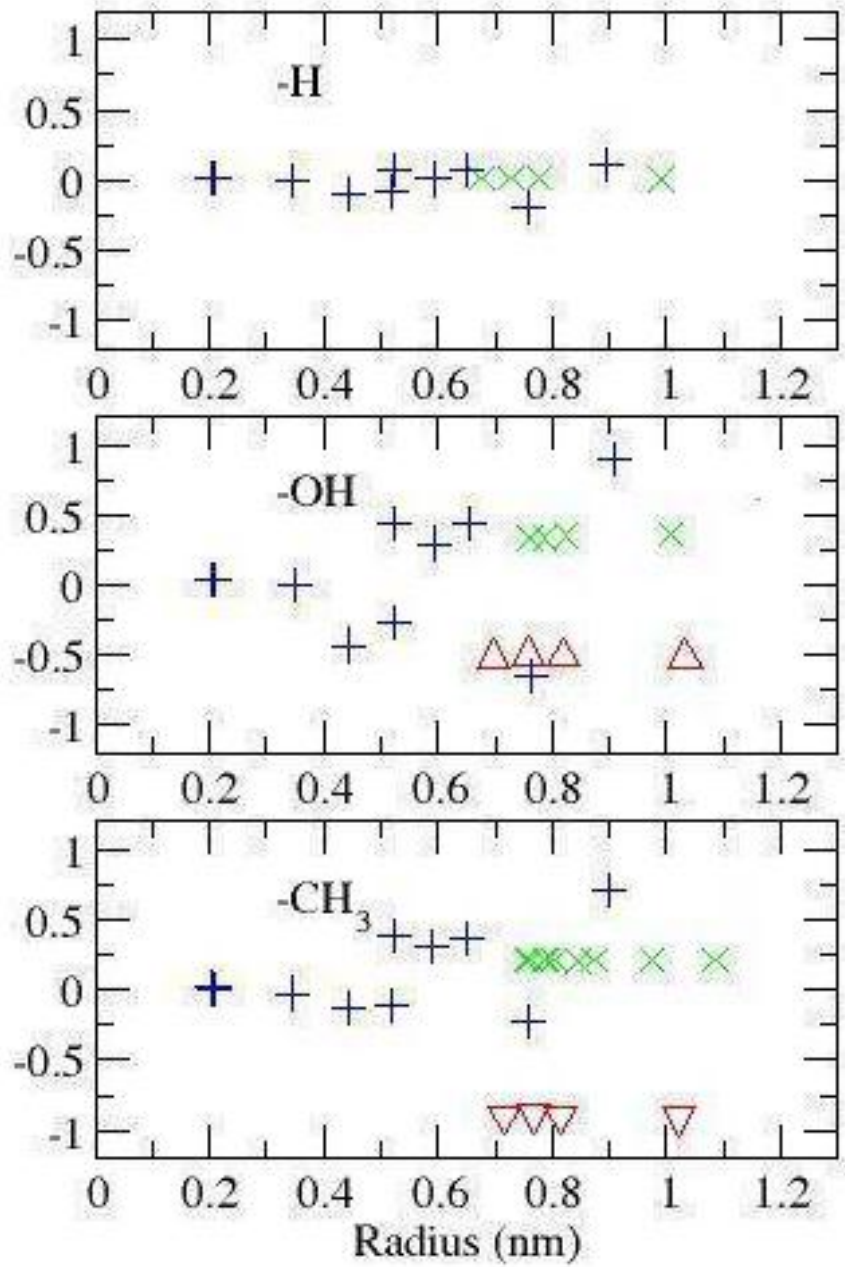
▽ carbon



<110>-aligned SiNWs

Mulliken population analysis results as a function of radial distance from center of SiNW.

Both hydroxyl and methyl passivation lead to both positive and negative charge on surface silicon atoms.



