Ab Initio Modeling Of Quantum Transport At The Nanoscale

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Quantum Mechanical Modeling Of Electronic Transport At Molecule/ Nanoscale Interface

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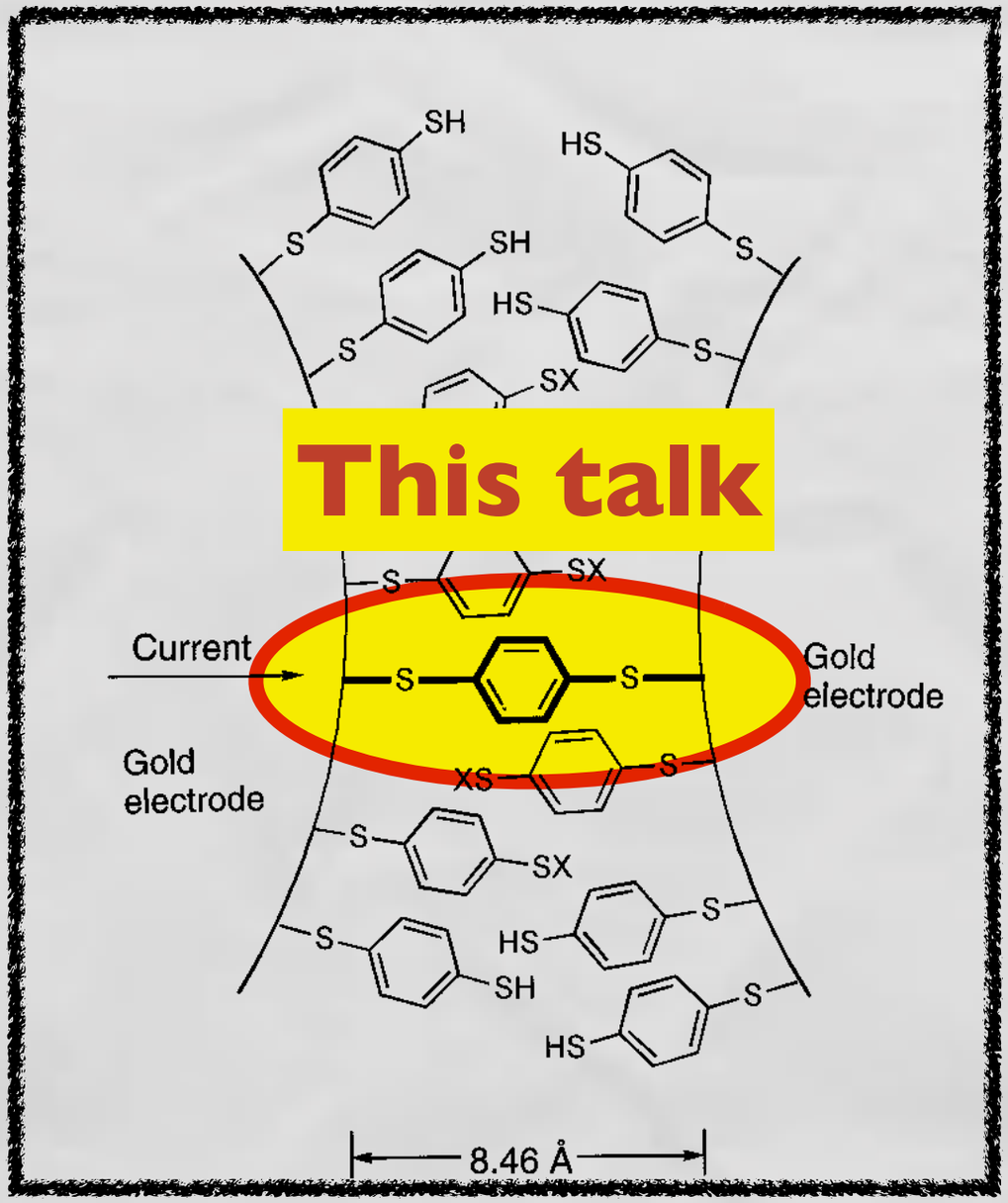
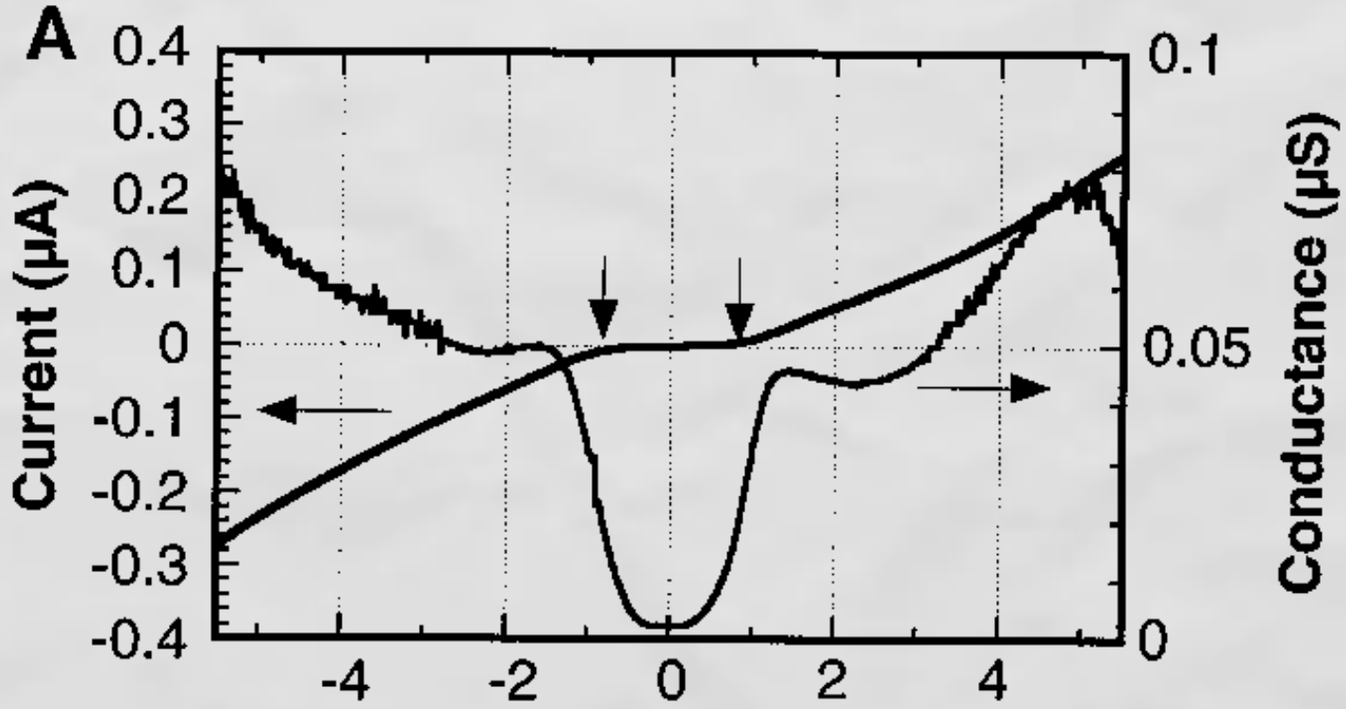
OUTLINE

- **Introduction to modeling QT**
  - Theory & Algorithms (knitting, patchworks,...)
- **Focus on quantum mechanical effects**
  - Negative Differential Resistance
  - Molecular Gating: Memory Effect
  - Chemical Sensing: DNA, small gas molecules, etc
  - Multiterminal: Interference and Scattering
  - More Networks
- **Some new results on GNR (graphitic nanoribbons)**

The Dawn of Molecular Electronics



This talk



Conductance of a Molecular Junction

M. A. Reed,* C. Zhou, C. J. Muller, T. P. Burgin, J. M. Tour*

SCIENCE • VOL. 278 • 10 OCTOBER 1997

nature nanotechnology

REVIEW ARTICLE

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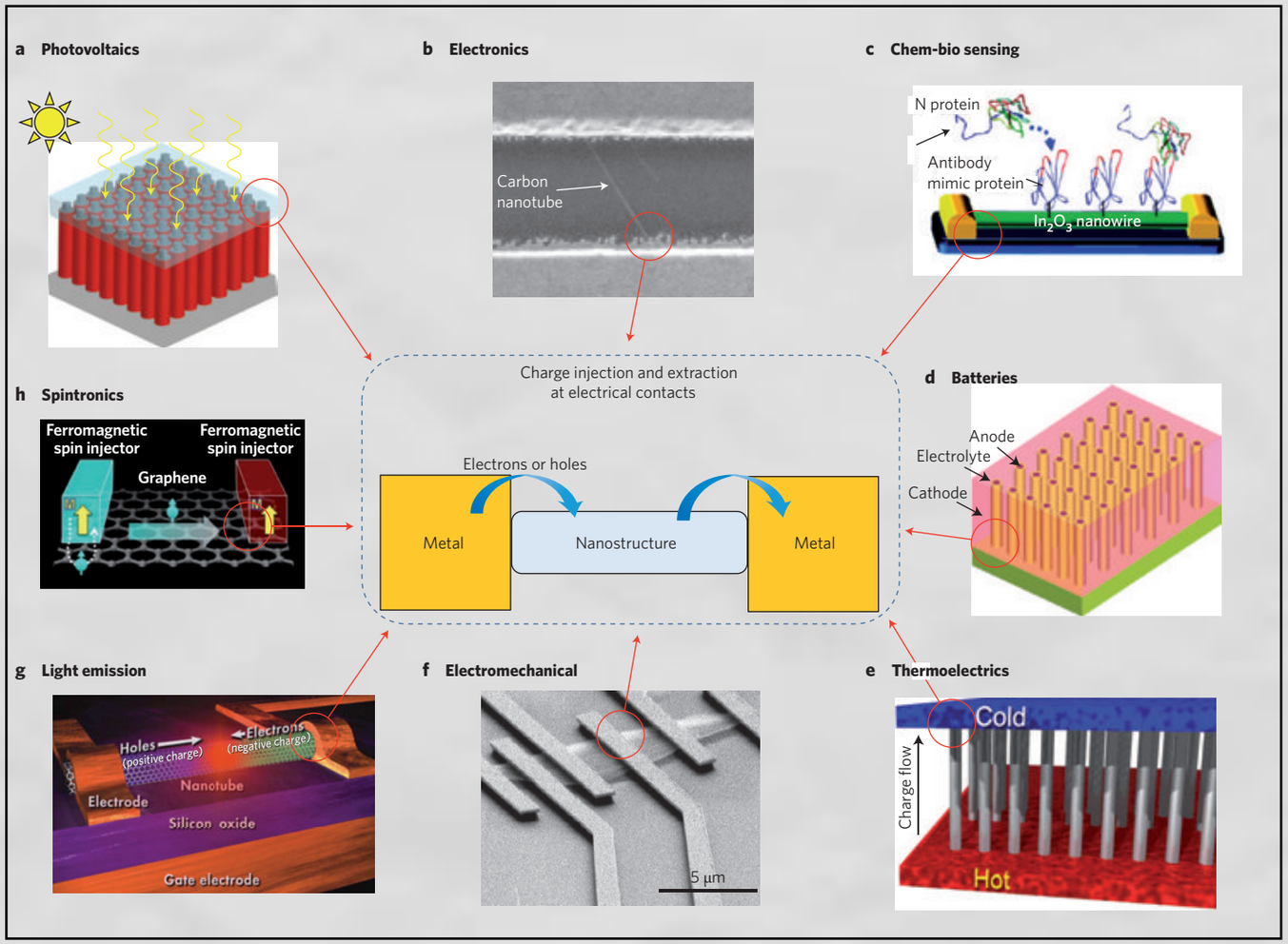
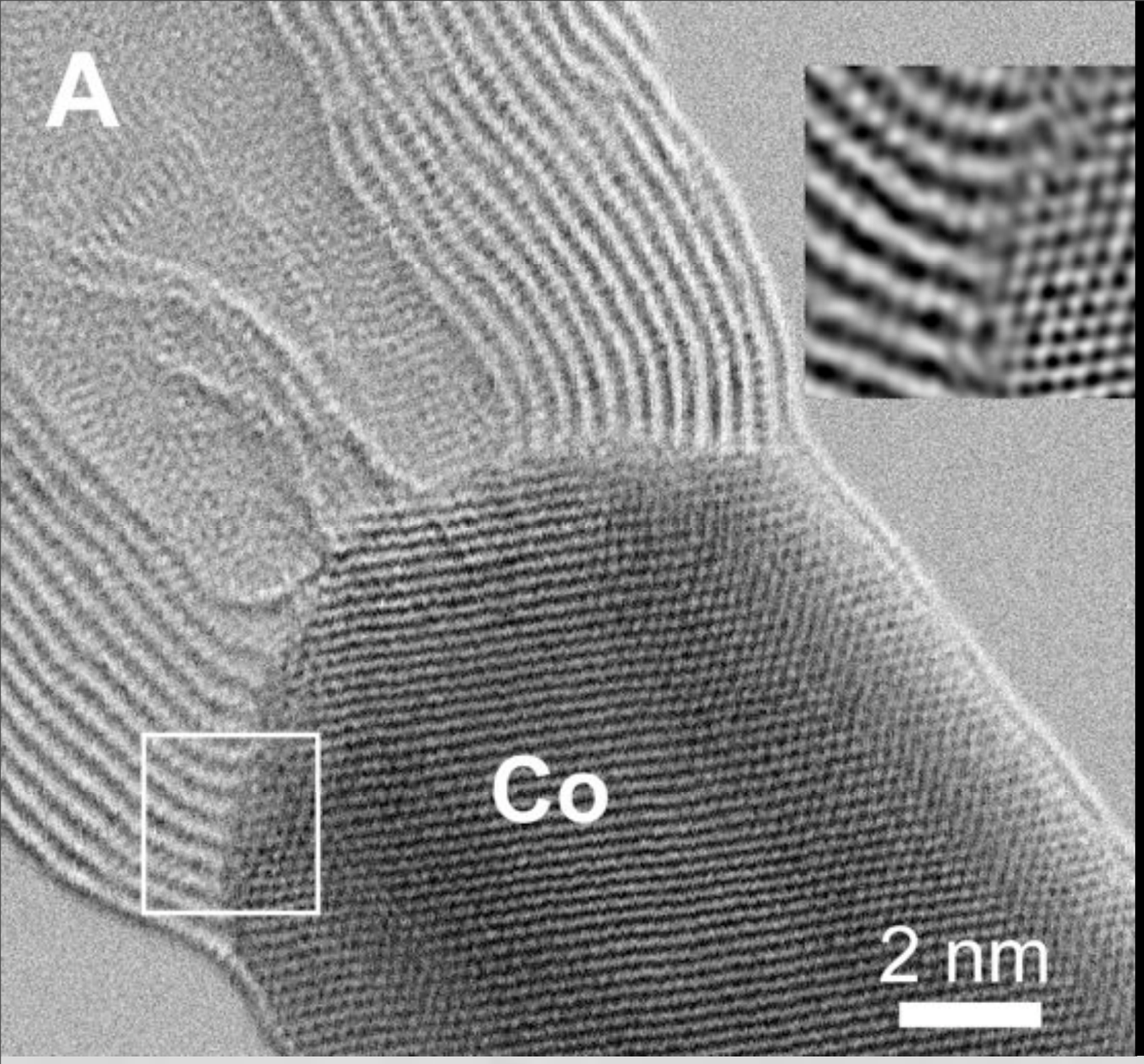
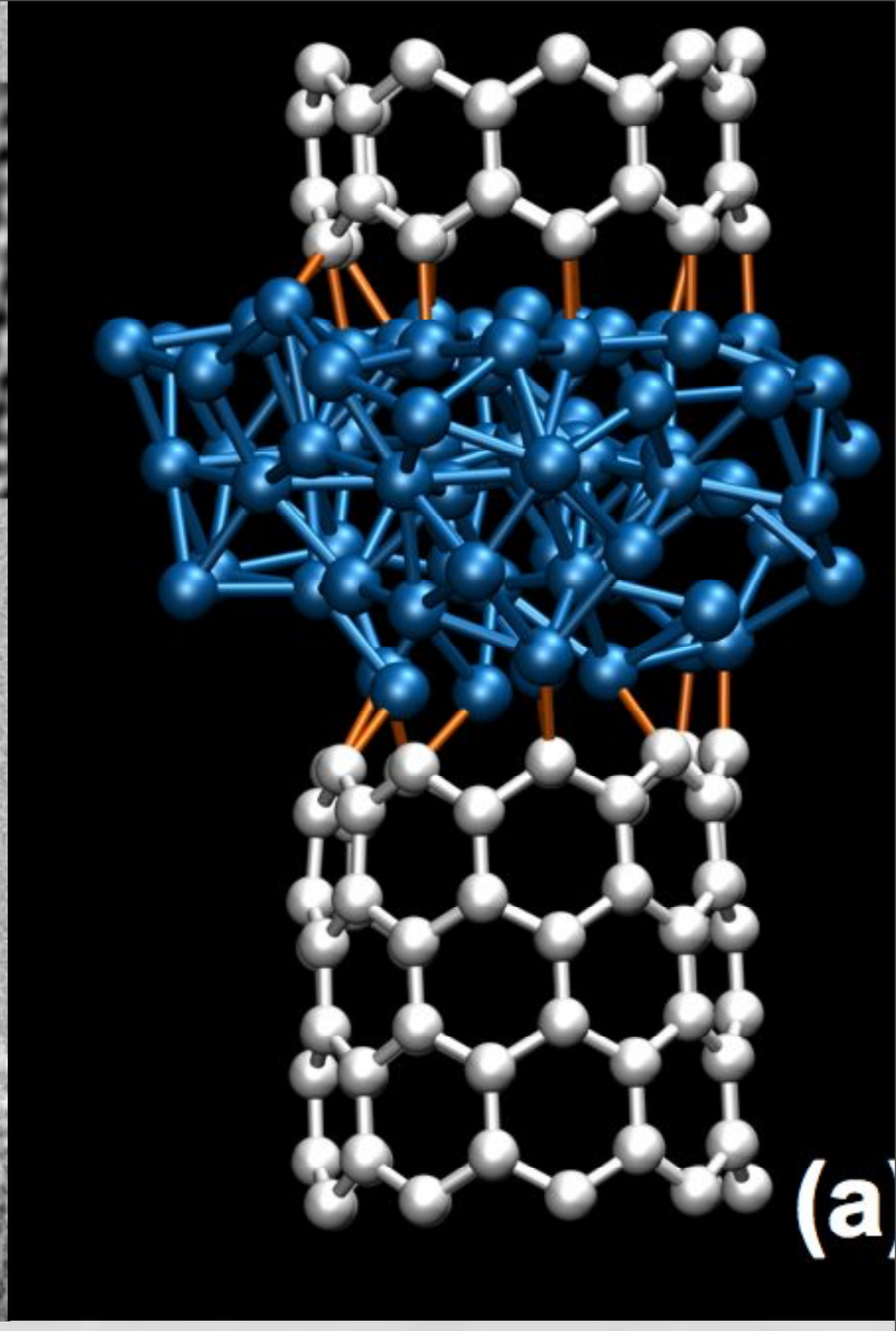
Electrical contacts to one- and two-dimensional nanomaterials

François Léonard[1] and A. Alec Talin[2]



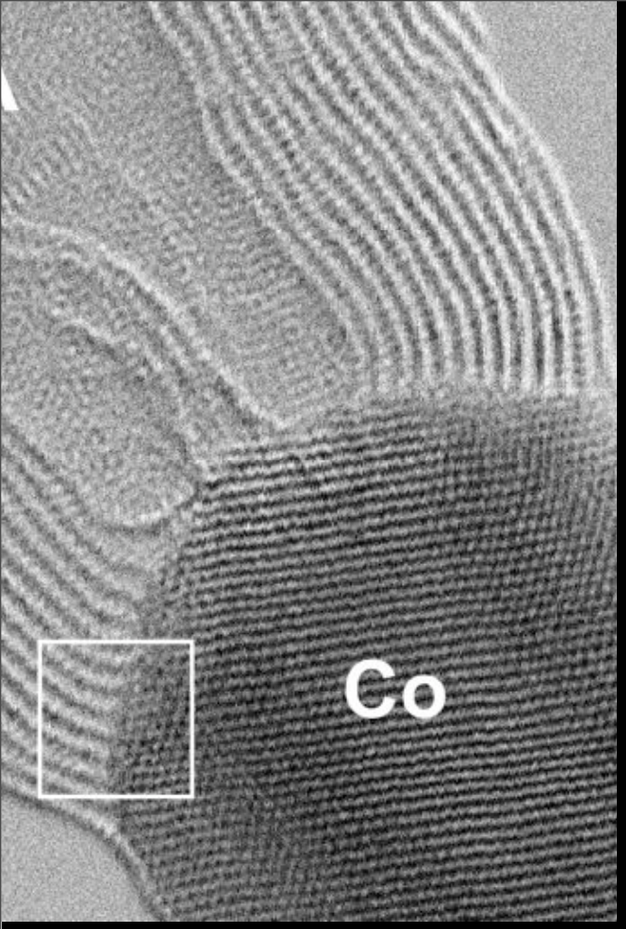


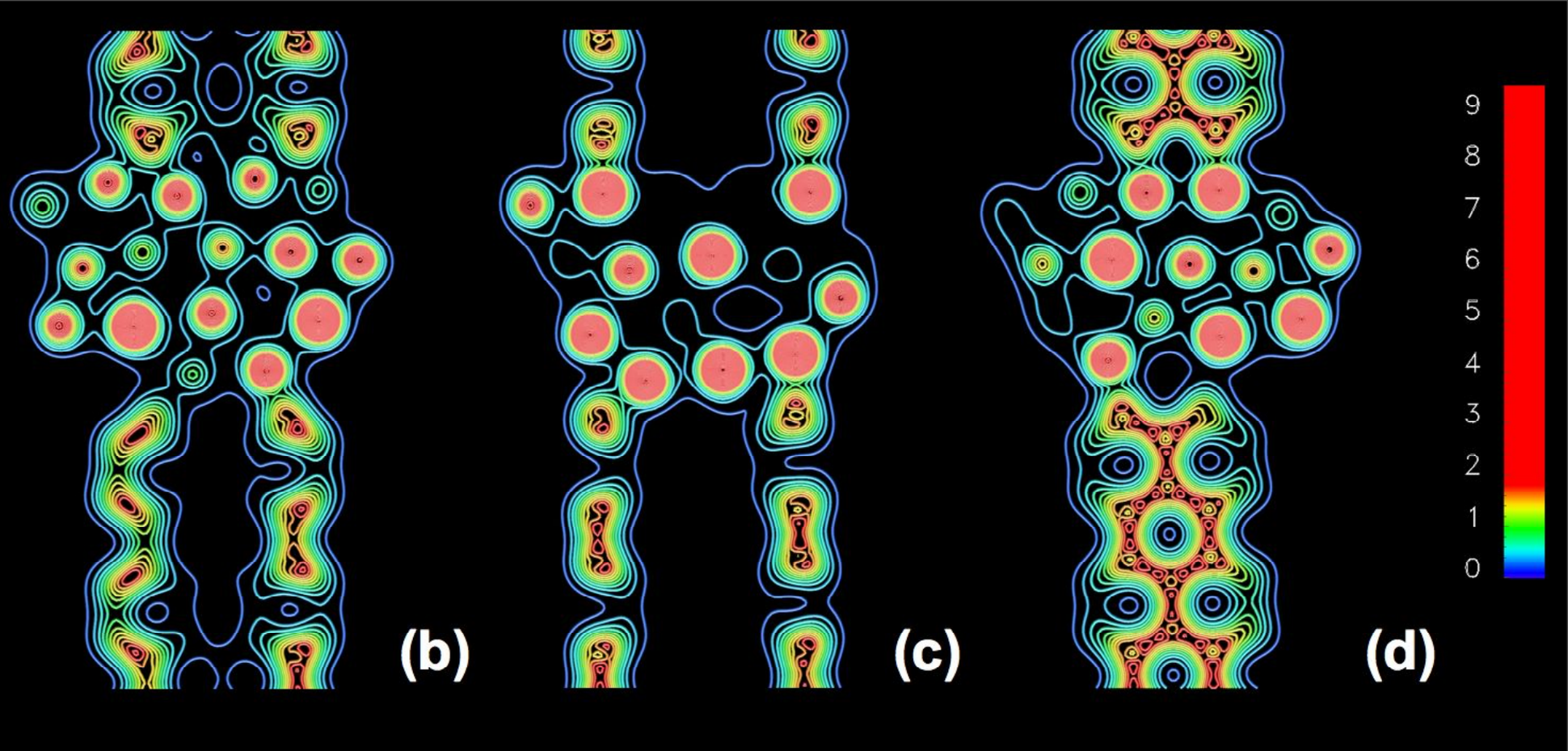


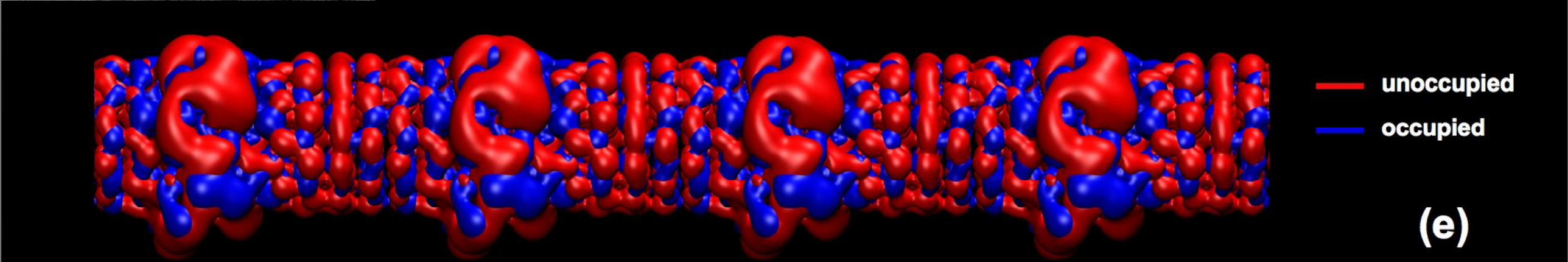
Heterojunctions between metals and carbon nanotubes as ultimate nanocontacts