+ silicon

x hydrogen

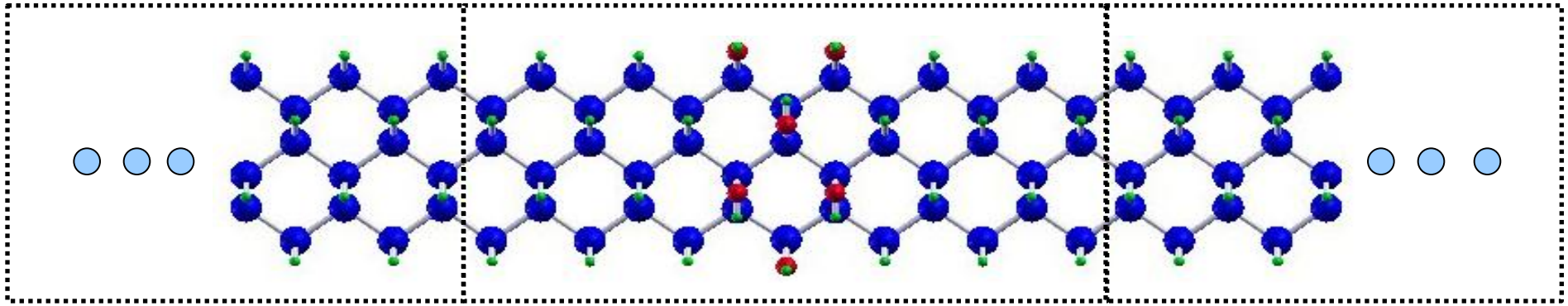
△ oxygen

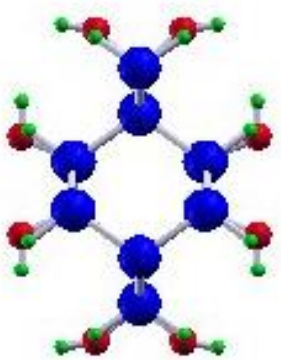
▽ carbon

Effective mass of silicon nanowires along <100> and <110> directions with various passivations

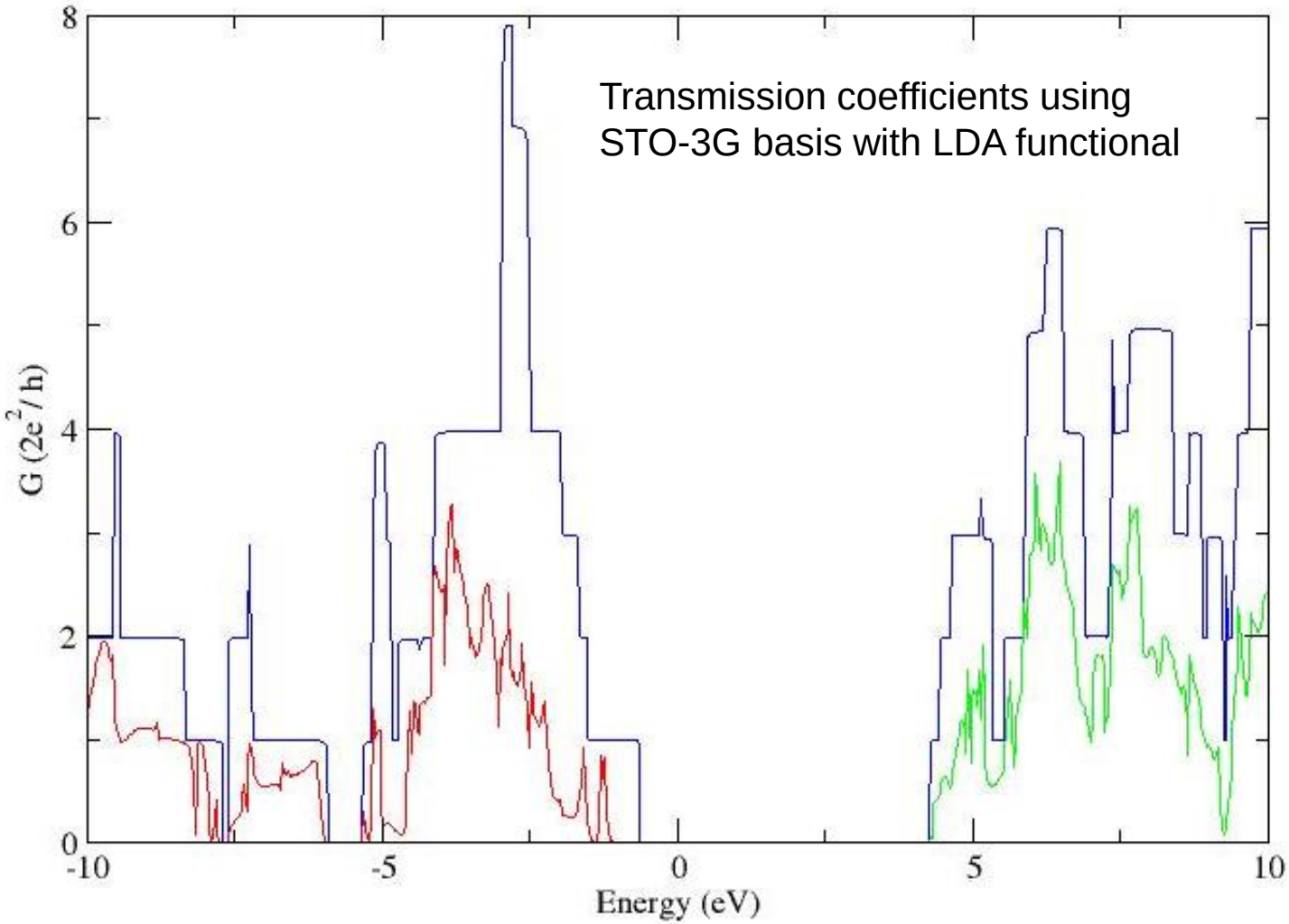
direction	diameter (nm)	effective mass (m_0)	H	OH	CH_3
[100]	0.43	m_e	0.56	0.39	2.51
		m_h	5.21	0.96	1.92
	0.87	m_e	0.30	0.40	1.12
		m_h	1.03	1.30	0.94
	1.30	m_e	0.22	0.29	1.13
		m_h	0.64	0.79	0.59
	1.73	m_e	0.30	0.31	1.13
		m_h	0.38	0.32	0.85
[110]	0.73	m_e	0.13	0.09	0.09
		m_h	0.13	0.11	0.13
	1.09	m_e	0.14	0.19	0.10
		m_h	0.13	0.10	0.13
	1.46	m_e	0.11	0.18	0.15
		m_h	0.12	0.18	0.14