Julio A. Rodríguez-Manzo[a], Florian Banhart[a,1], Mauricio Terrones[b], Humberto Terrones[b], Nicole Grobert[c], Pulickel M. Ajayan[d], Bobby G. Sumpter[e], Vincent Meunier[e], Mingsheng Wang[f], Yoshio Bando[f], and Dmitri Golberg[f]

PNAS PNAS PNAS







Heterojunctions between metals and carbon nanotubes as ultimate nanocontacts

Julio A. Rodríguez-Manzo[a], Florian Banhart[a,1], Mauricio Terrones[b], Humberto Terrones[b], Nicole Grobert[c], Pulickel M. Ajayan[d], Bobby G. Sumpter[e], Vincent Meunier[e], Mingsheng Wang[f], Yoshio Bando[f], and Dmitri Golberg[f]

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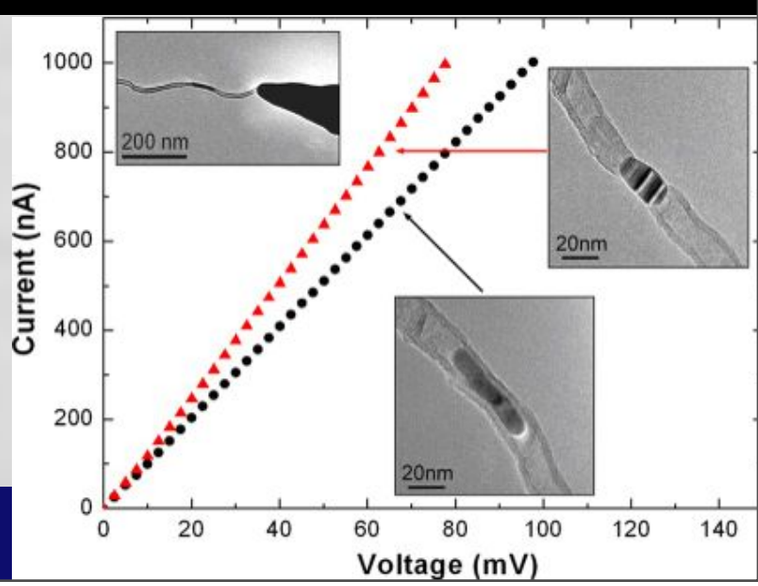


QUANTUM MECHANICAL APPROACH USED IN THIS WORK

$$\hat{H}_{ele}\Psi_n(r;R) = \epsilon_n(R)\Psi_n(r;R)$$

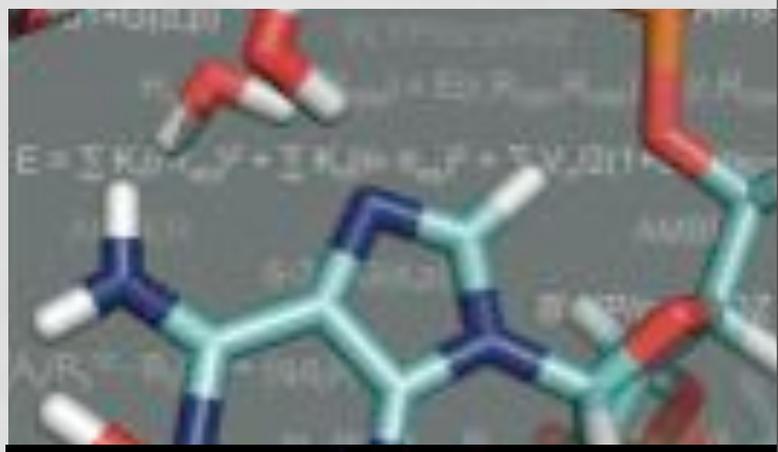
$$\hat{H}_{ele} = -\sum_{i}^{electrons} \frac{\nabla_i^2}{2} - \sum^{nuclei}\sum^{electrons} \frac{Z_i}{r_{..}} + \sum^{electrons}\sum \frac{1}{r_{..}}$$

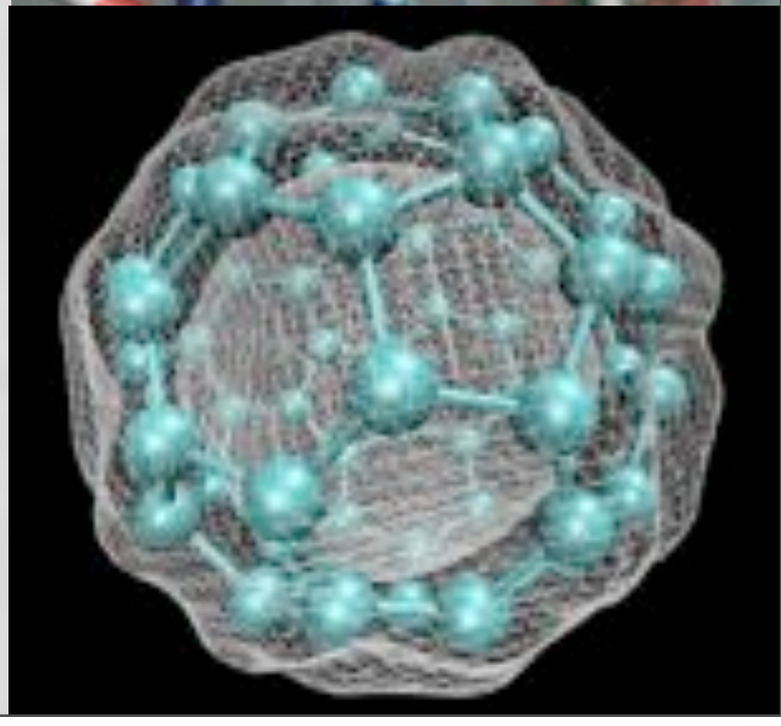
DFT

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_s(\vec{r})\right]\phi_i(\vec{r}) = \epsilon_i\phi_i(\vec{r})$$

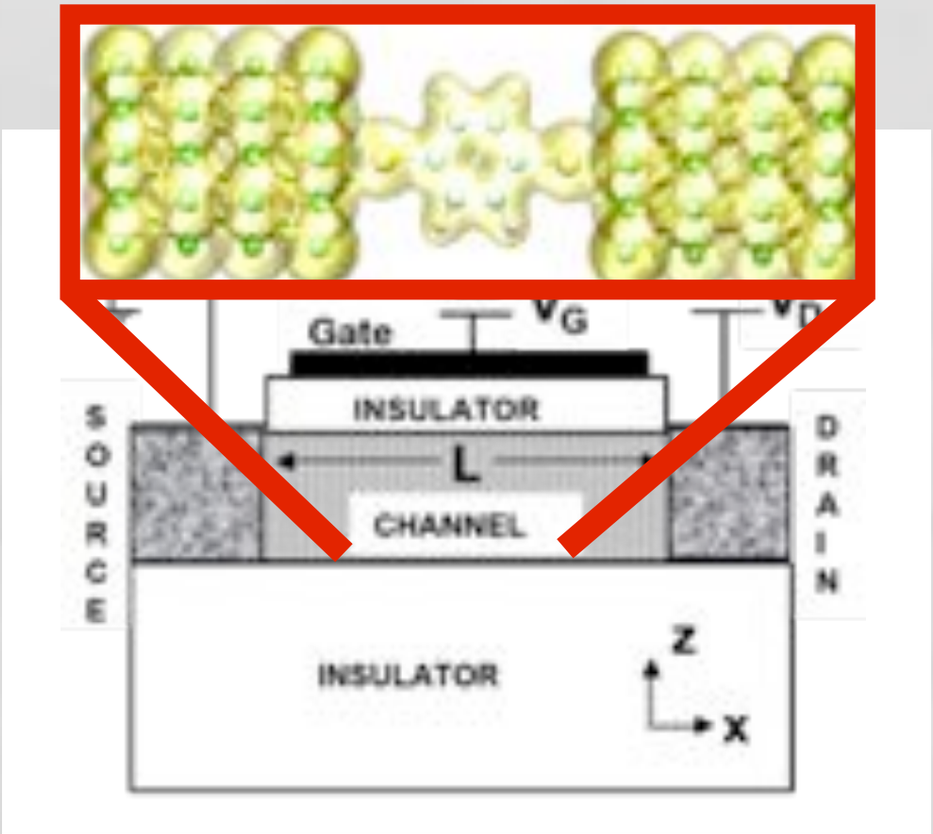
$$V_s(\vec{r}) = V(\vec{r}) + \int \frac{e^2 n_s(\vec{r}\,')}{|\vec{r} - \vec{r}\,'|}\mathrm{d}^3r' + V_{\mathrm{XC}}[n_s(\vec{r})]$$

$$E_{XC}^{\mathrm{GGA}}[n_\uparrow, n_\downarrow] = \int \epsilon_{XC}(n_\uparrow, n_\downarrow, \vec{\nabla}n_\uparrow, \vec{\nabla}n_\downarrow)n(\vec{r})\mathrm{d}^3r.$$

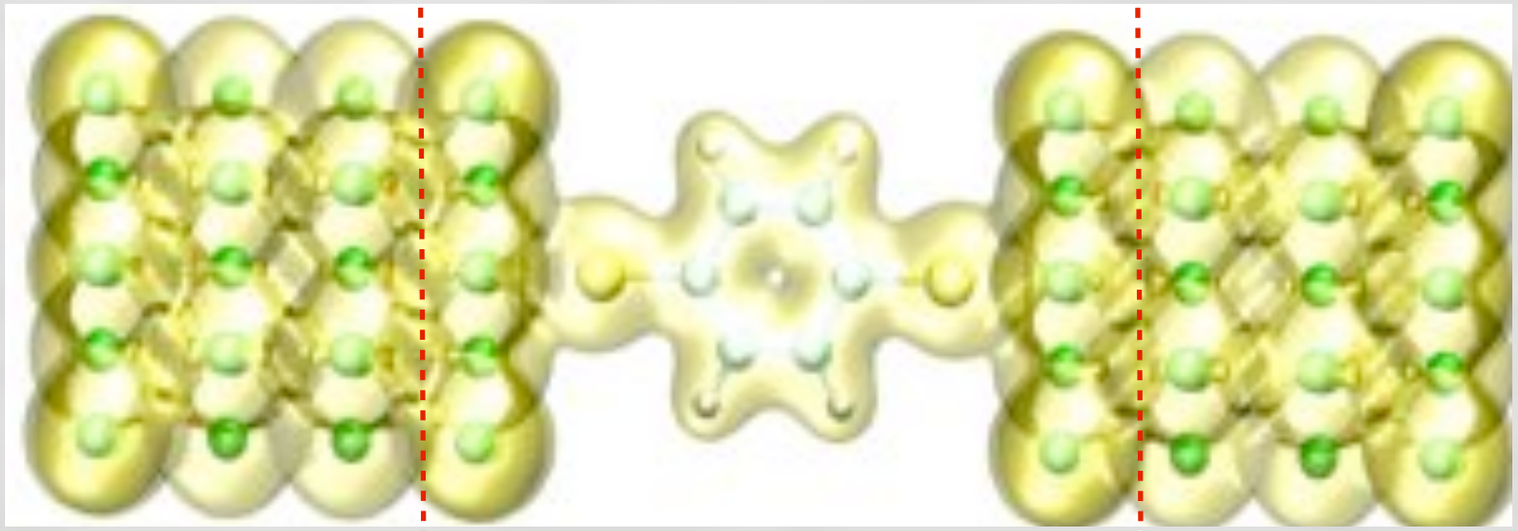


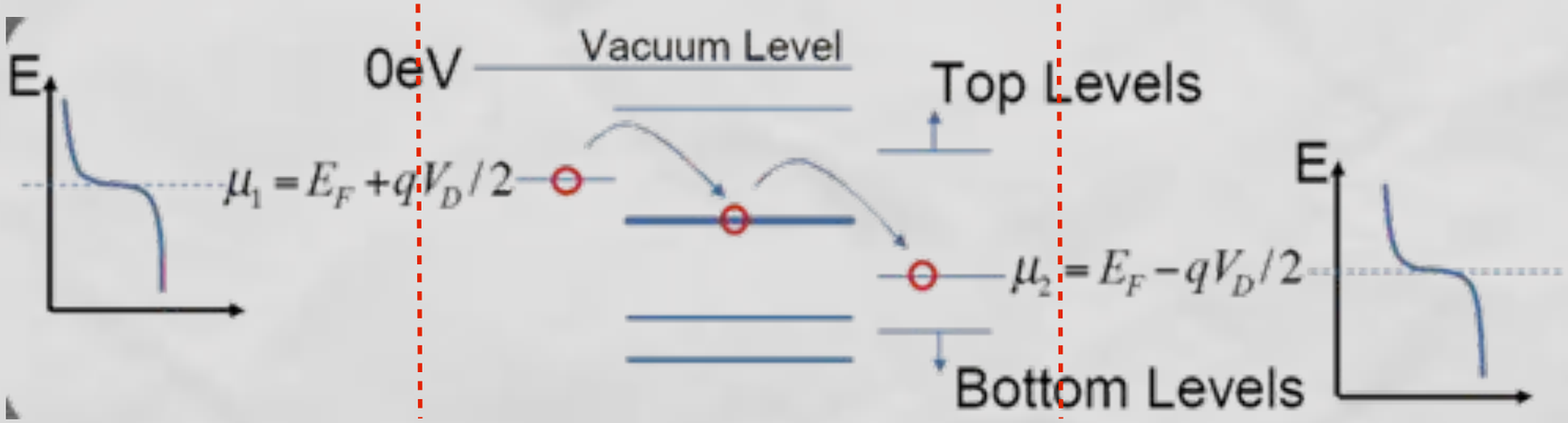


QUANTUM TRANSPORT



QUANTUM TRANSPORT





Current flows if

- there is a region with differing Fermi distributions on L/R ⟶ ***- STATISTICS (Landauer, NEGF)***

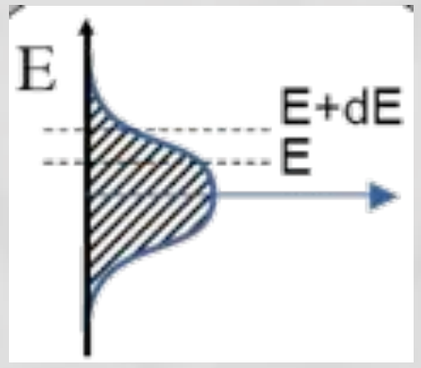
- there are *states available* in that region ⟶ ***- ELECTRONIC STATES (QM)***

ORIGIN OF FINITE RESISTANCE

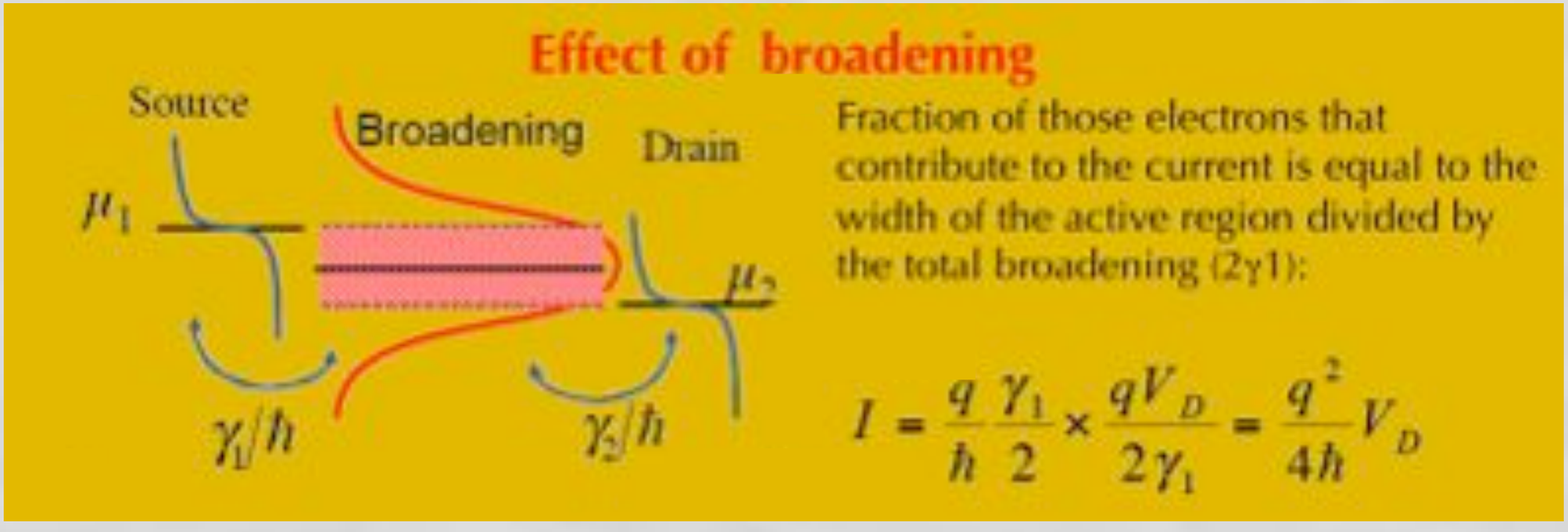
No coupling: wave function is given by $\psi \propto e^{-iEt/\hbar}$ (sharp peak in the energy domain, i.e. probability of finding an electron at a given place is constant.)

With coupling, i.e. finite probability for the electron to escape the channel (i.e. finite lifetime for the electron in the channel)

$$\psi \propto e^{-iEt/\hbar} e^{-t/2\tau}$$



In energy space, this corresponds to a **Lorentzian broadening**.

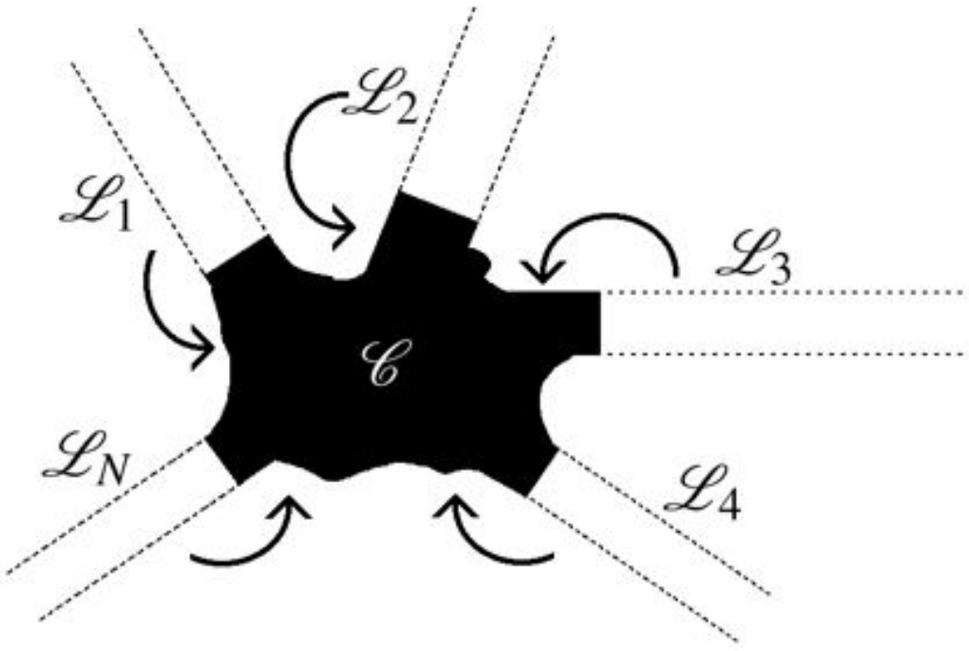


LANDAUER-BUTTIKER

$$G_C = (\epsilon I_C - H_C - \Sigma_1 - \Sigma_2 - ... - \Sigma_N)^{-1}$$

$$\Sigma_i = h_{Ci} g_i h_{iC} \qquad g_i = (\epsilon I_i - H_i)^{-1}$$

$$\Gamma_i = i(\Sigma_i^r - \Sigma_i^a)$$



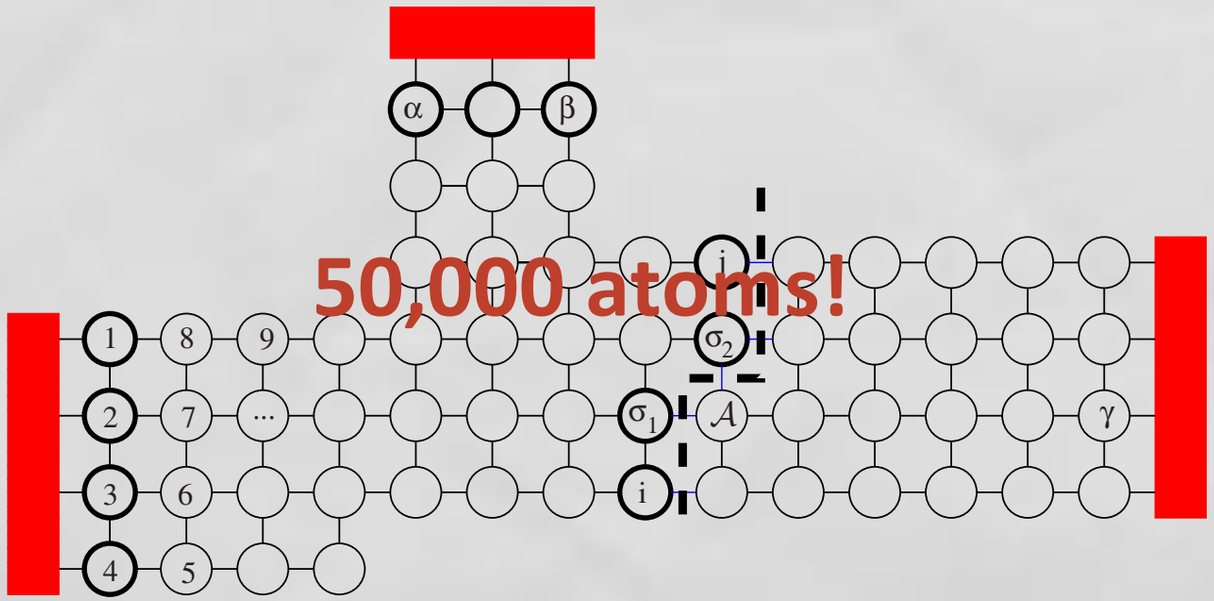
$$G^{n\to m}(E) = \frac{2e^2}{h}\mathcal{T}_{nm}(E)$$