Calculation of electron transport through passivation-defect region

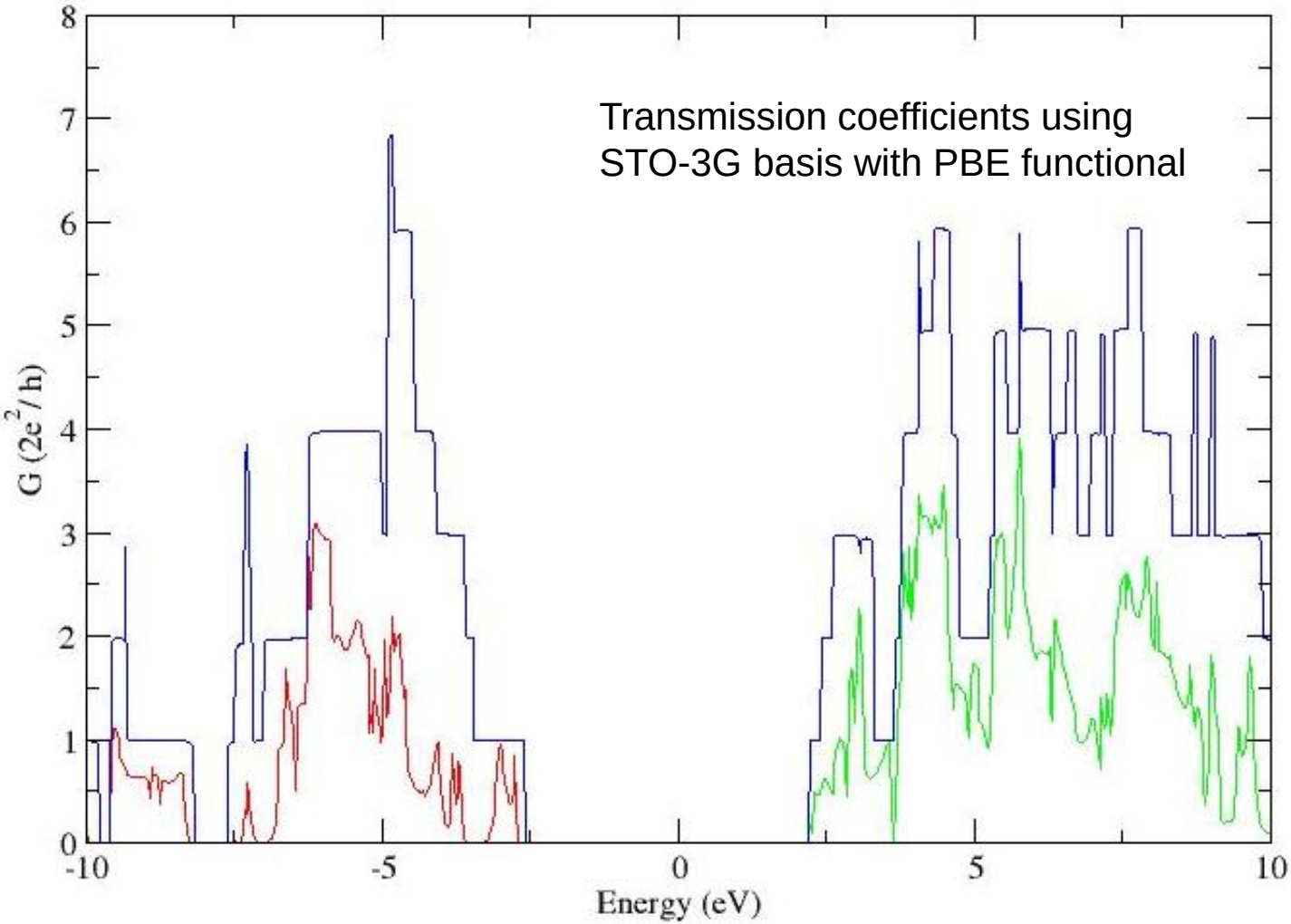




- Each principal layer consists of five helical cells aligned along <110> direction, of sufficient length to neglect next-nearest layer interactions.
- Leads are two semi-infinite H-passivated Si nanowires.
- Conductor region contains three helical cells passivated by OH, attached to one H-passivated unit cell on each side
- Transmission coefficients calculated using Landauer-Büttiker approach and STO-3G basis with LDA and PBE functionals



J. W. Li, T. Jayasekera, V. Meunier, and J. W. Mintmire, Int. J. Quantum Chem., in press.



J. W. Li, T. Jayasekera, V. Meunier, and J. W. Mintmire, Int. J. Quantum Chem., in press.

Chemical Passivation of Silicon Nanowires

- Passivation with OH groups leads to substantial reduction in the band gaps of the SiNWs for both <100> and <110> orientations.
- Passivation with methyl groups leads to reduced band gaps in both orientations, and indirect band gaps (albeit only slightly smaller than the direct gap) in <100> orientations.
- Passivation with methyl groups leads to flatter bands closest to Fermi level and concomitant increase in effective mass.
- Charge transfer shows qualitative differences between <100> and <110> aligned SiNWs.
- Preliminary results for small diameter SiNWs show marked effects on electron transport of small regions of different passivation.

Optoelectronic Properties of Carbon Nanostructures

- Research issues and goals
- Approach: quasi-one-dimensional nanostructures
  - Use of helical symmetry
  - Use of first-principles band structure methods for helical polymers
- Current research projects
  - ✓ Polymers for photovoltaic bulk heterojunctions
  - ✓ Graphene nanoribbons
  - ✓ Silicon/inorganic nanowires
  - ✓ Double-walled carbon nanotubes
- Research plans
  - TDDFT for quasi-1D systems
    better estimates of electron excitation energies
  - Transport in electroactive polymers

Electron Properties

in

Fluorinated Chiral-Single Wall Carbon Nanotubes

Thushari Jayasekera, Junwen Li, J. W. Mintmire

Oklahoma State University, Stillwater, OK

Vincent Meunier

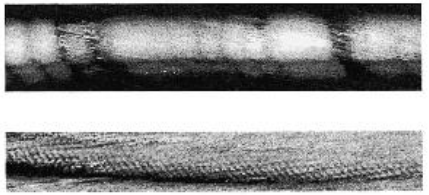
Oak Ridge National Laboratory, Oak Ridge, TN

Computational Materials Physics

Background and Motivation

- Fluorination of SWNTs – 1998.

Mickelson et.al Chem.Phys. Lett ,296,(1998), 188



K. F. Kelly et.al Chem.Phys. Lett ,313,(1999), 445

- Sidewall functionalization can be used to engineer the electronic properties of carbon nanotubes.

APPLIED PHYSICS LETTERS VOLUME 77, NUMBER 9 28 AUGUST 2000

Molecular wires, solenoids, and capacitors by sidewall functionalization of carbon nanotubes

Gotthard Seifert,[a] Thomas Köhler, and Thomas Frauenheim
Fachbereich Physik, Theoretische Physik, Universität Paderborn, 33098 Paderborn, Germany

(Received 18 April 2000; accepted for publication 22 June 2000)

Fluorotubes as Cathodes in Lithium Electrochemical Cells

Haiqing Peng, Zhenning Gu, Jiping Yang, J. L. Zimmerman, P. A. Willis, M. J. Bronikowski, R. E. Smalley, R. H. Hauge, and J. L. Margrave

Nano Letters, **2001**, 1 (11), 625-629 • DOI: 10.1021/nl010053u

Objective

• Understand the atomic structure, electronic structure and electronic transport properties of fluorinated chiral SWNTS

Literature

• Energetics of F-SWNTS were studied by Bauschlicher for single and pair fluorination. Chem Phys Lett **322**, 237-241 (2000)

• The electronic structures were studied for different patterns of fluorine decorations

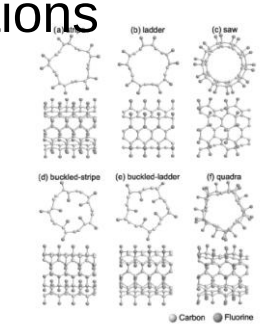
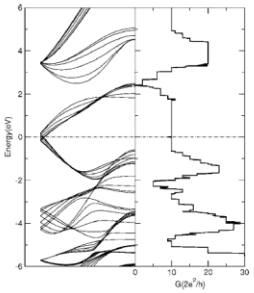


FIG. 2. Various isomers of the fluorinated (5,5) armchair nanotube at coverage of 0.5.

Ah Park et. al,
Phys. Rev. B, **68,** 045429 (2003)

• The electron transport properties were also studied on armchair and zigzag fluorinated SWNTs.



N. Ranjan et. al,
Phys. Rev. B, **73,** 153408 (2006)

Most of these studies are carried out for small radii armchair and zigzag tubes with C_2F stoichiometry.

Our goal is to study the effect of an isolated fluorination site in a pristine SWNT for a better fundamental understanding of these materials.

Computational Materials Physics

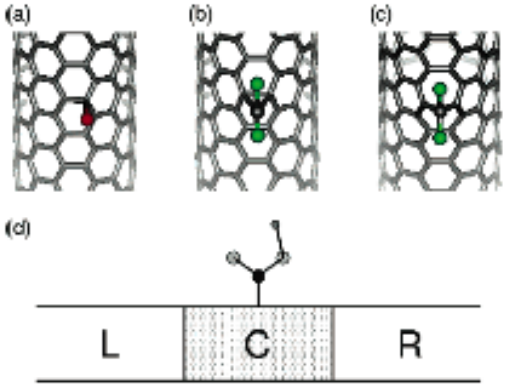
Effect of Isolated Fluorine Substitution

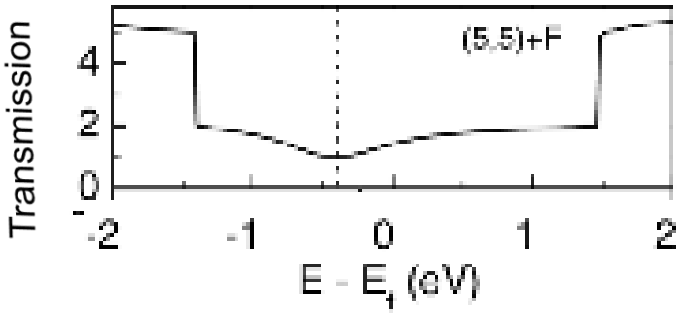
INSTITUTE OF PHYSICS PUBLISHING NANOTECHNOLOGY
Nanotechnology 16 (2005) 635–638 doi:10.1088/0957-4484/16/6/003