$$\mathcal{T}_{nm} = Tr(\Gamma_i G_C^r \Gamma_j G_C^a)$$

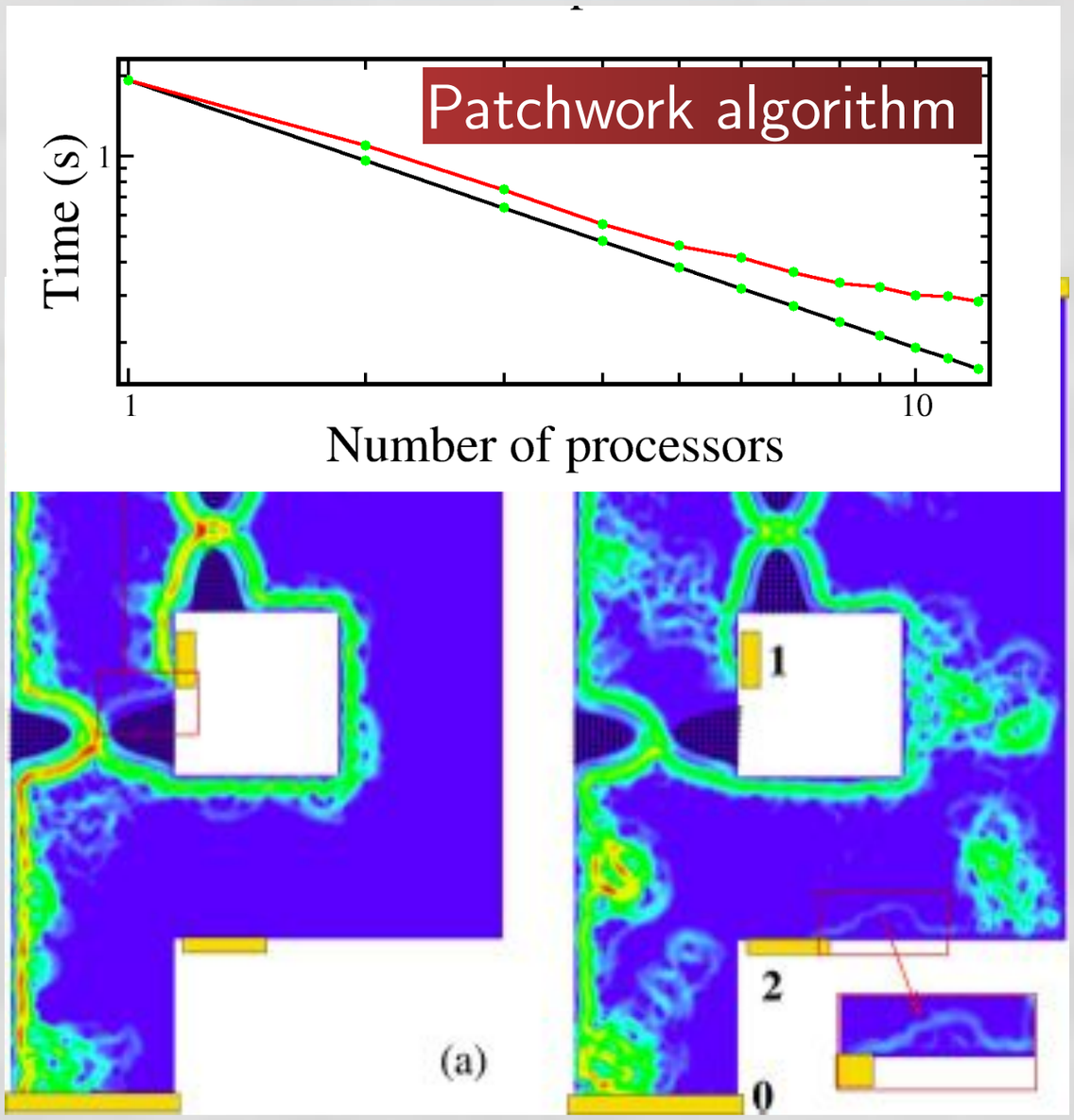
KNITTING ALGORITHM

Dyson equation

$$G_{ij} = g_{ij} + \sum_{kl} g_{ik} V_{kl} G_{lj}.$$

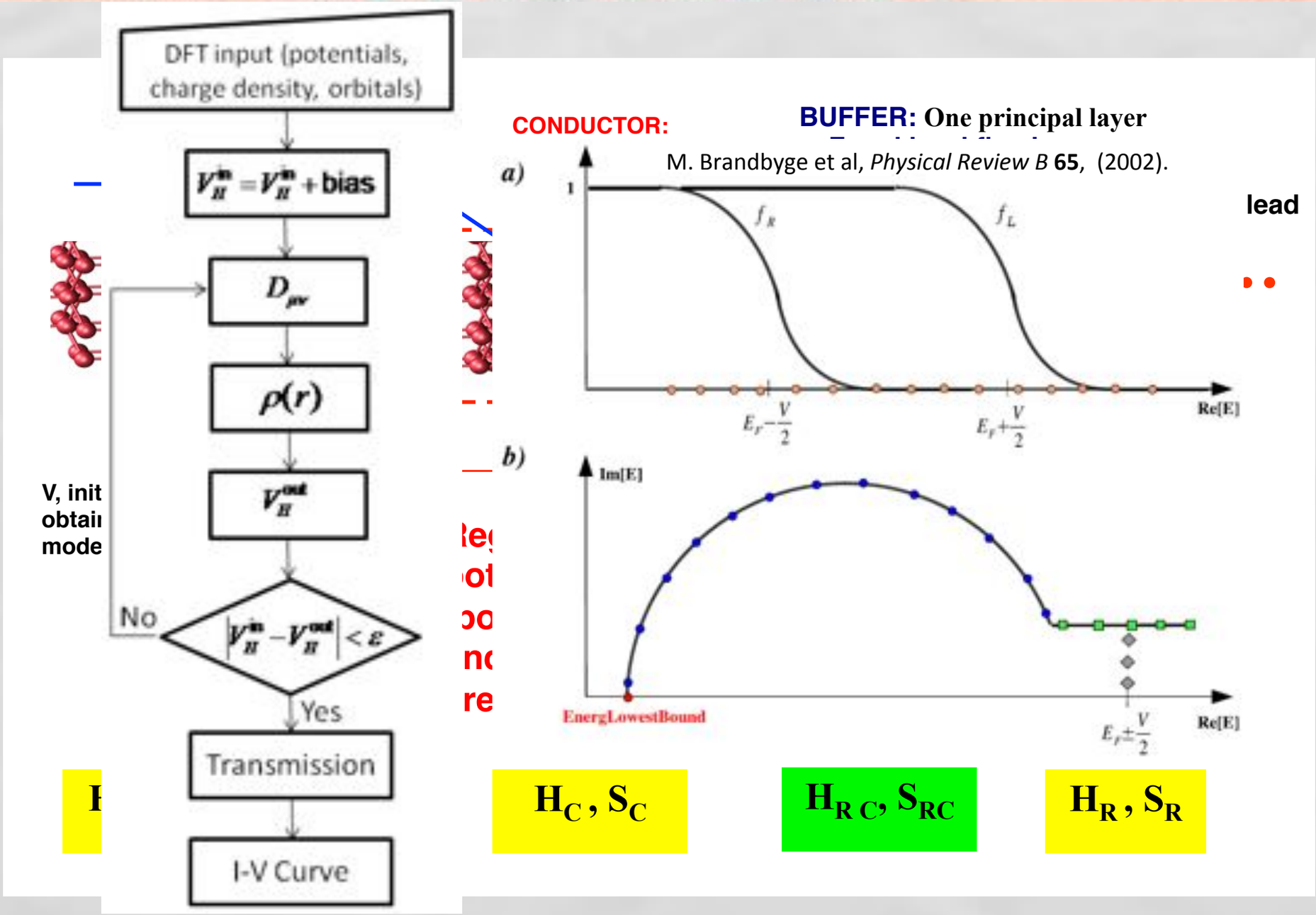


50,000 atoms!



Waintal et al, PRB 77, 115119 (2008)

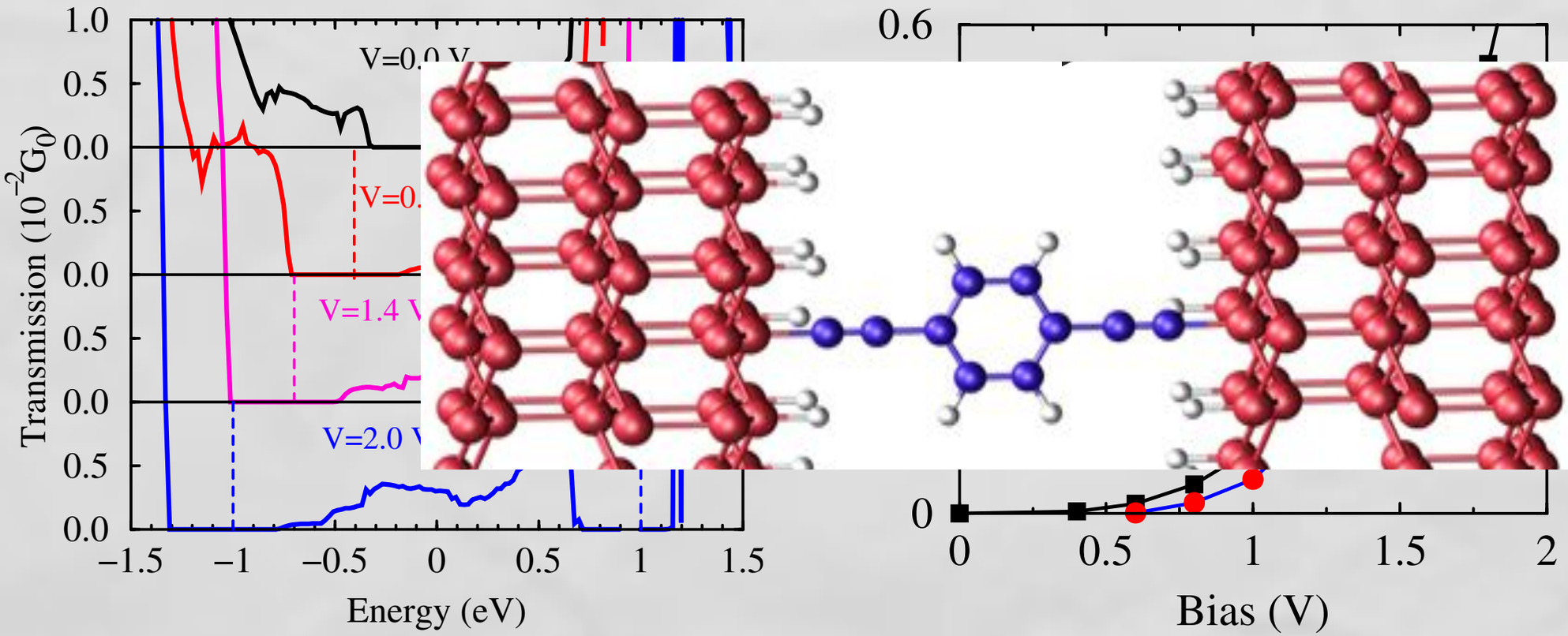
NON-EQUILIBRIUM TRANSPORT



Main reference: Phys. Rev. Lett 95 206805 (2005)

Our Generalization to multiterminal: Phys. Rev. B, 81, 125420 (2010); .J. Chem. Phys, 131, 164105 (2009)

NONEQUILIBRIUM QT OF ORGANIC MOLECULES ON SILICON



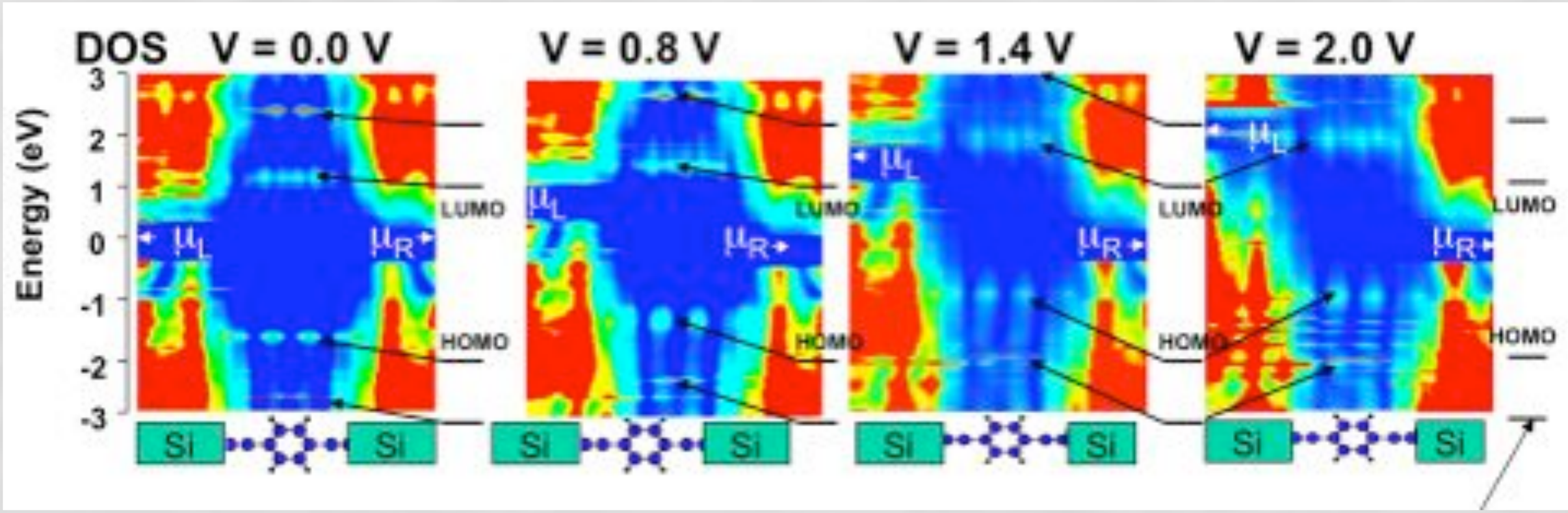
Transmission arises from HOMO and LUMO tail

NDR appears around 1.6 eV

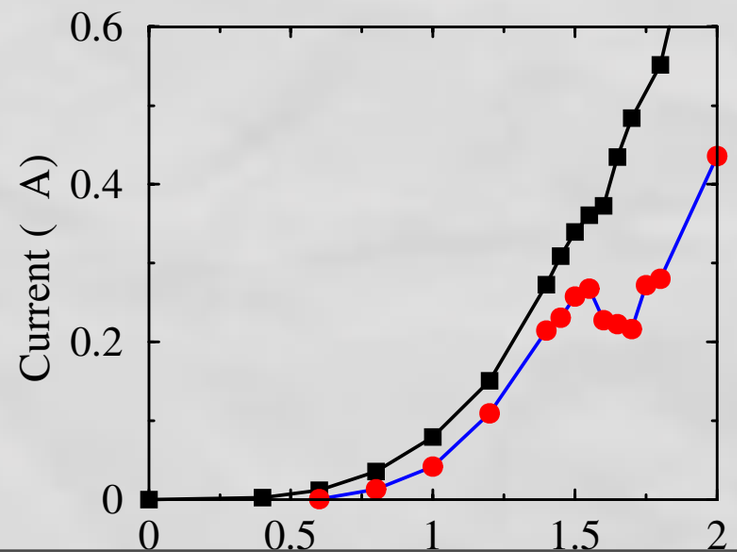
Importance of SCF under large bias

Phys. Rev. Lett **95** 206805 (2005)

QUASI MOLECULAR ORBITAL PICTURE OF ELECTRONIC TRANSMISSION

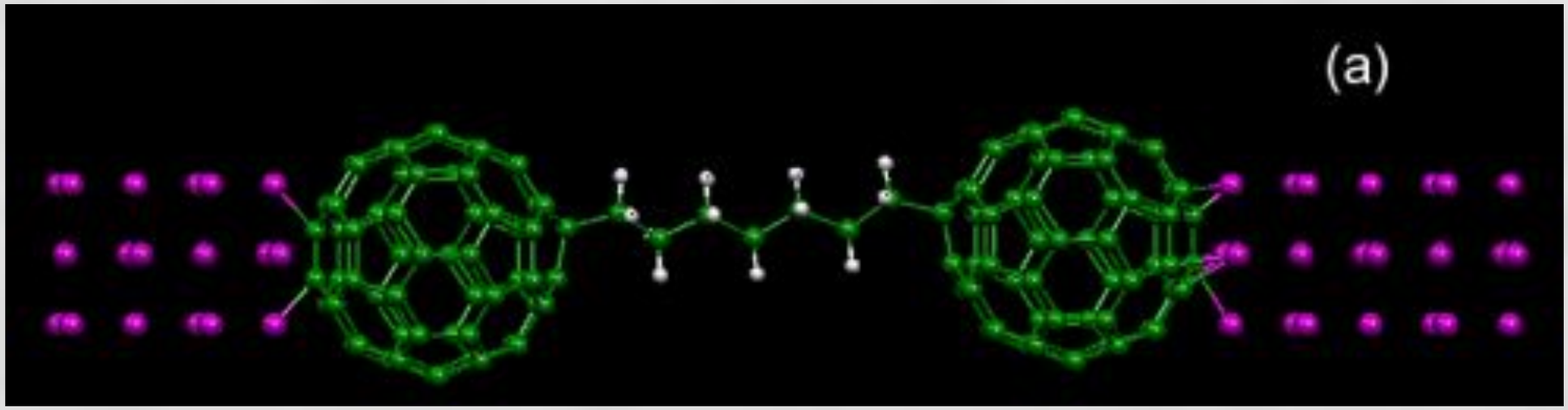


- Molecular orbitals **broaden** with applied bias
- When molecular orbitals match the band edge, a peak appears in the I-V curve
- When molecular orbitals fall into the band gap of Si, **the current drops**, i.e., **negative differential resistance (NDR) occurs.**



Phys. Rev. Lett **95** 206805 (2005)

BRIDGED C60

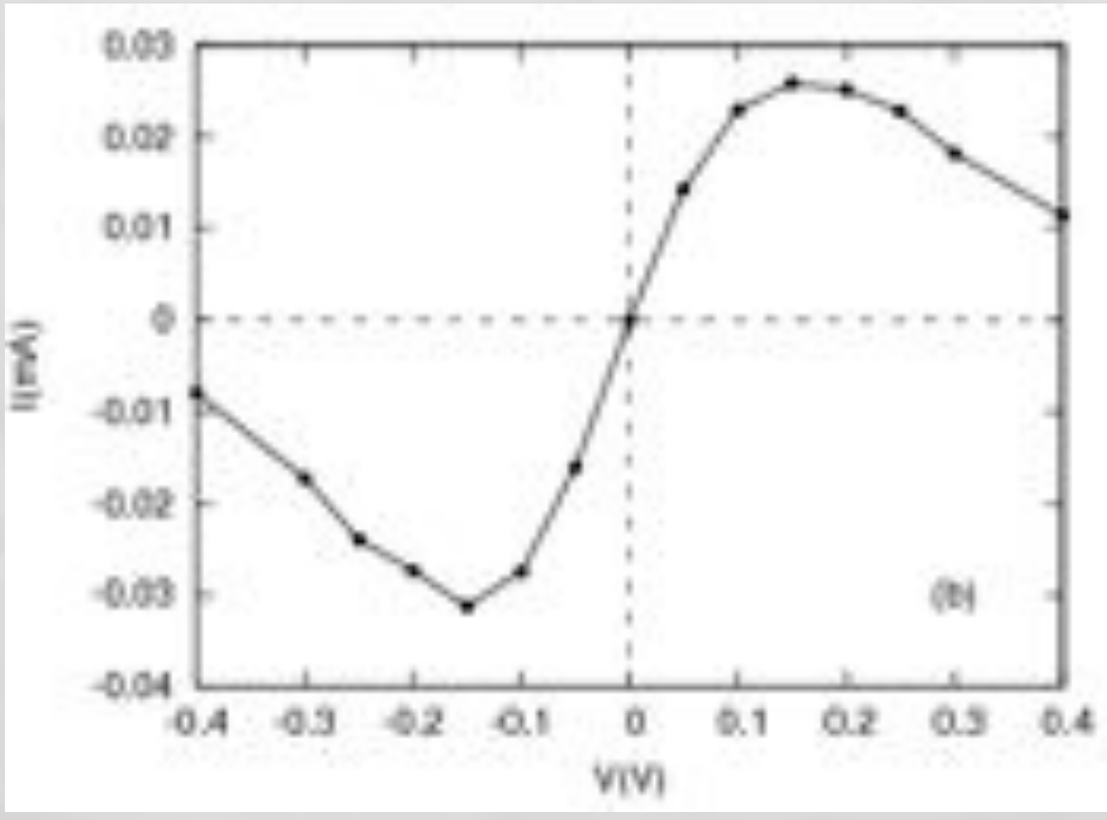


Two C_{60}s connected by an alkane chain are sandwiched between two Aluminum electrodes.

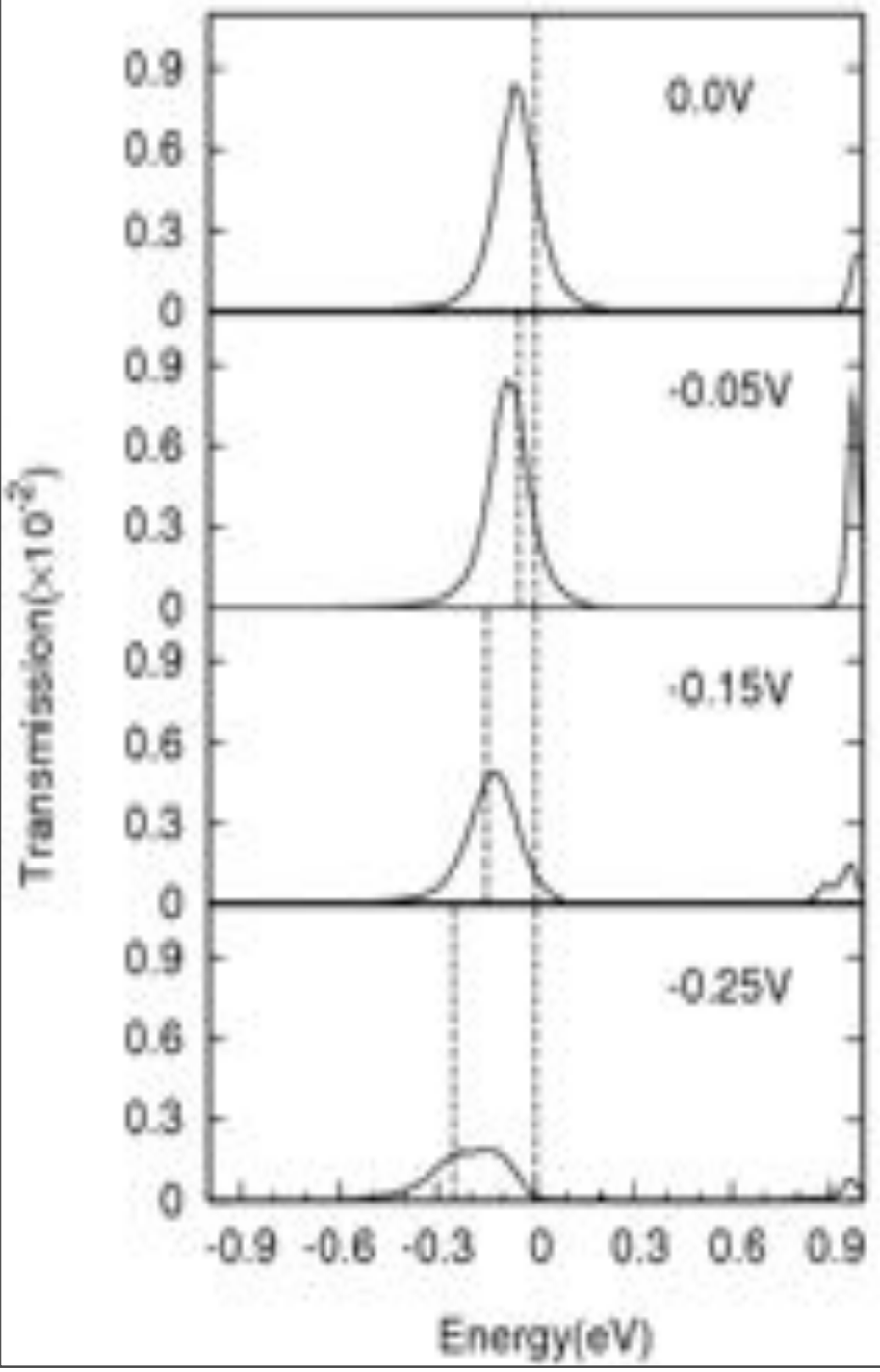
The I-V curve: NDR at very low bias
(V = +0.15V and -0.15V)

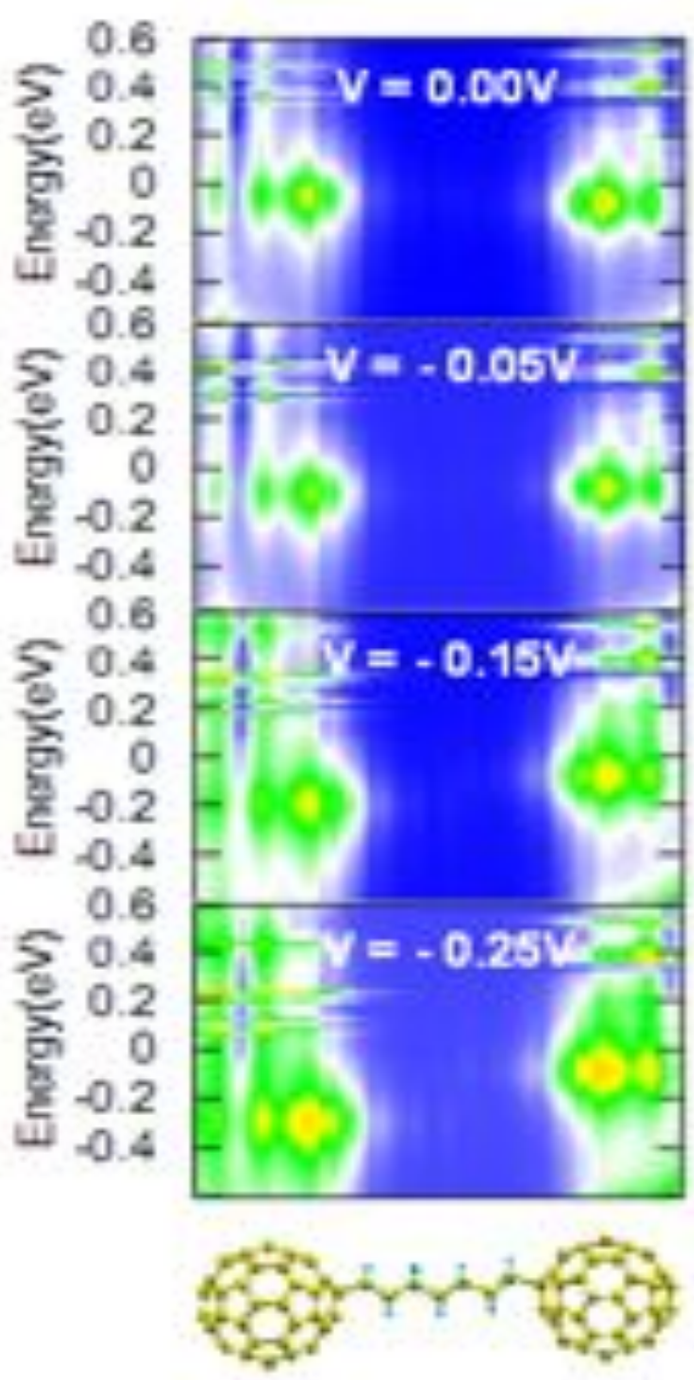
Resonant tunneling at a low bias through the LUMO

ACS Nano 4 (12), 2010



BIAS DEPENDENT COUPLING: QMO PICTURE





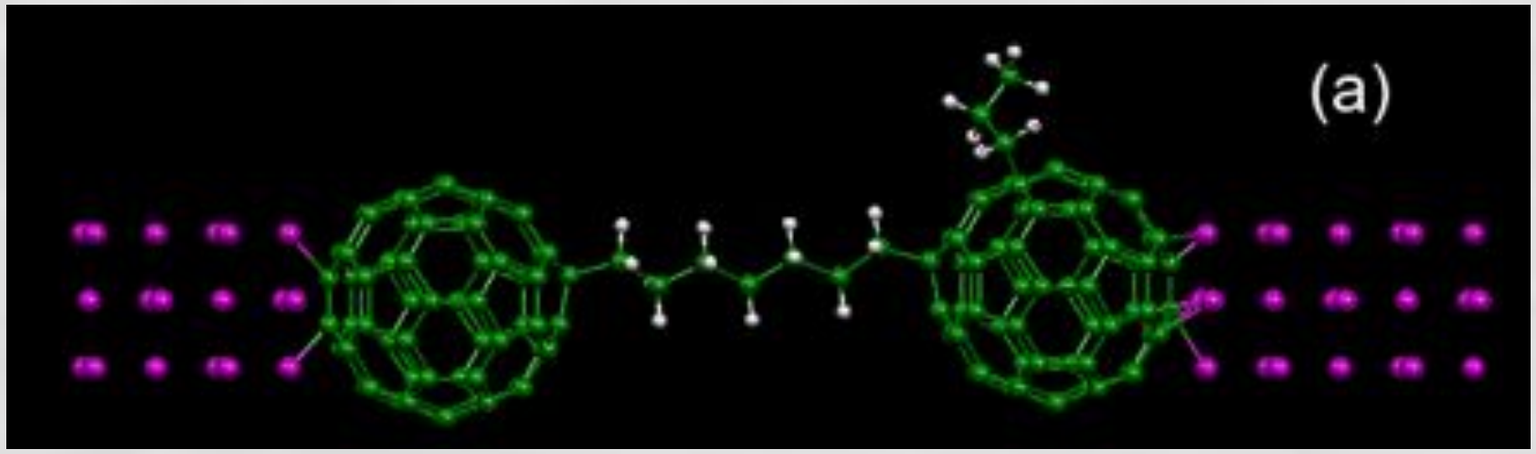
The LUMOs of the C_{60}s.

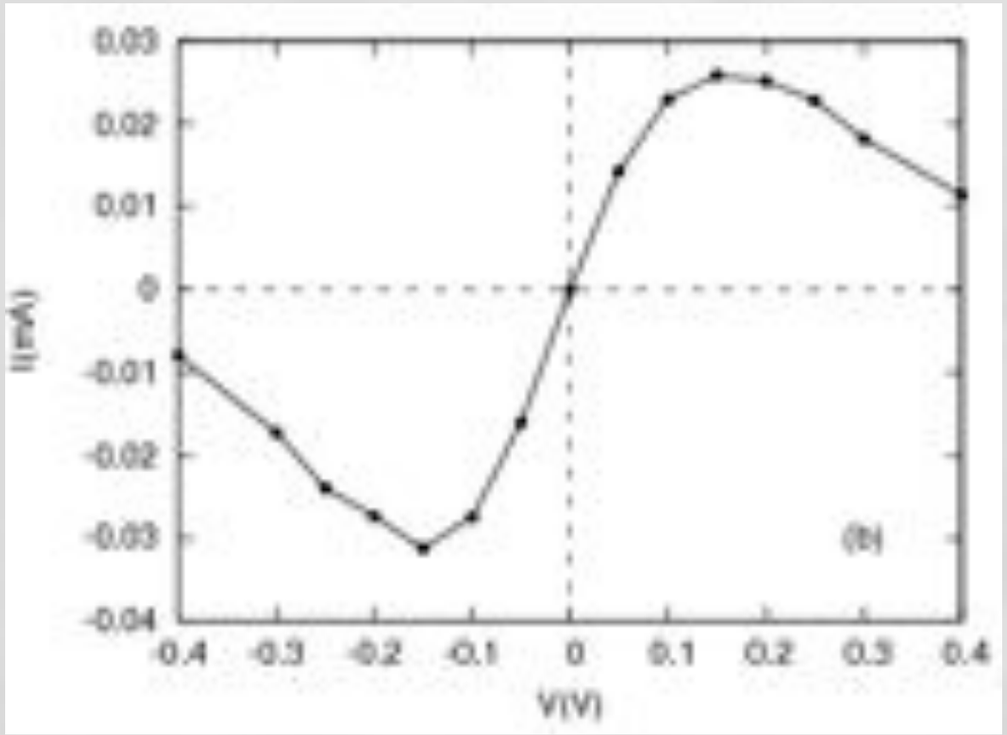
Due to charge transfer from the electrode to C_{60}, the LUMOs are partially filled.

At zero bias, the LUMO of the C_{60}s align with each other very well. This gives rise to the main peak in the transmission.

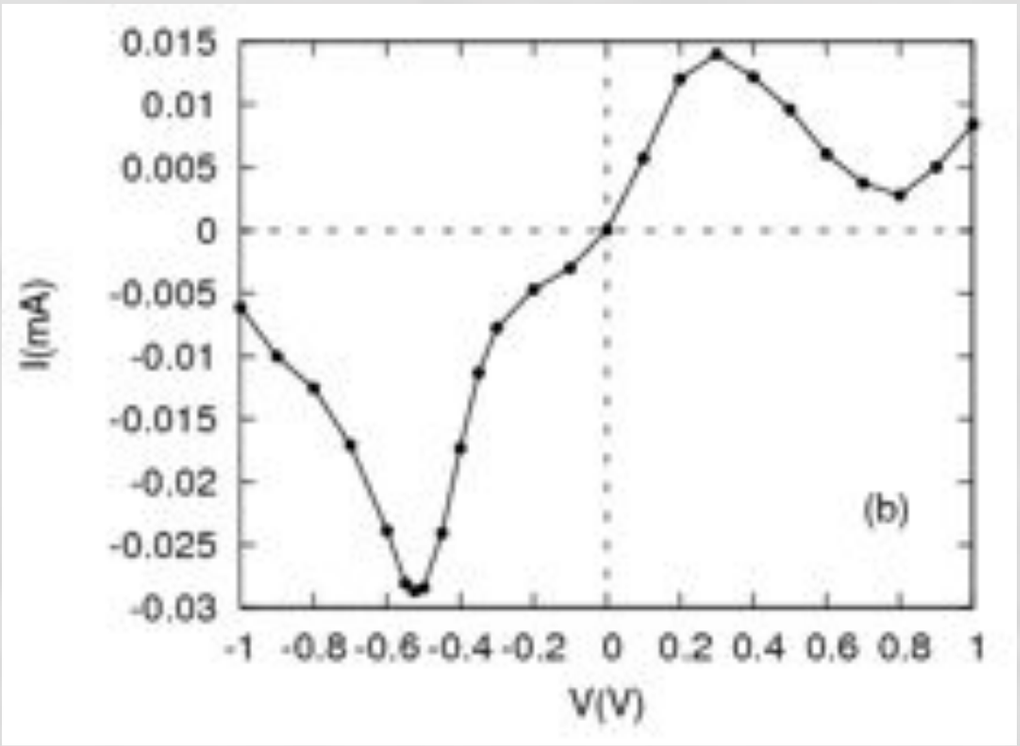
The LUMOs are shifted away from each other under finite bias. The coupling between them becomes weaker and the transmission decreases.

FURTHER TUNING:A C3H8 MOLECULE IS ATTACHED TO THE RIGHT C60



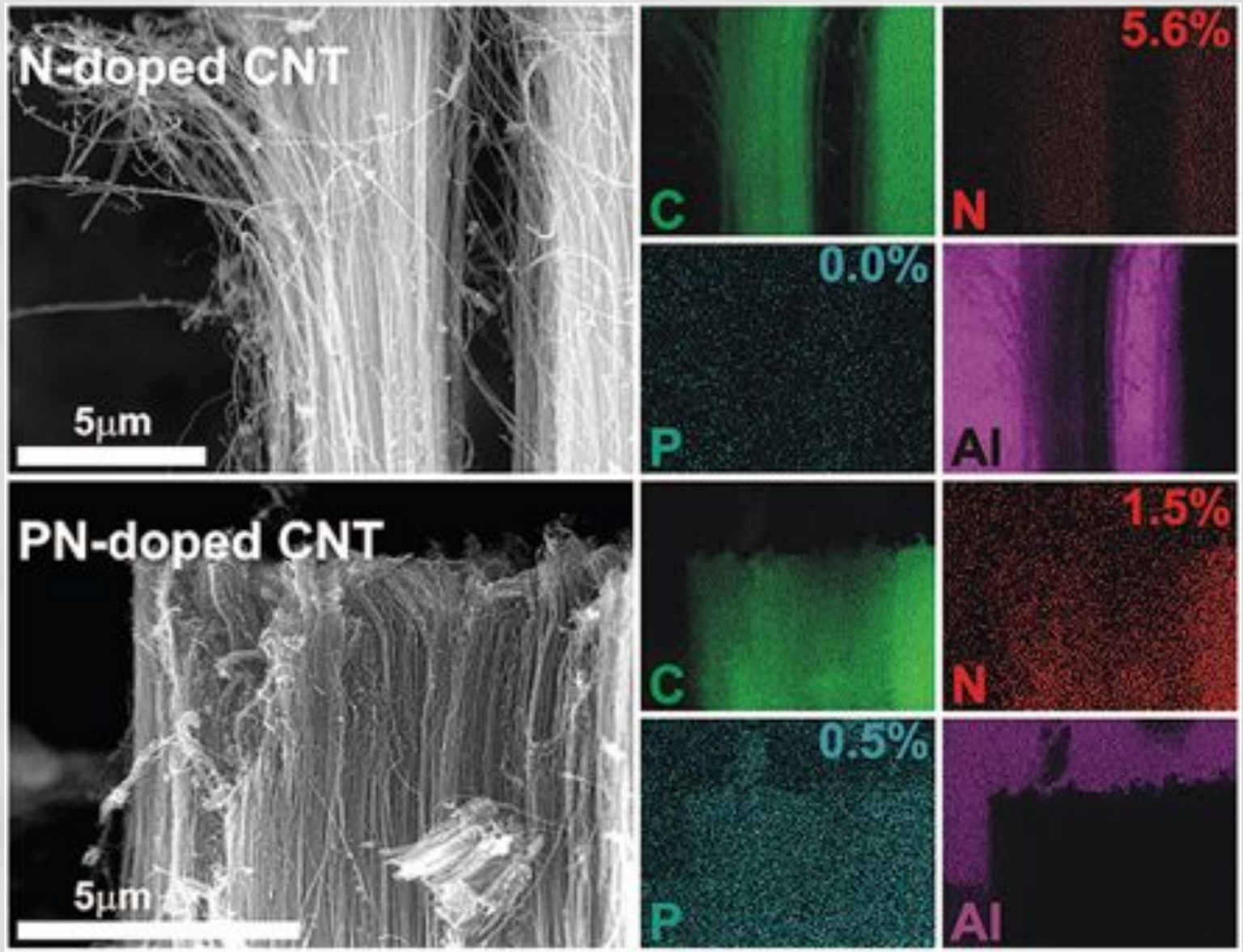


No adsorption:
Symmetrical I-V
NDR at low bias: +0.15V and -0.15V

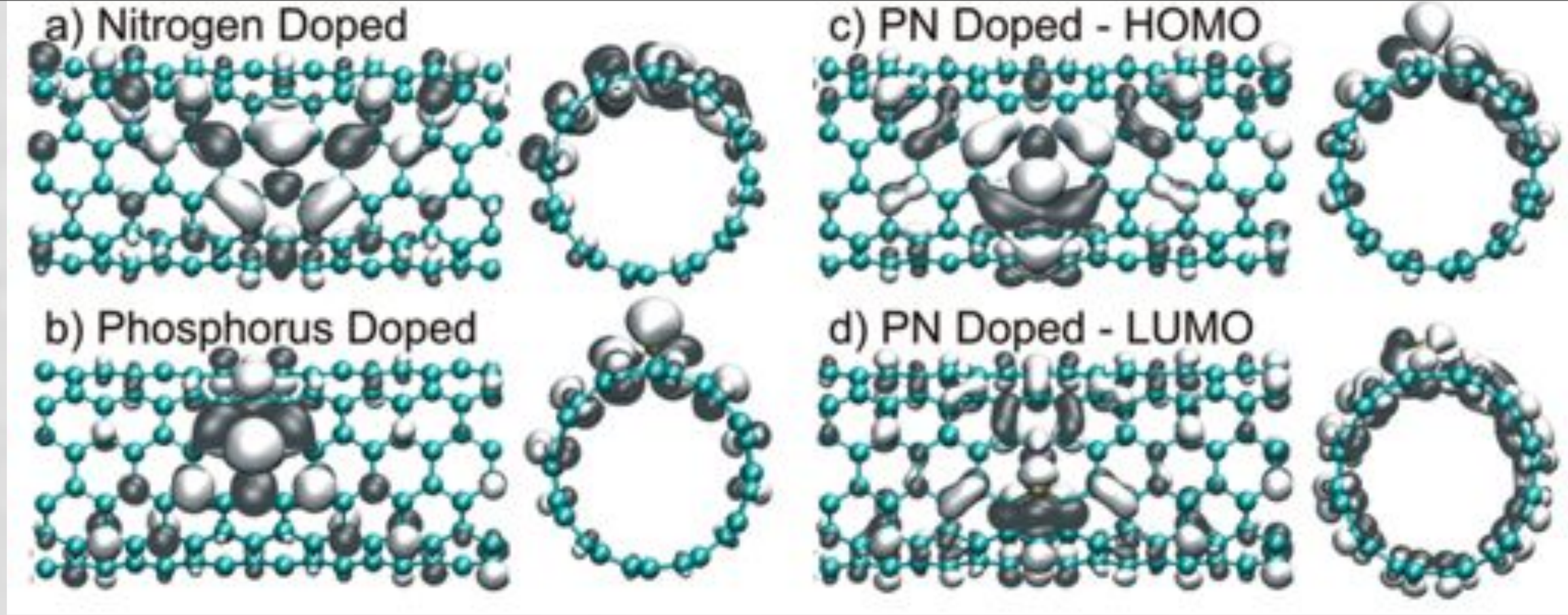


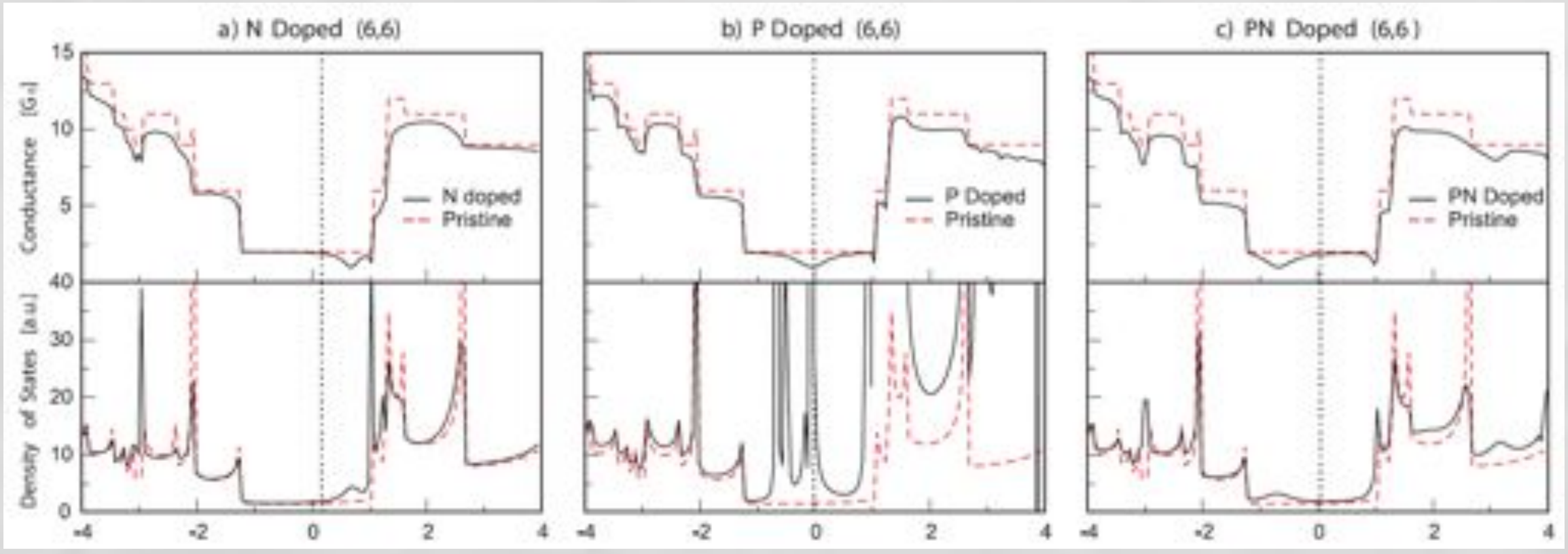
Adsorption:
Asymmetrical I-V
NDR at higher bias: +0.30V and -0.55V

CHEMICAL HETERODOPING: PHOSPHORUS NITROGEN



ACS Nano 2, 441-448 (2008)
ACS Nano 3, 1913-1921 (2009)



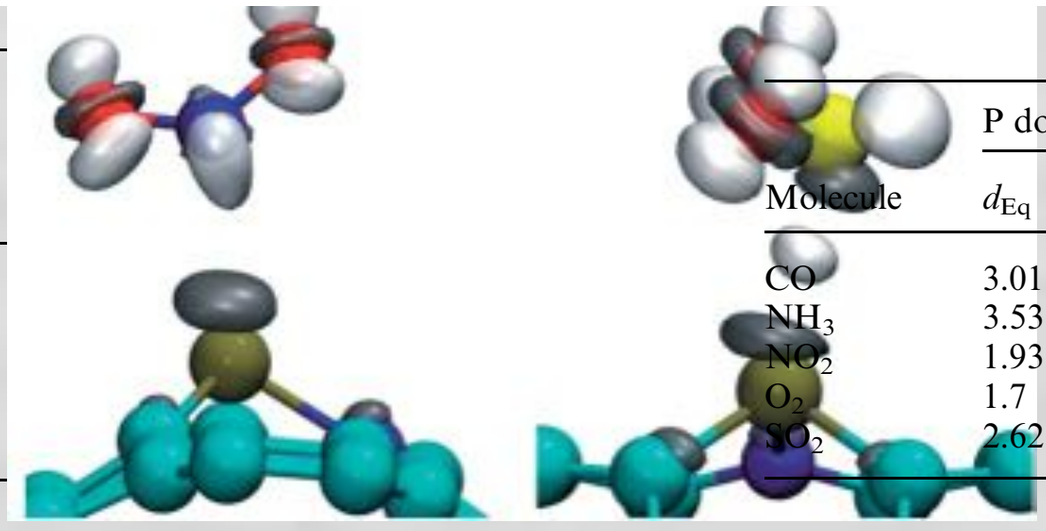


ACS Nano 3, 1913-1921 (2009)

P AND P-N DOPING FOR ULTRASENTIVE DETECTION

- Substitutional P atoms have affinity towards acceptor molecules
- P–N co-dopants have a reduced affinity for acceptor molecules
- P–N bond can also take up charge, resulting in affinity towards donor molecules