Distinct properties of single-wall carbon nanotubes with monovalent sidewall additions

Hyoungki Park, Jijun Zhao and Jian Ping Lu[1]

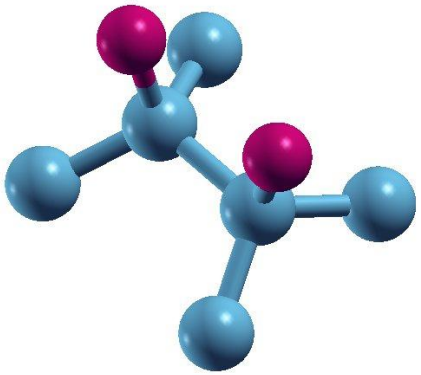
Department of Physics and Astronomy, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599, USA





- The effect of isolated functionalized site on electron transport in the system
- The calculations are limited to armchair and zigzag SWNTs.
- Also their electron transport calculation is based on tight binding matrix elements

Effect of Pair-Fluorination on Chiral Single-Wall Carbon Nanotubes



- Addition of fluorine pairs is energetically more favorable than the addition of two isolated single fluorine atoms.

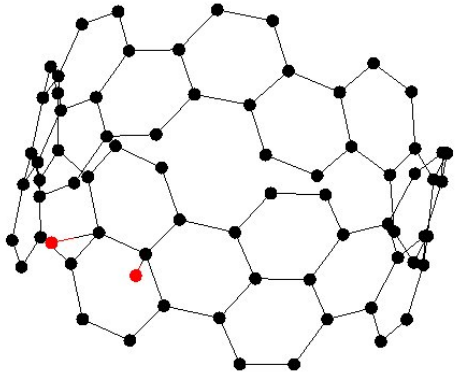
Bauschlicher, Chem Phys Lett **322**, 237-241 (2000)

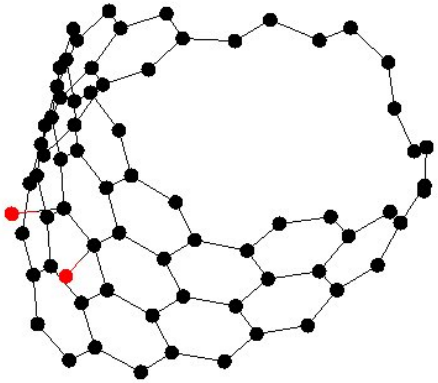
We study the effect of pair fluorination on chiral single-wall nanotubes.

- Geometry Optimization
- Electronic Structure
- Electronic Transport

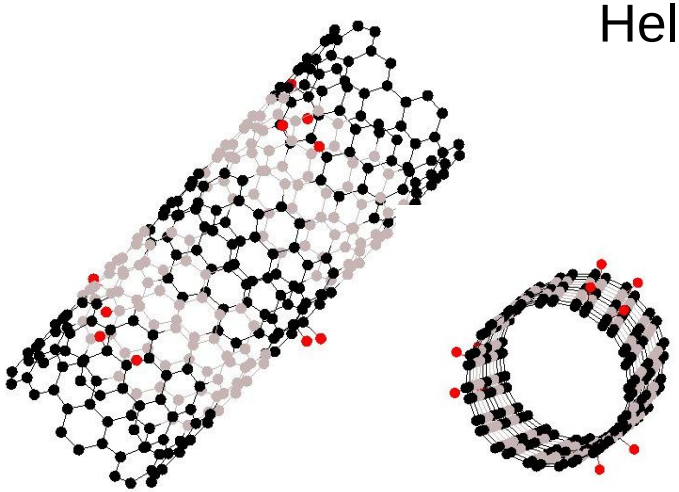
Helical Symmetry in Electronic Transport Calculations