P-doped	ΔG
NO_2	57%
O_2	57%
SO_2	41%
PN-doped	
CO	0%
NH_3	−10%
NO_2	−1%
SO_2	4%

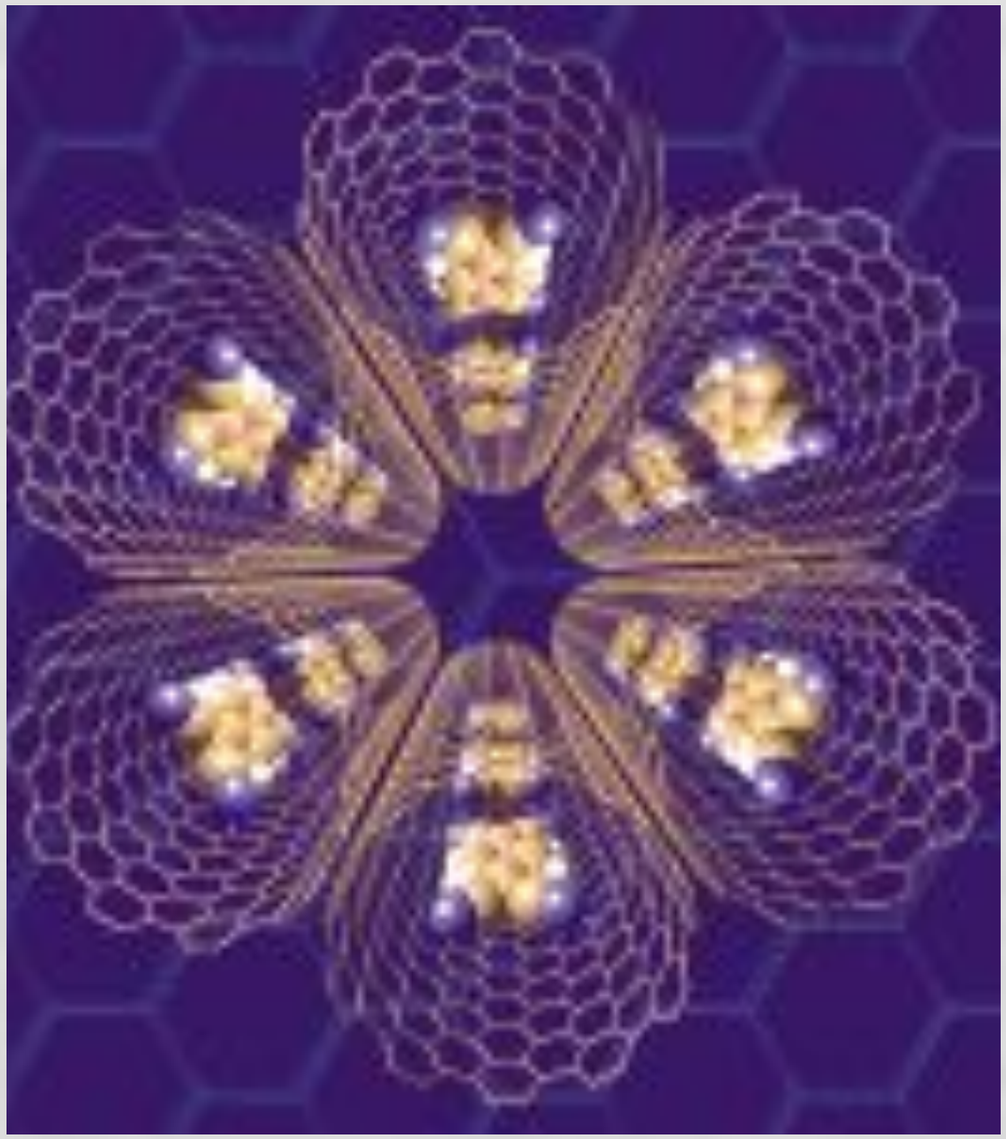


	P doped CNT			PN doped CNT		
Molecule	d_{Eq}	E_{Bind}	Δq_{mol}	d_{Eq}	E_{Bind}	Δq_{mol}
CO	3.01	0.088	0.02	2.38	0.203	−0.04
NH_3	3.53	0.064	0.00	2.41	0.444	−0.16
NO_2	1.93	1.545	0.07	2.65	0.232	0.15
O_2	1.7	0.756	0.27	3.07	0.061	0.03
SO_2	2.62	0.435	0.27	2.73	0.335	0.25

Nanoscale, 3, 1008 (2011)

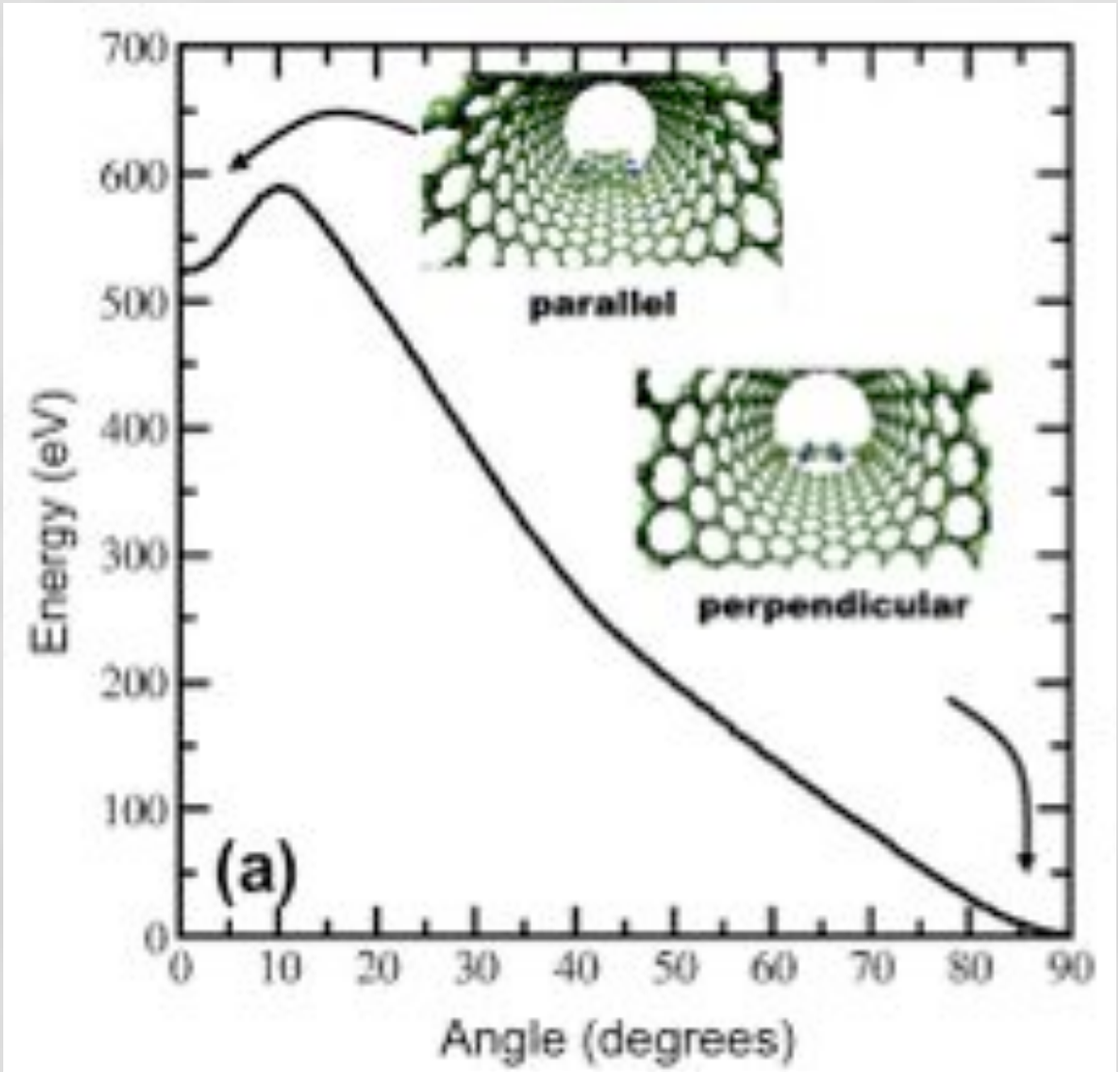
MOLECULAR GATING

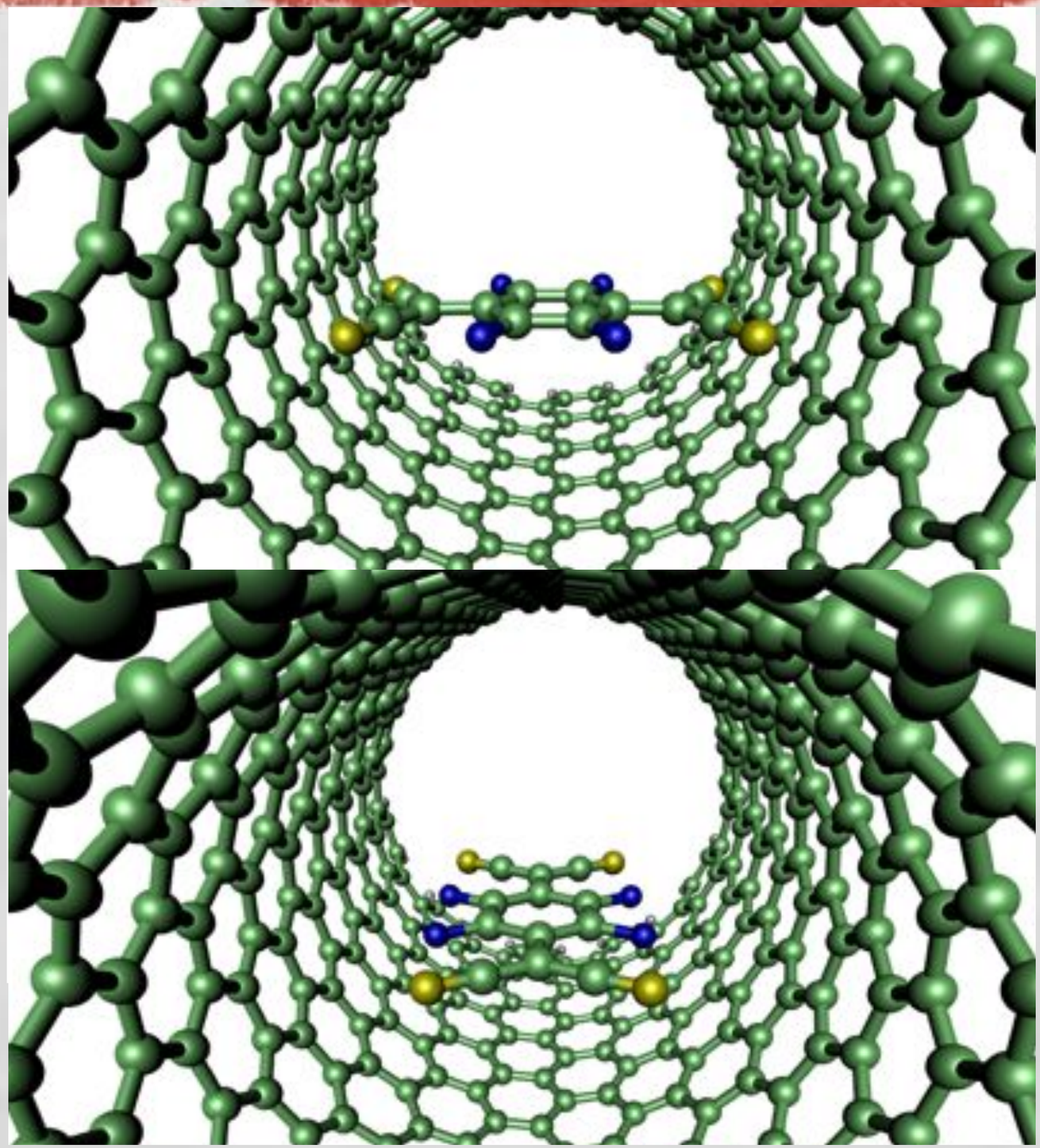
ENDOHEDRAL MOLECULES



Takenobu et al. Nat. Mat (2003)

ENCAPSULATION AND FUNCTIONALITY

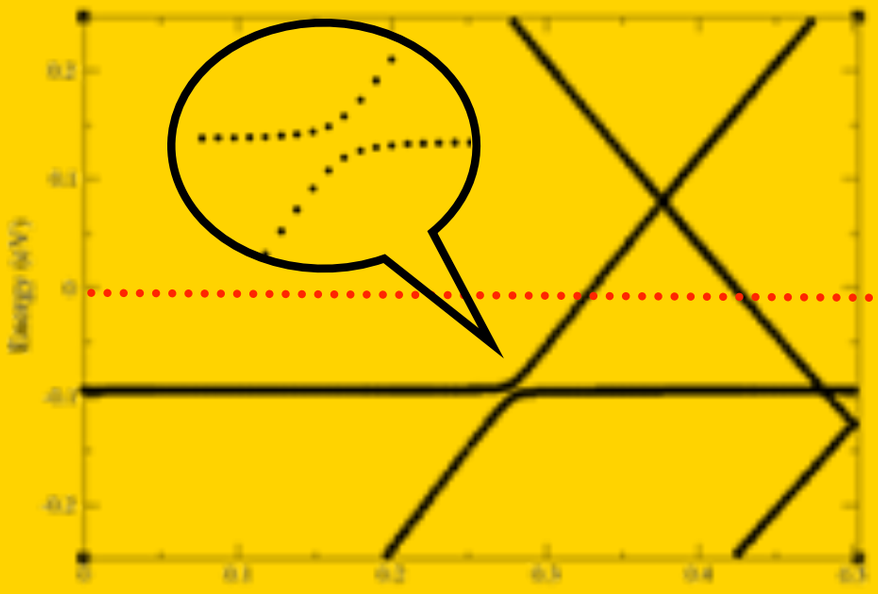


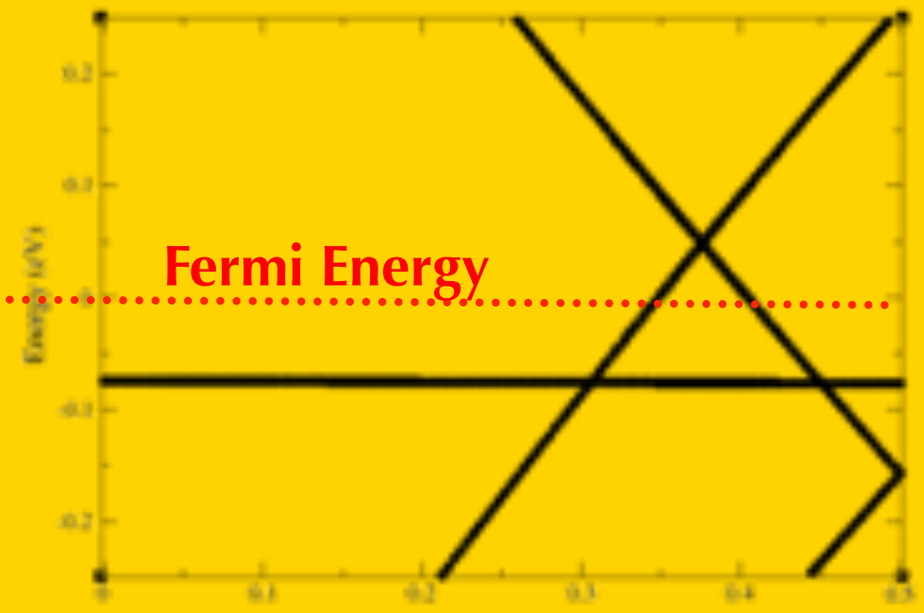


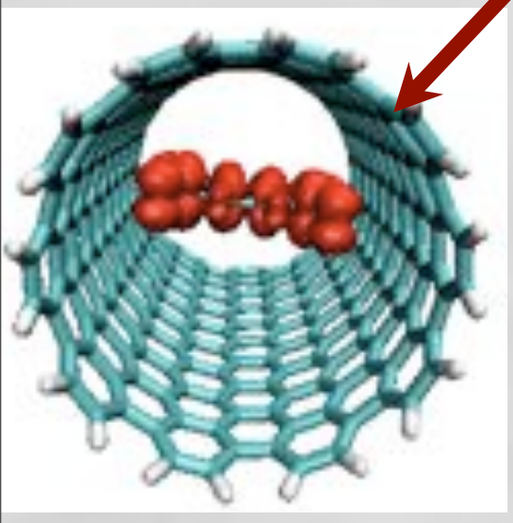
PRL 98, 056401 (2007)

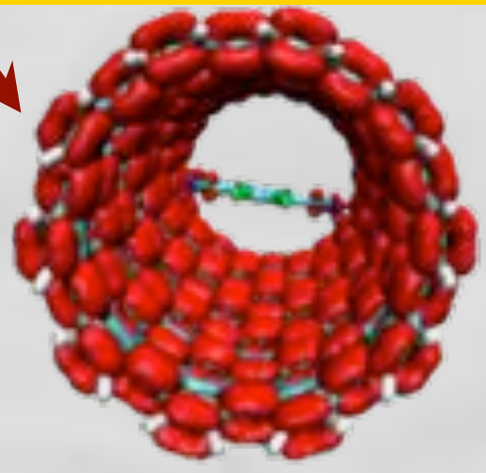
DETAILS OF THE LOCAL INTERACTIONS PROVIDE AN UNDESTANDING OF THE ORIGIN FOR THE ON/OFF STATES

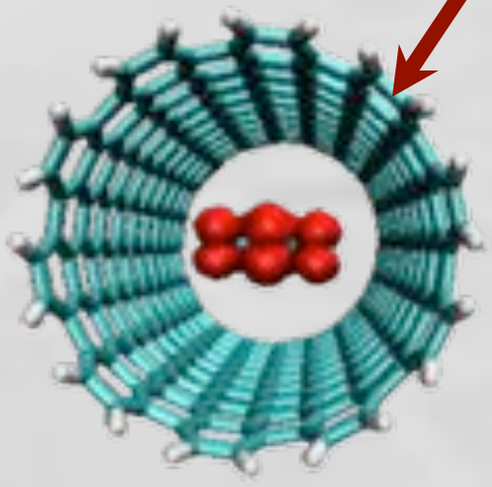
Plane-wave band-structure (periodic calculation)

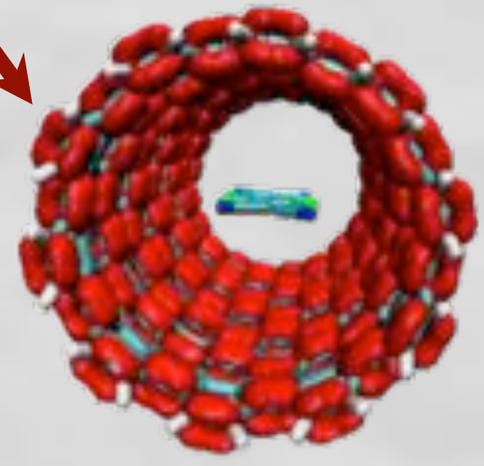








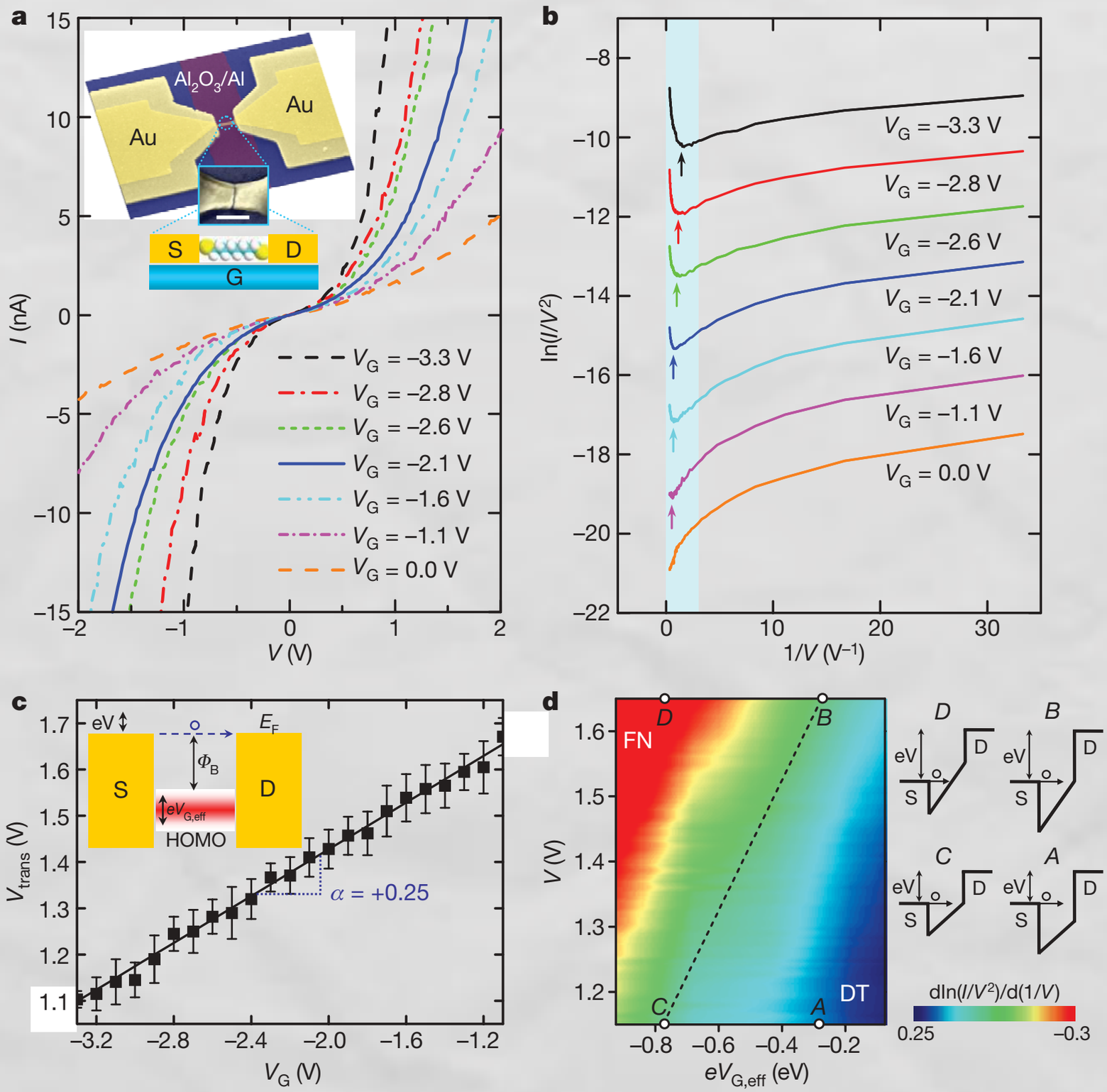




nature

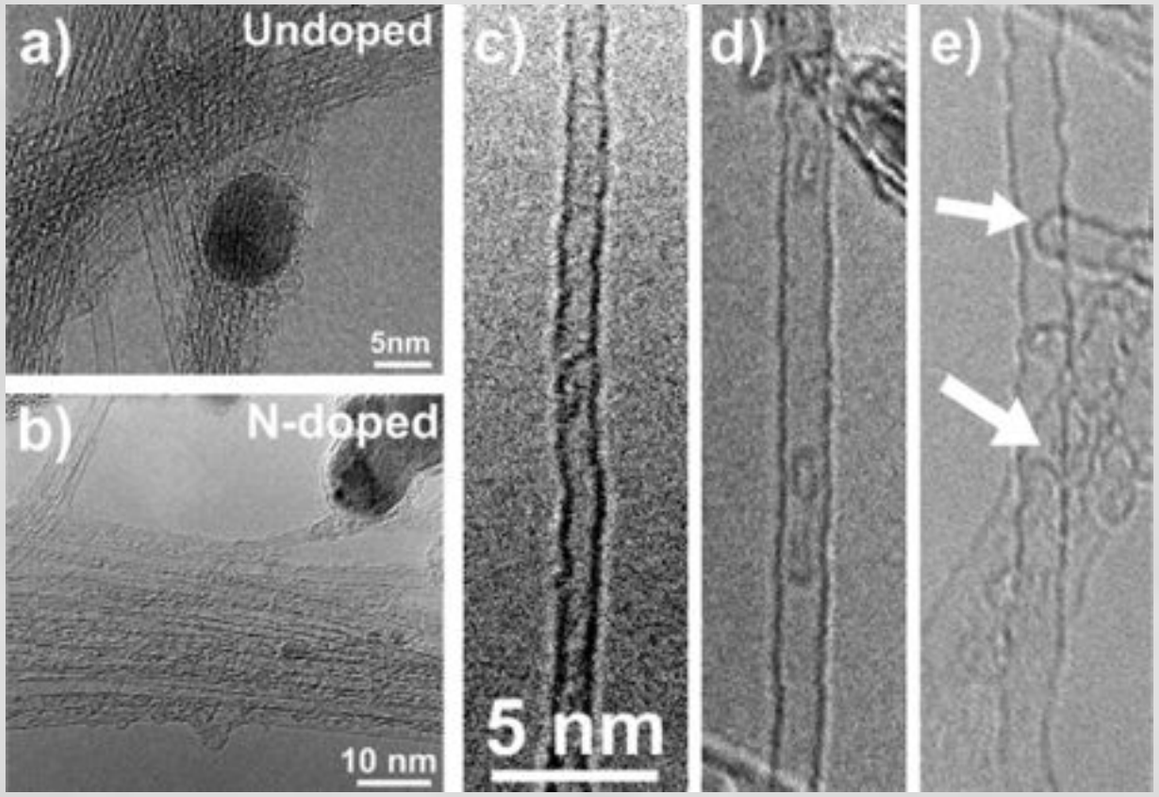
Observation of molecular orbital gating

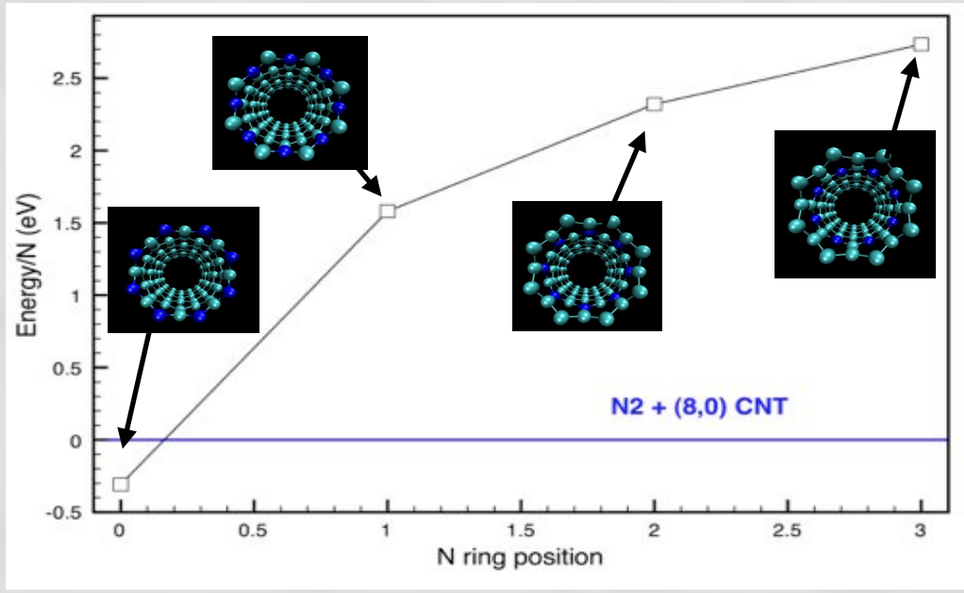
Hyunwook Song[1,2], Youngsang Kim[3]†, Yun Hee Jang[2], Heejun Jeong[3], Mark A. Reed[4] & Takhee Lee[1,2]

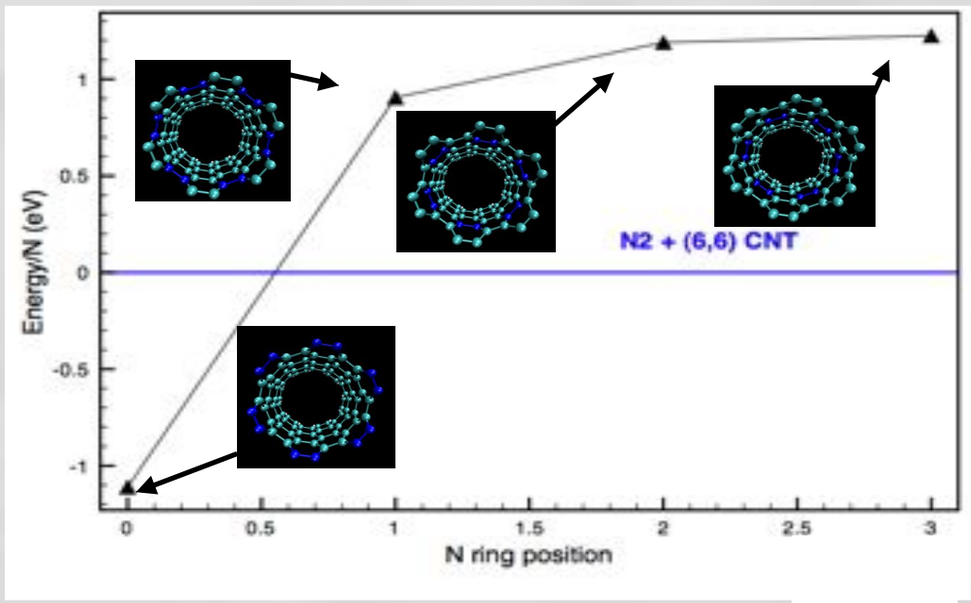


MOLECULE-ENHANCED COUPLING

NITROGEN DOPING: BAMBOOS AND CLOSING

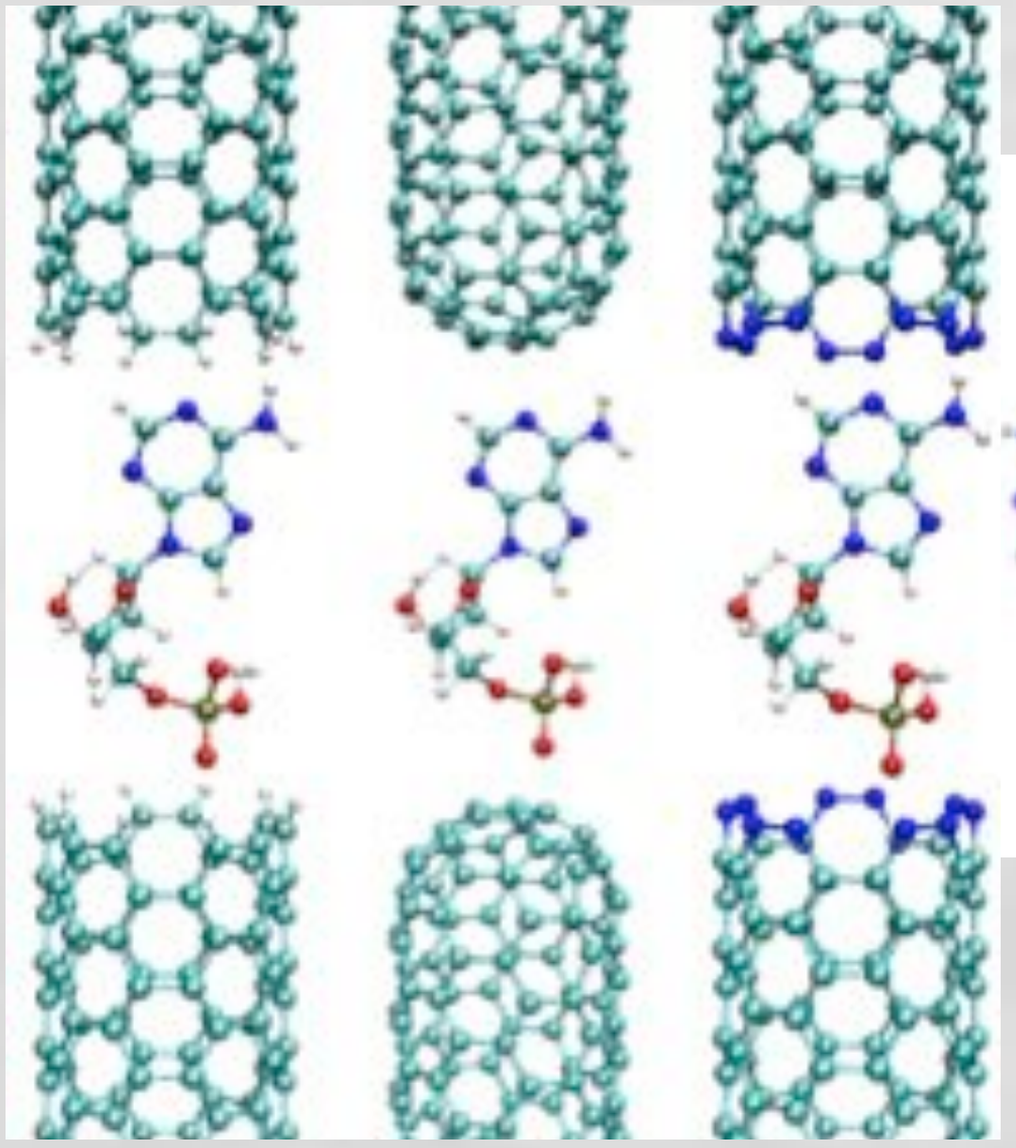


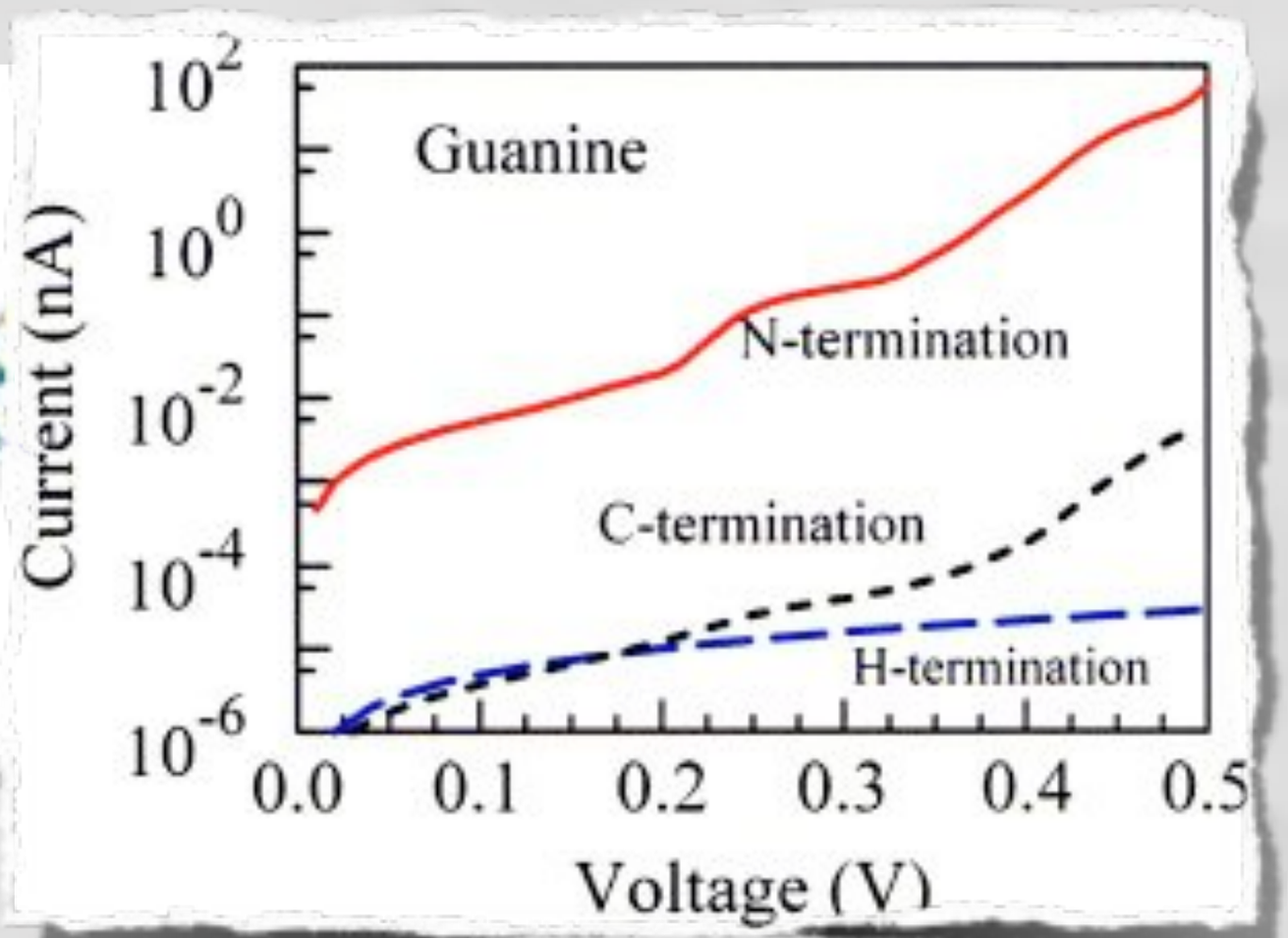




ACS Nano 1, 369 (2007)

N-DOPING INCREASE COUPLONG FOR DNA SEQUENCING





Meunier and Kirstic, JCP08, US Patent

WHAT HAVE WE LEARNED SO FAR?

- We looked into molecule/nanoscale electrode interface
- We found out that the details of M.O. distribution at the interface brings about non-classical effects (e.g. NDR)
- We also shown some strong effects on local electornic properties and modifications of the transmission probability along certain conduction channels.
- The coupling can be enhanced by the presence of molecules at the interface

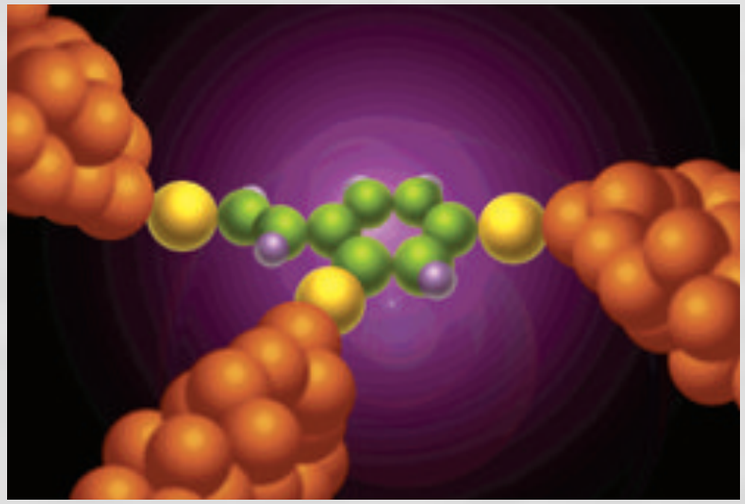
INTERFERENCE EFFECTS

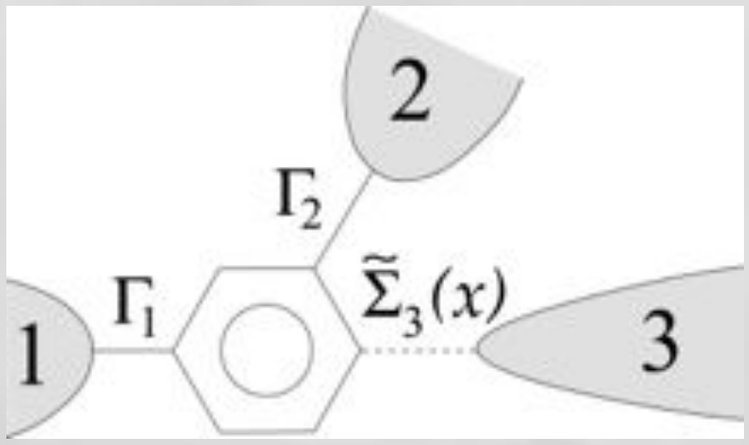
NANO LETTERS

2006
Vol. 6, No. 11
2422−2426

Controlling Quantum Transport through a Single Molecule

David M. Cardamone,* Charles A. Stafford, and Sumit Mazumdar





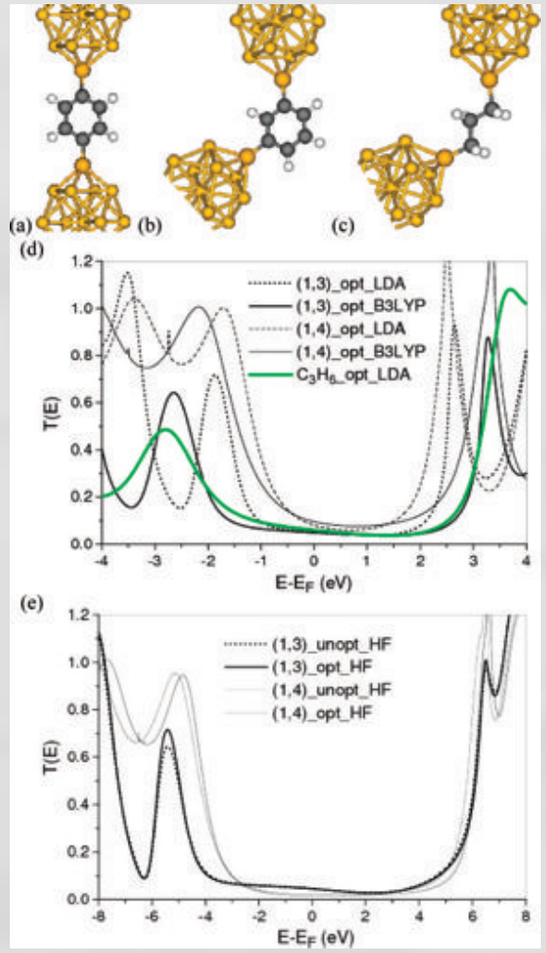
See also: Works presented by this morning's speakers