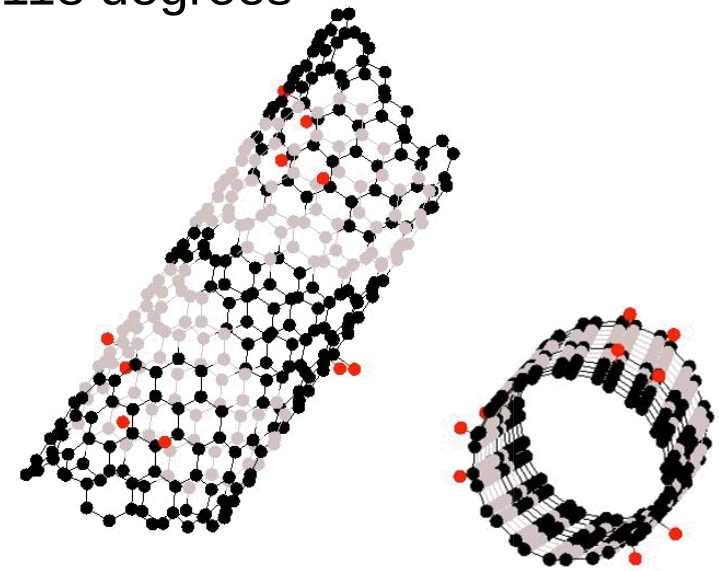
Two representations of helical unit cell for (8,7) SWNT $C_{70}F_2$ configuration