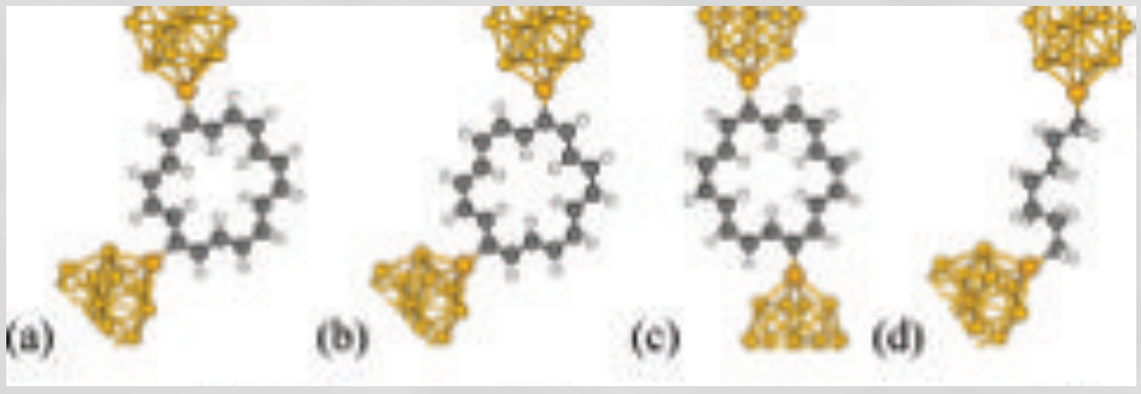
NANO LETTERS

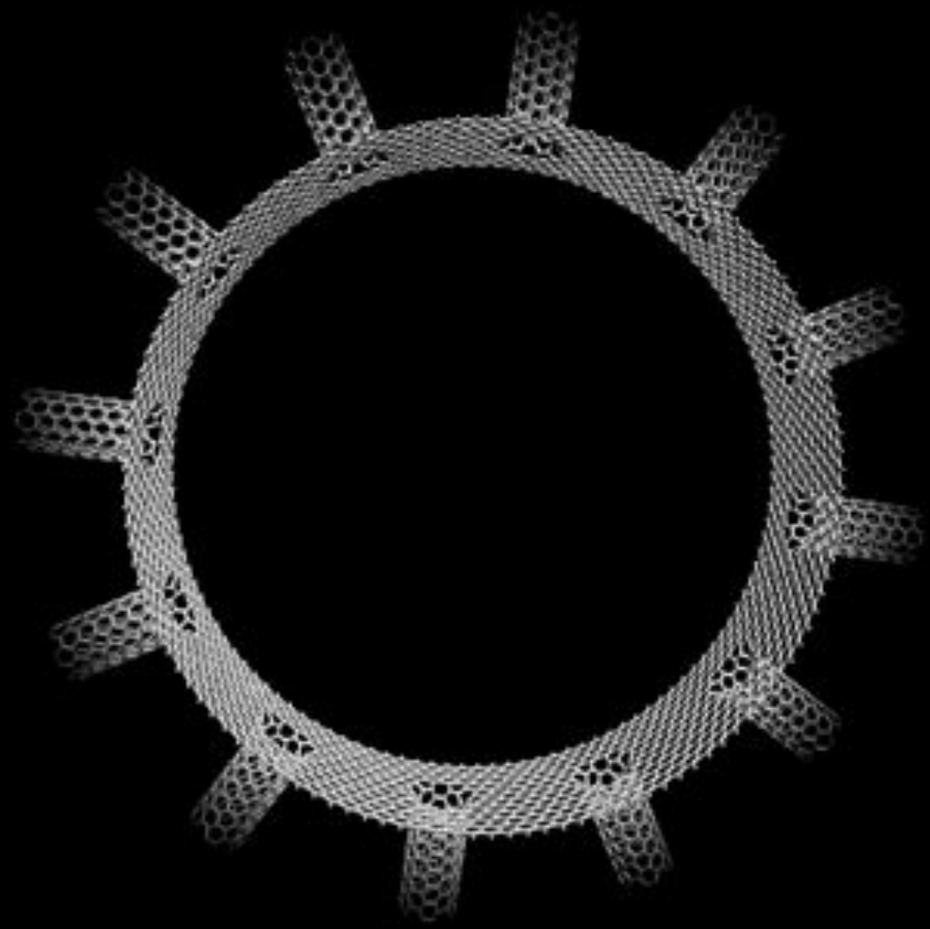
2008
Vol. 8, No. 10
3257-3261

Quantum-Interference-Controlled Molecular Electronics

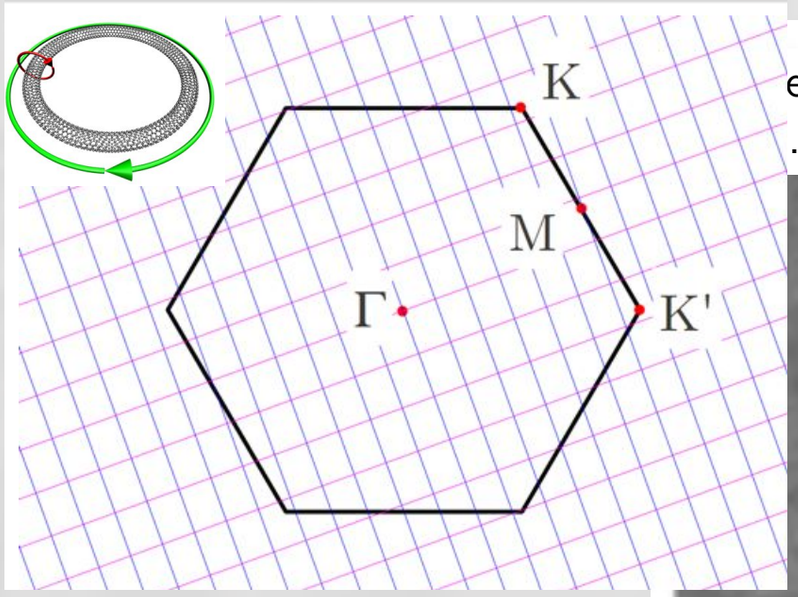
San-Huang Ke* and Weitao Yang



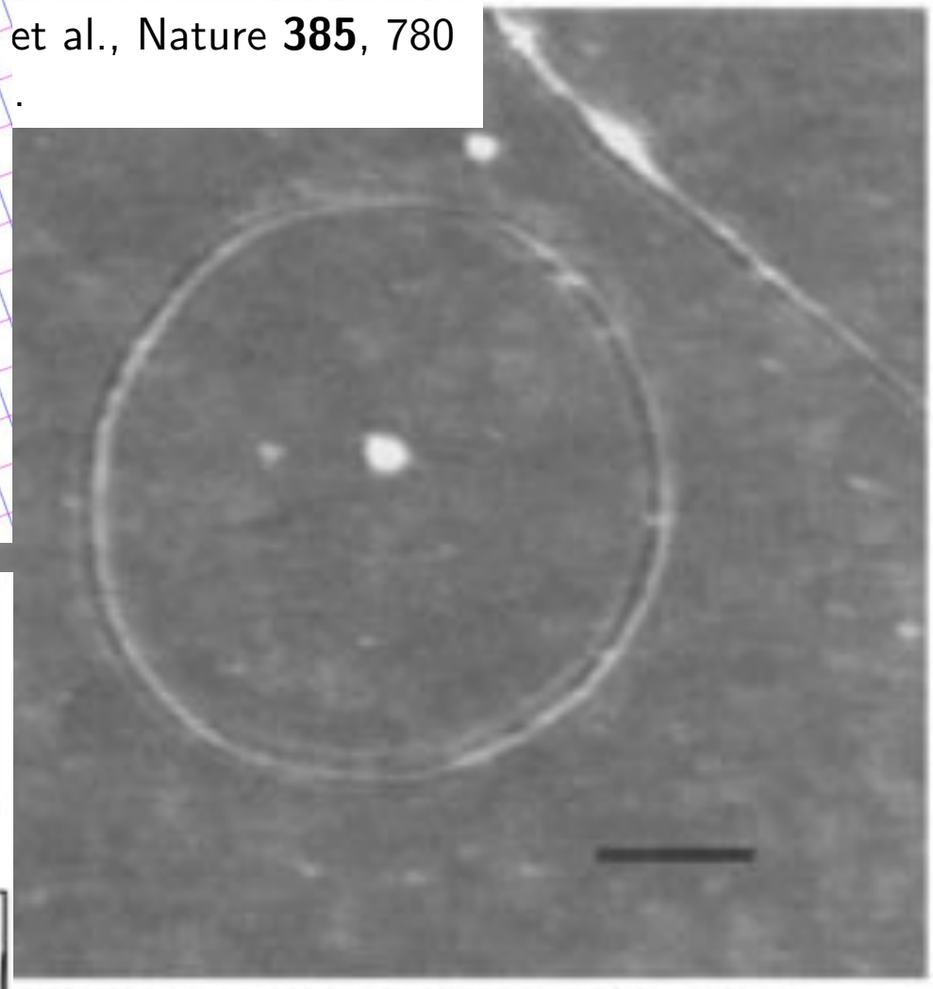


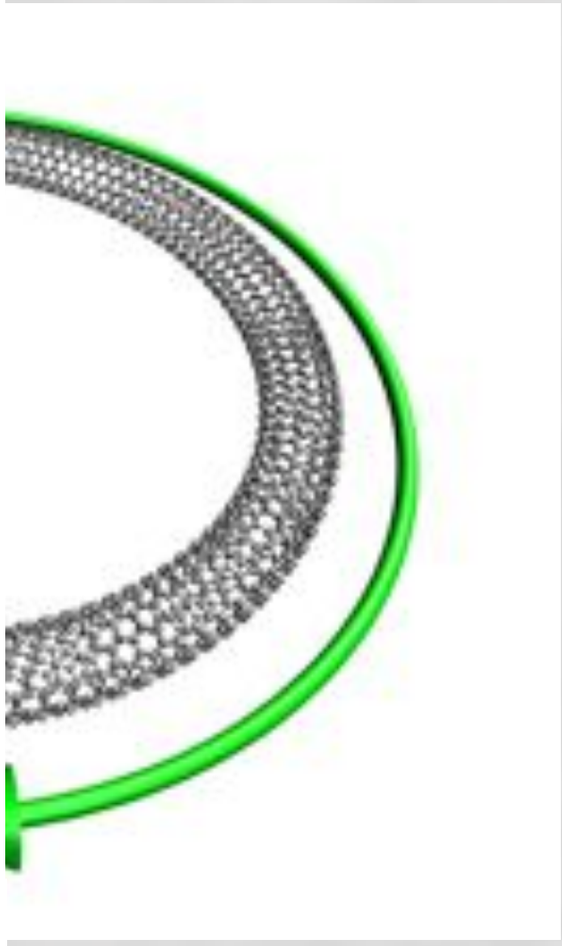


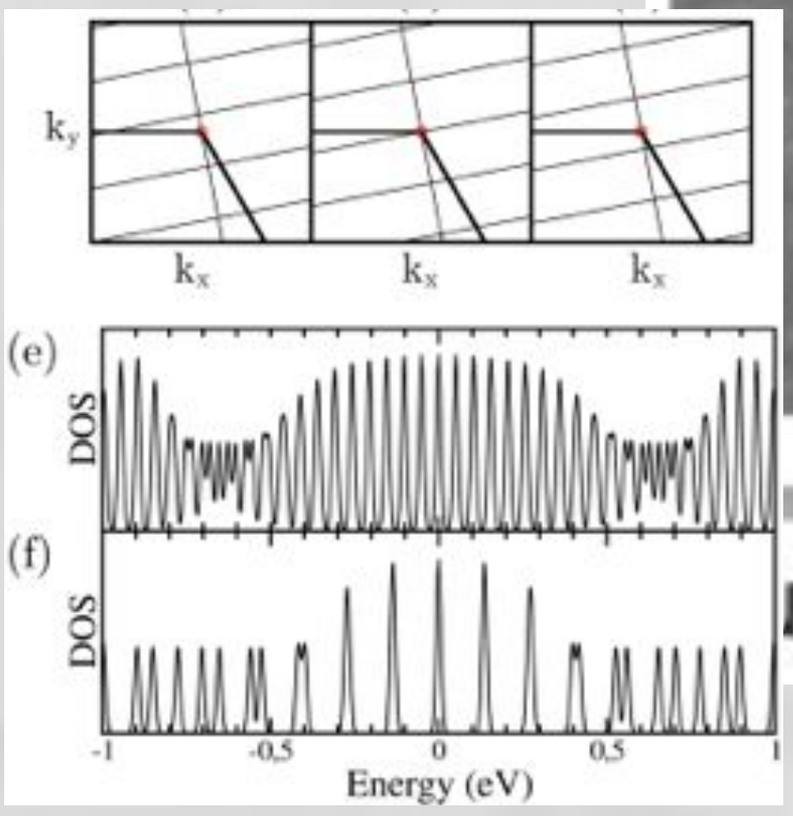
PERFECT INTERFERENCE TESTBED: RINGS



et al., Nature **385**, 780
.

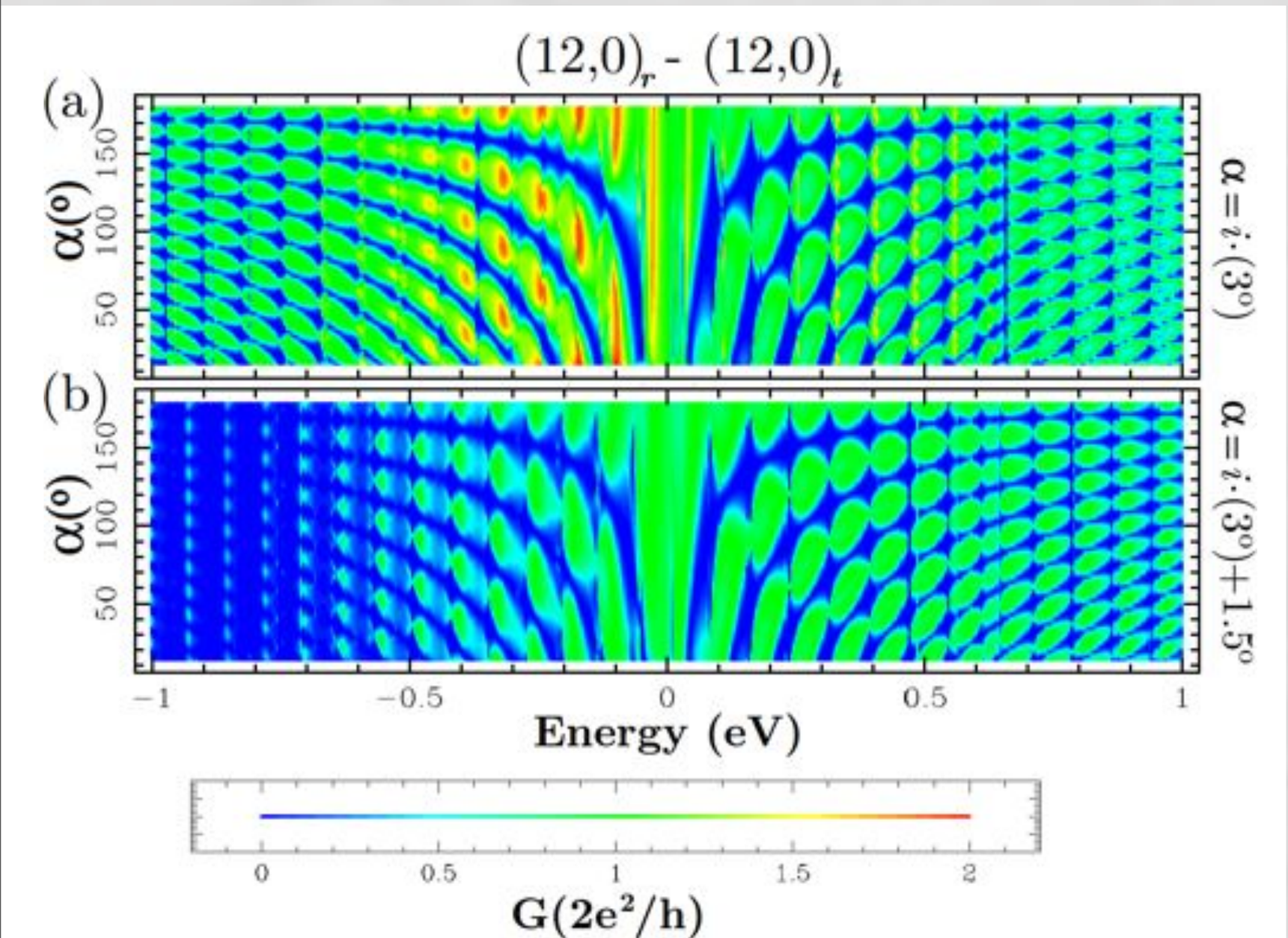


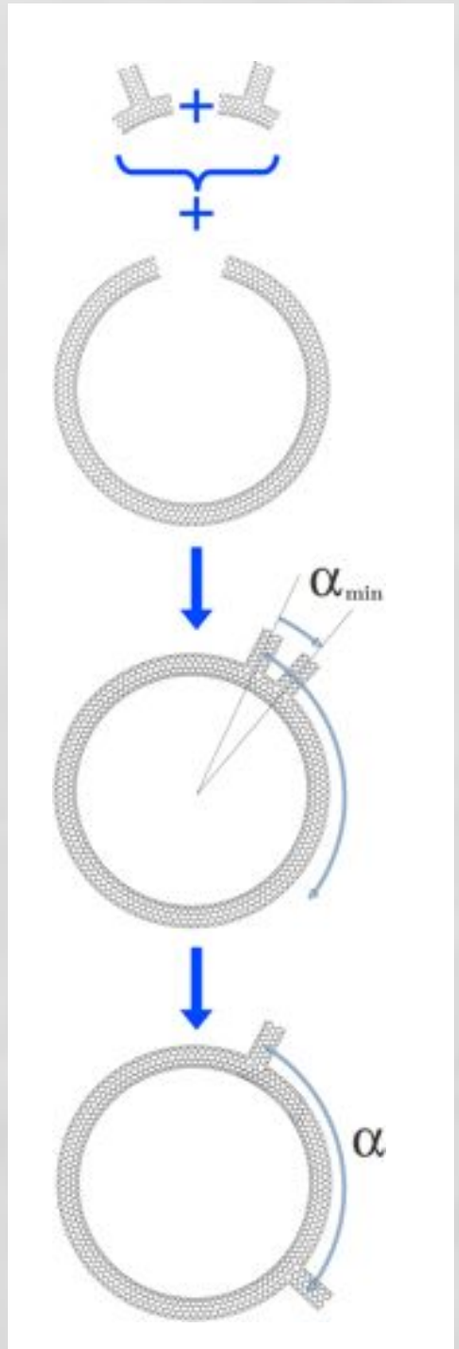




llerene 'crop circles'

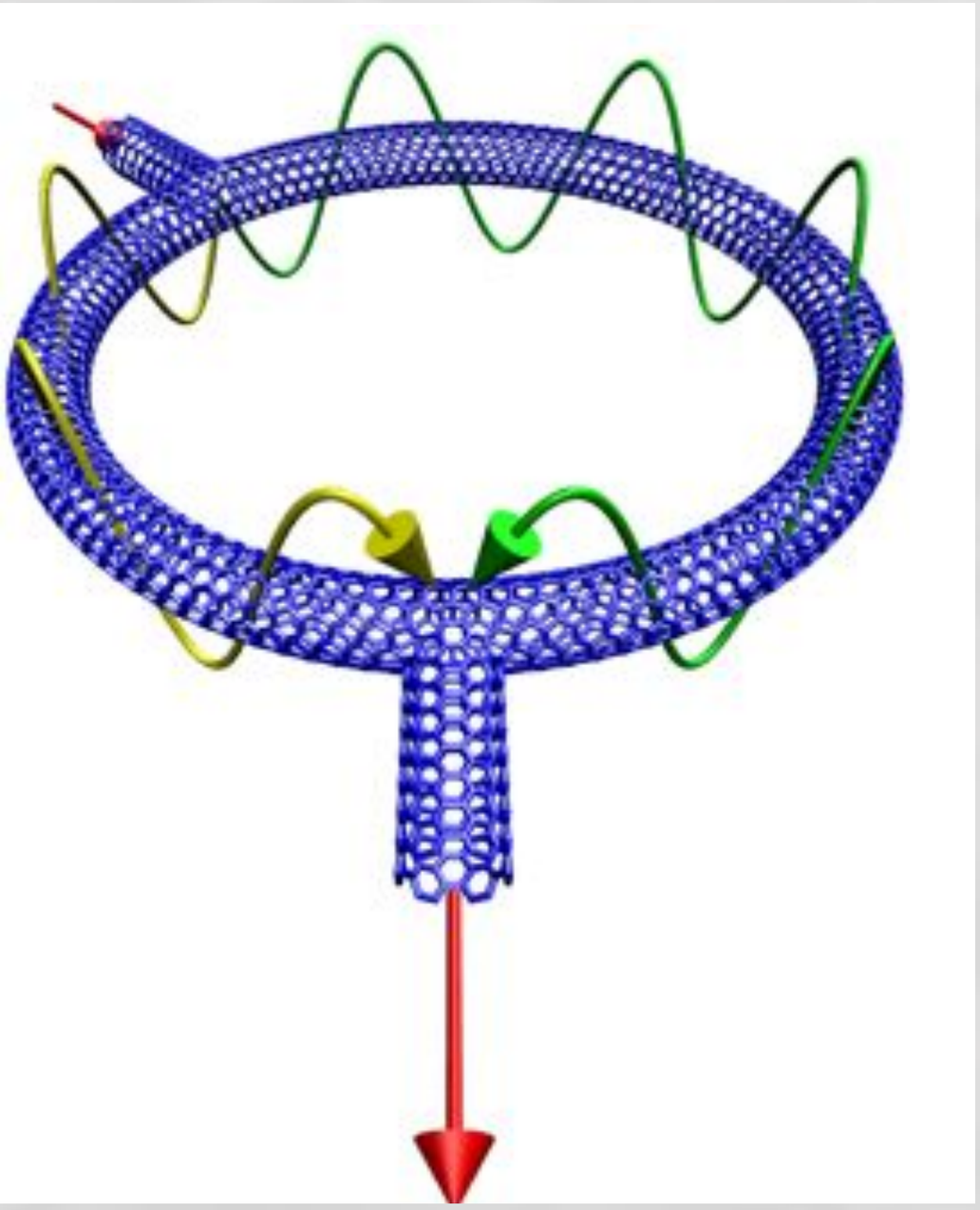
HOW TO PROBE LOCAL PHASE

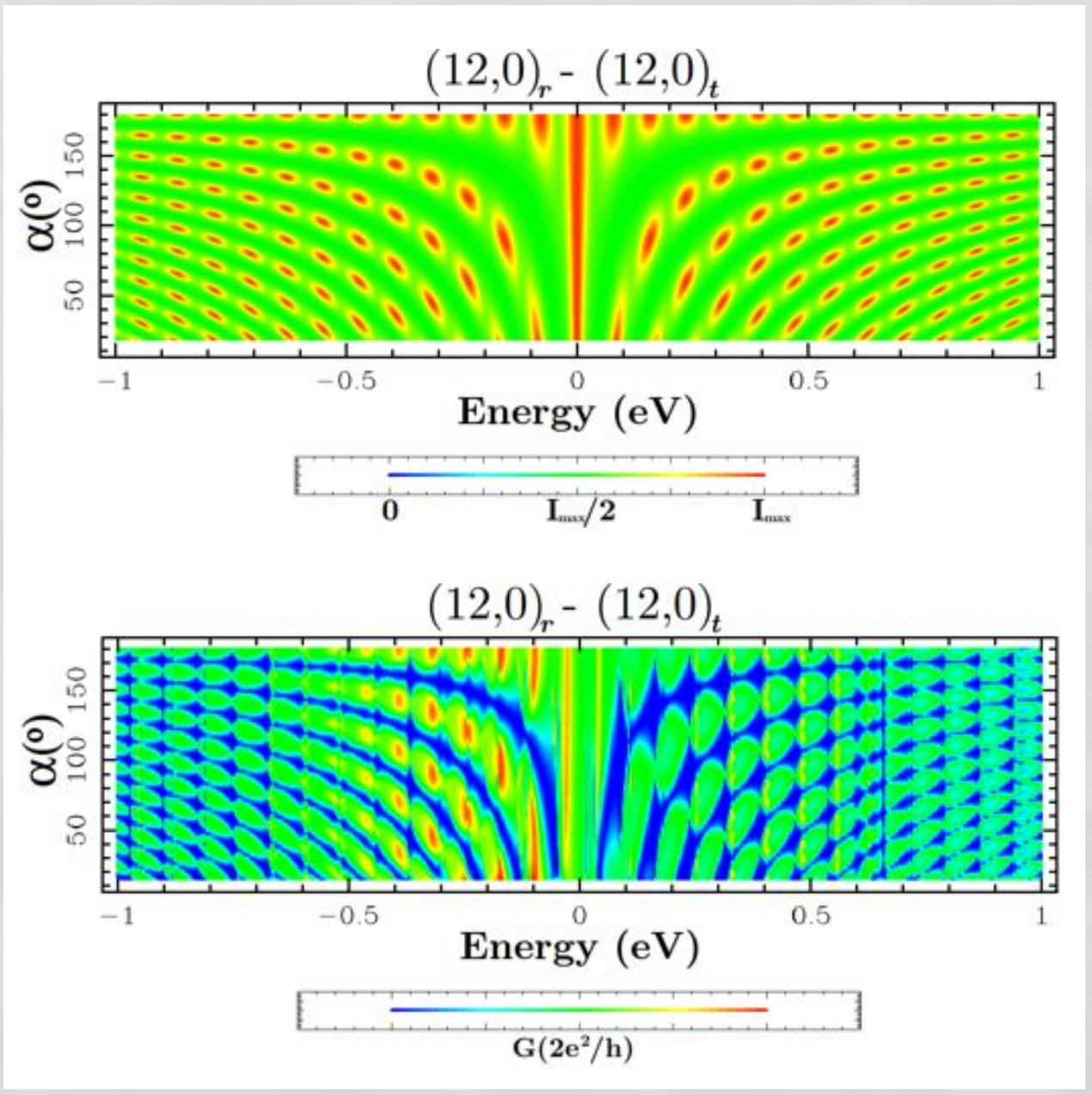




Nanotechnology **22**, 075701 (2011)