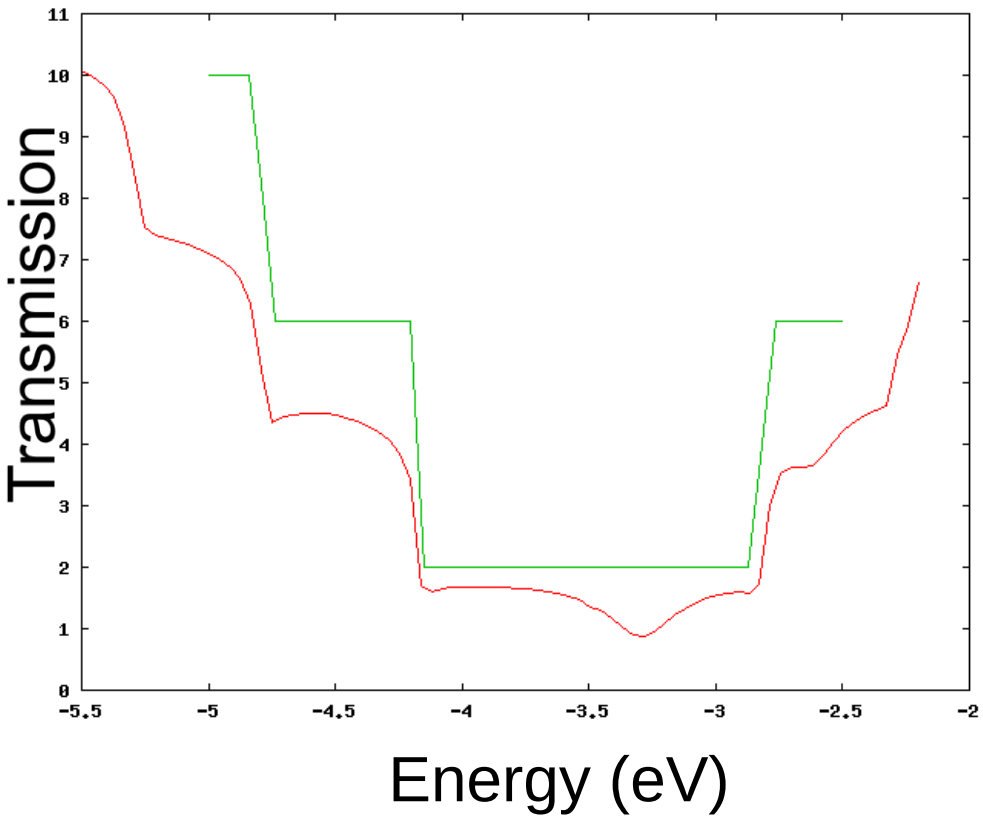


Helical Pitch=5.82 Angstroms
Helical Angle=118 degrees





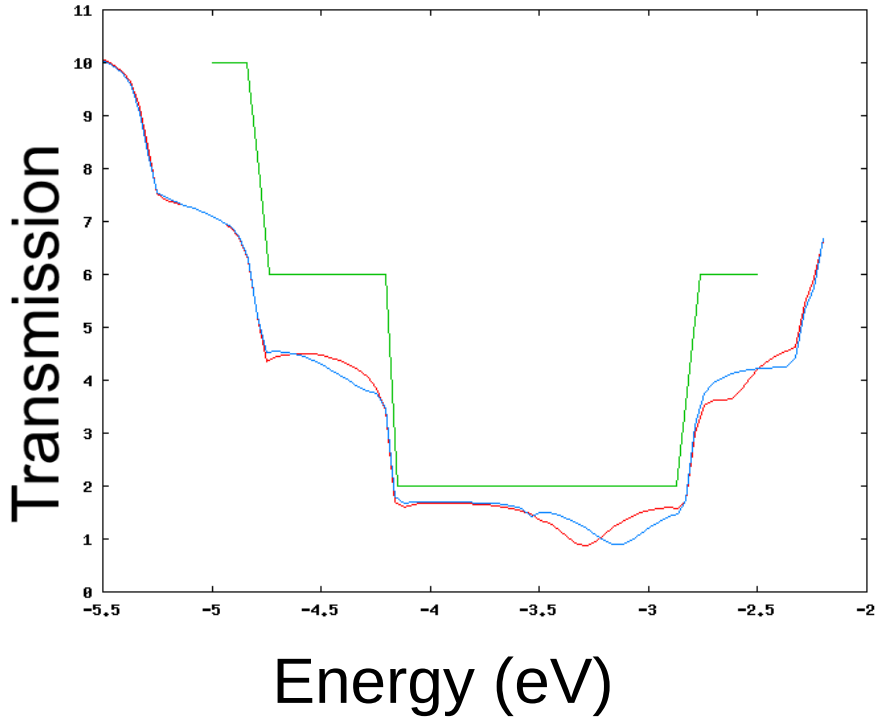
Results: Electronic Transport Calculations



Transmission through a pristine (10,13) SWNT

Transmission through a fluorinated (10,13) SWNT (as it is calculated using a $C_{74}F_2$ super cell)

Results: Electronic Transport Calculations



Transmission through a pristine (10,13) SWNT

Transmission through a fluorinated (10,13) SWNT (calculated using a $C_{74}F_2$ super cell)

Transmission through a fluorinated (10,13) SWNT (calculated using a $C_{70}F_2$ super cell)

Publications

“First-Principles Properties of Organic Photovoltaic Materials", T. Jayasekera, M. S. Monigold, S. L. Elizondo, and J. W. Mintmire, Int. J. Quantum Chem. **107**, 3120 (2007).

"Lattice Vacancy Effects on Electron Transport in Multiterminal Graphene Nanodevices", T. Jayasekera and J. W. Mintmire, Int. J. Quantum Chem. **207**, 3071 (2007).

"Hidden One-Electron Interactions in Carbon Nanotubes Revealed in Graphene Nanostrips", C. T. White, J. W. Li, D. Gunlycke, and J. W. Mintmire, Nano Lett. **7**, 825 (2007).

"Transport in Multiterminal Graphene Nanodevices", T. Jayasekera and J. W. Mintmire, Nanotechnology **18**, 424033 (2007).

"Altering Low-Bias Transport in Zigzag-Edge Graphene Nanostrips with Edge Chemistry", D. Gunlycke, J. W. Li, J. W. Mintmire, and C. T. White, Appl. Phys. Lett. **91**, 112108 (2007).

"Graphene Nanostrip Digital Memory Device", D. Gunlycke, D. A. Areshkin, J. W. Li, J. W. Mintmire, and C. T. White, Nano Lett. **7**, 3608 (2007).

"First-Principles Study of the Optical Properties of ZnO Single-Wall Nanotubes", S. L. Elizondo and J. W. Mintmire, J. Phys. Chem. C **111**, 17821 (2007).

“Effect of Phase-Breaking Events on Electron Transport in Mesoscopic and Nanodevices”, T. Jayasekera, P.K. Pillalamarri, J.W. Mintmire, and V. Meunier, Int. J. Quantum Chem. **108**, 2896 (2008).

"First-Principles Simulations of Chiral Double-Wall Carbon Nanotubes", T. Jayasekera, B. A. Landis, and J.W. Mintmire, Int. J. Quantum Chem., **108**, 2943 (2008).

“Electron Transport of Silicon Nanowires with Surface Defects", J. W. Li, T. Jayasekera, V. Meunier, and J. W. Mintmire, Int. J. Quantum Chem., in press.

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