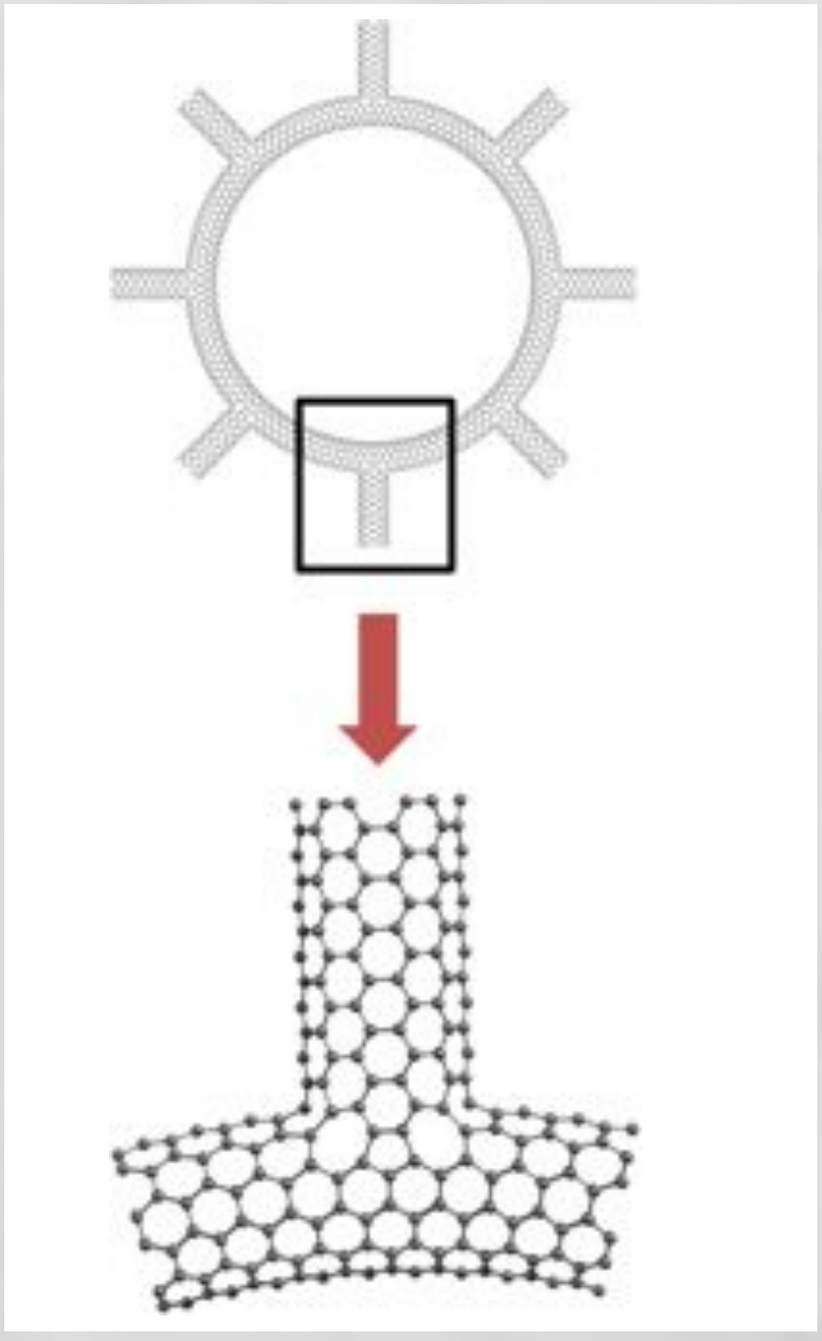
IT IS (ALMOST) ALL ABOUT INTERFERENCE

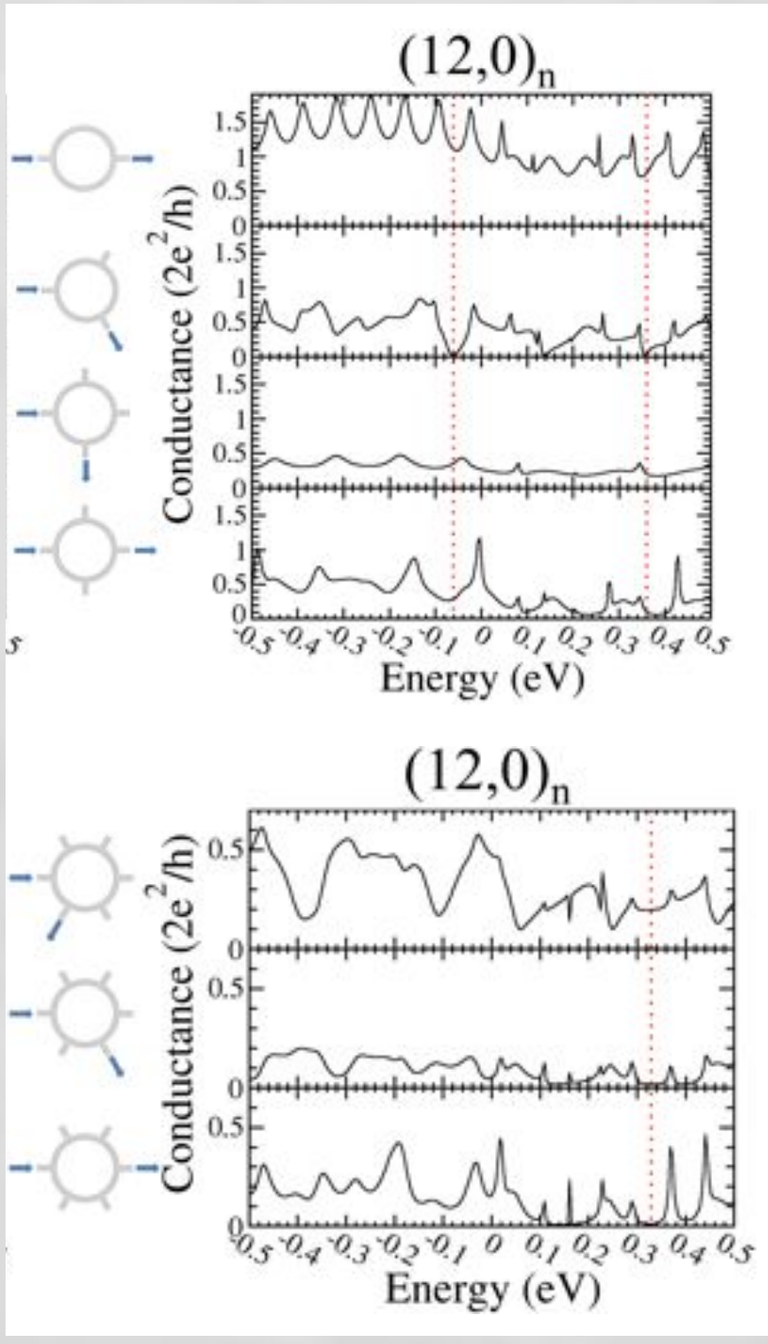




Nanotechnology **22**, 075701 (2011)

PROBING PHASES LOCALLY, ALL AT ONCE



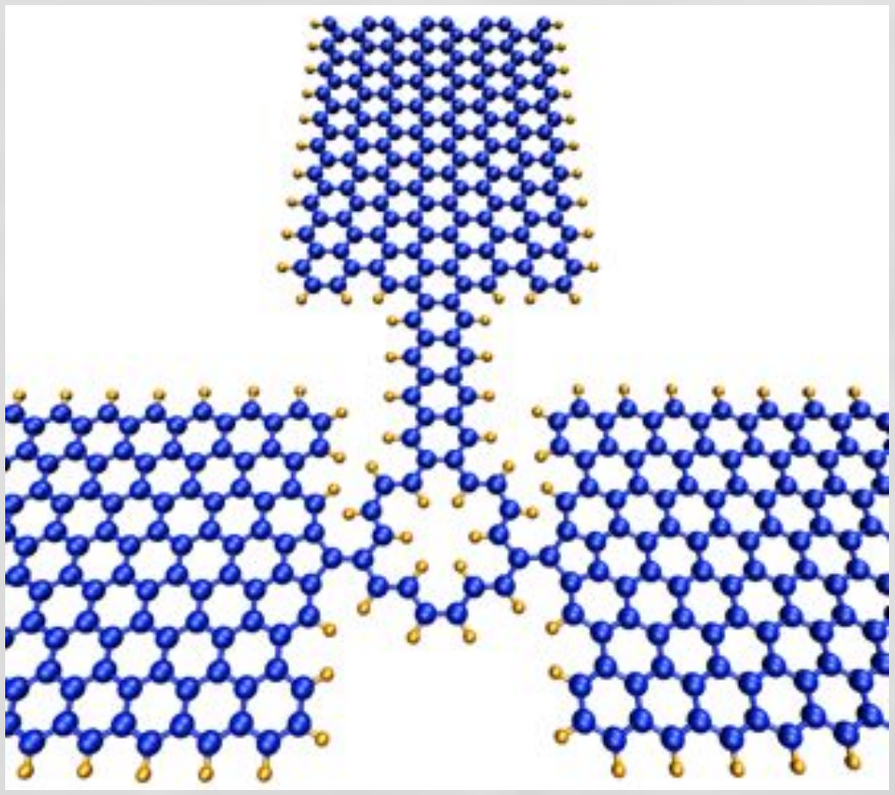


Applied Physics Letters **98**, 6951 (2011).

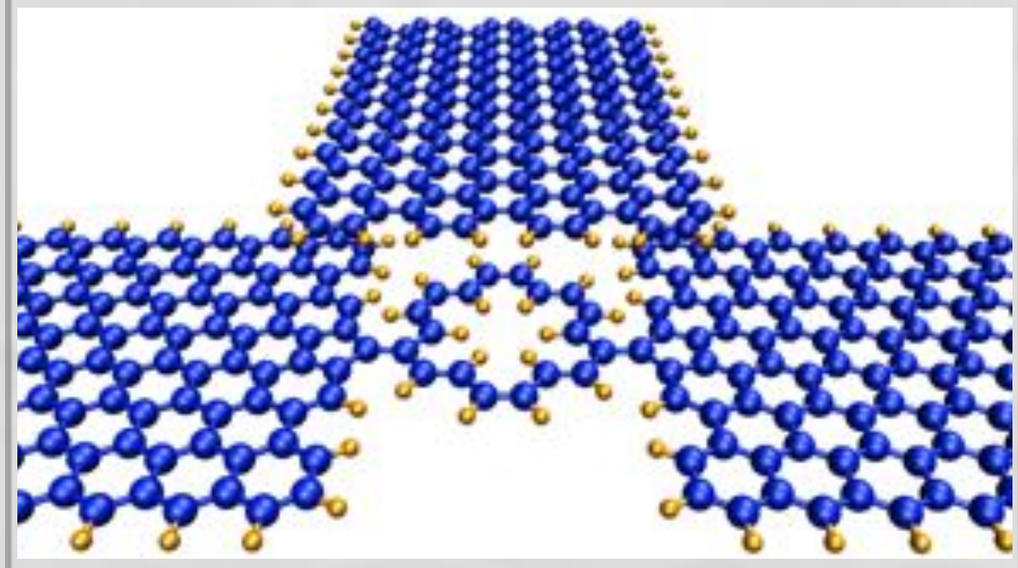
ACTUAL MOLECULAR INTERFOREMETER

CAN WE TUNE THE CURRENT ON IN DESTRUCTIVE SETUP BY SOMEHOW CONTROLLING THE QUANTUM-INTERFERENCE-EFFECT?

Yes, this is possible if we can change the electron path, thereby modifying the phases of their paths, by connecting a third electrode to the system and applying bias-voltage through it as well.



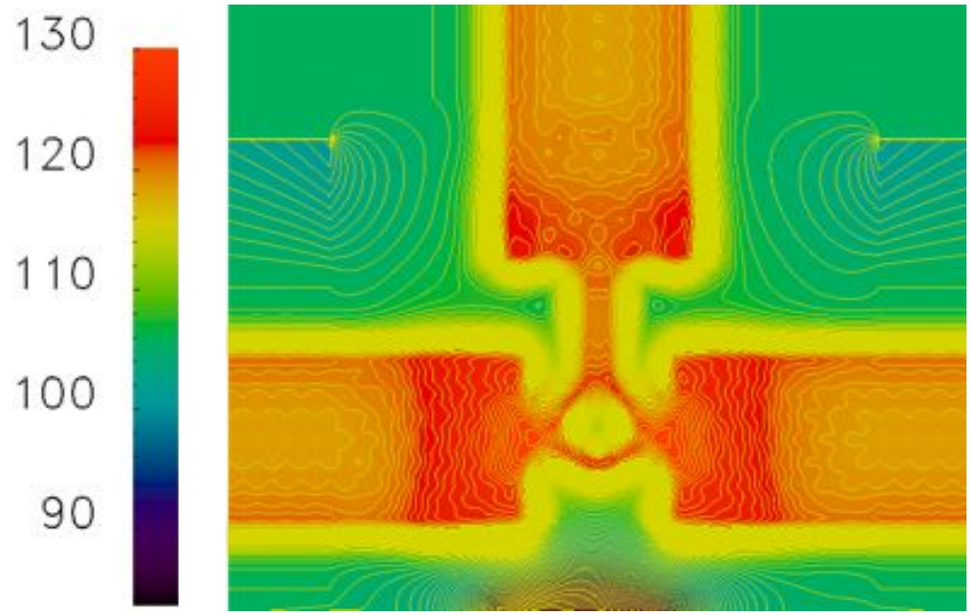
Attached third electrode

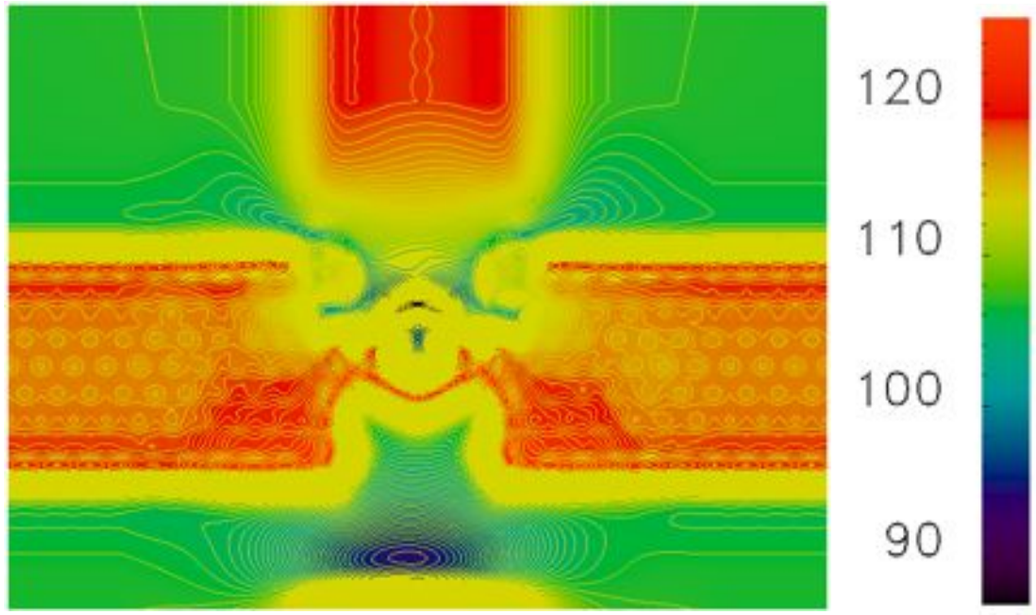


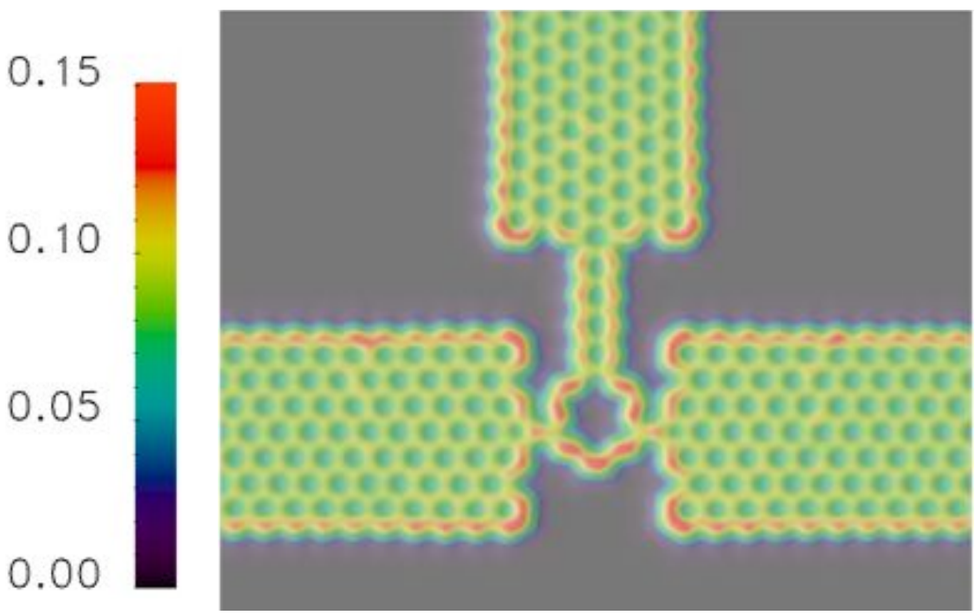
'Air gap' third gate electrode

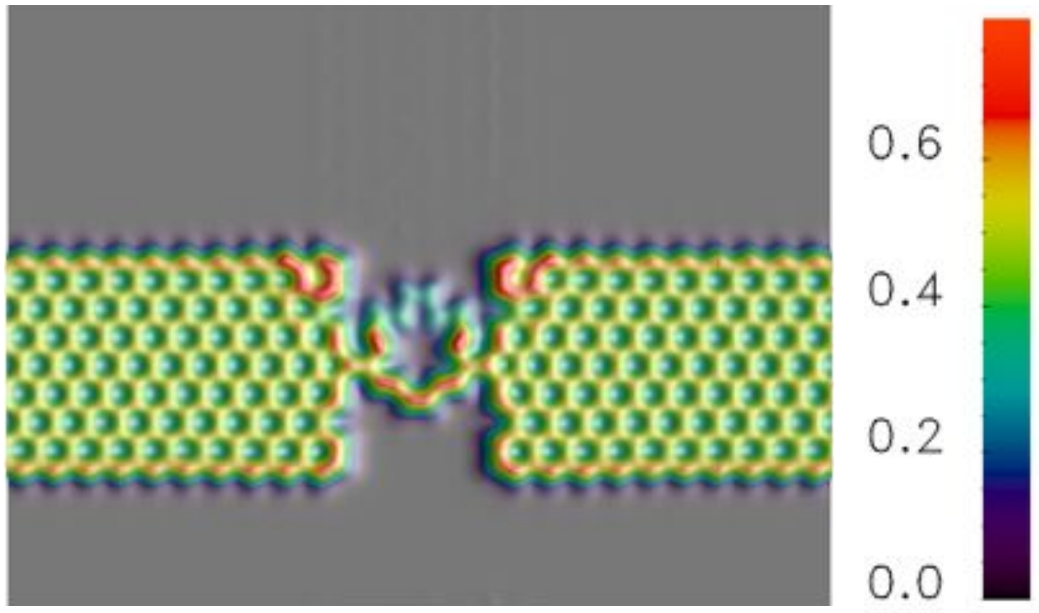
Phys. Rev. Lett. **105**, 236803 (2010)

HARTREE POTENTIAL AND CHARGE DENSITY IN EQUILIRBIUM



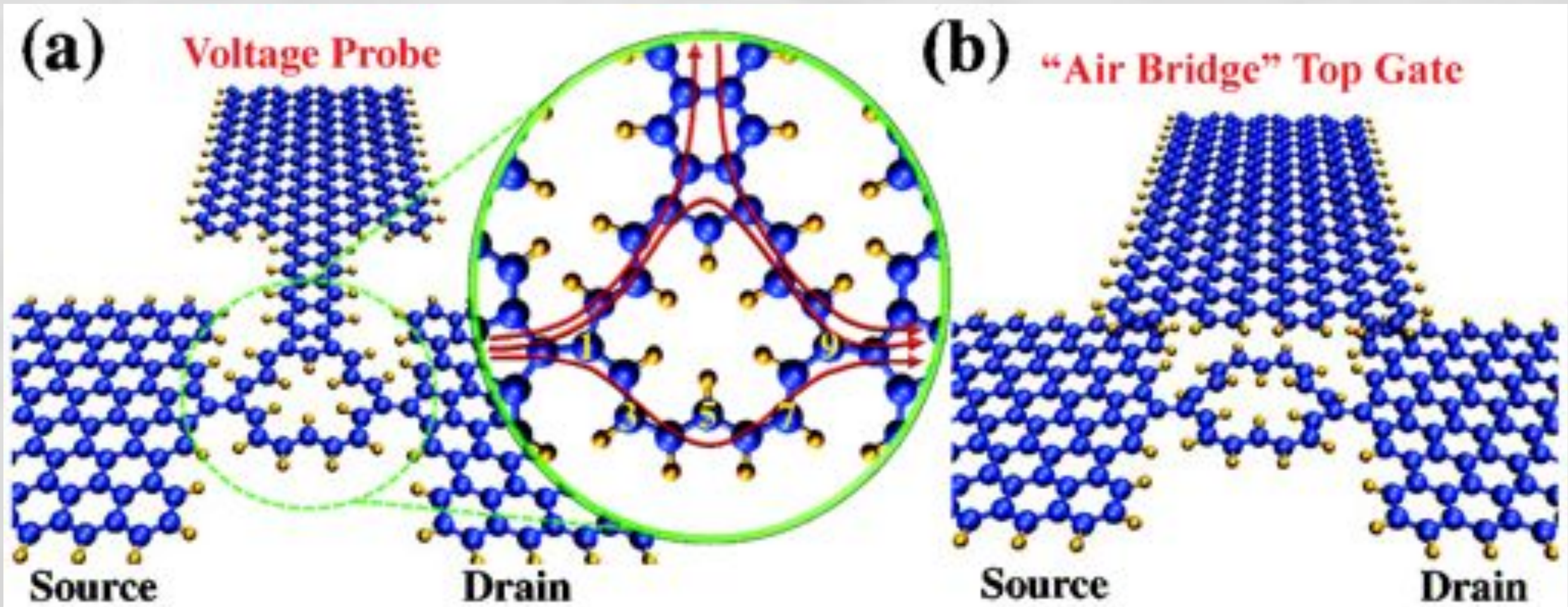






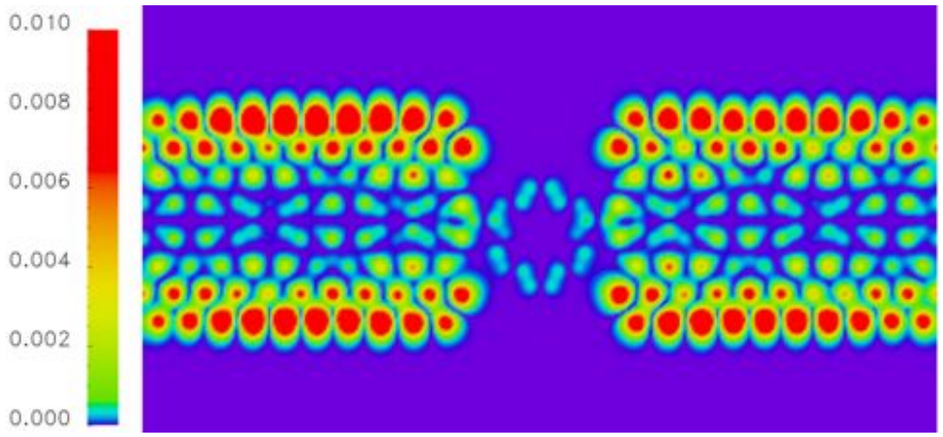
Phys. Rev. B, 81, 125420 (2010); .J. Chem. Phys, 131, 164105 (2009)

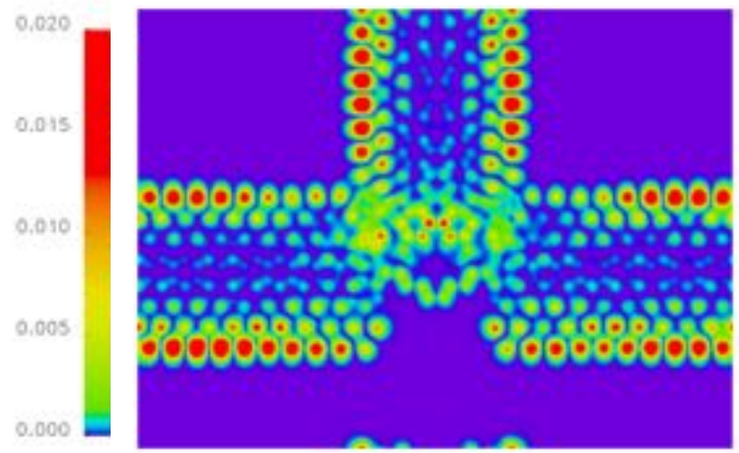
QUANTUM-INTERFERENCE-CONTROLLED MOLECULAR TRANSISTORS



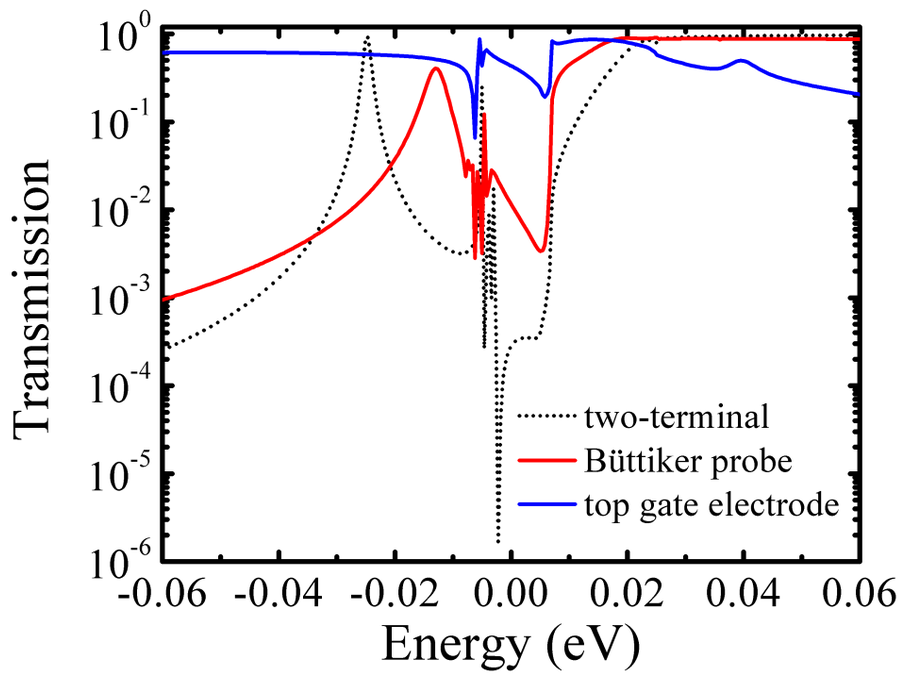
Phys. Rev. Lett., 105, 256803 (2010)

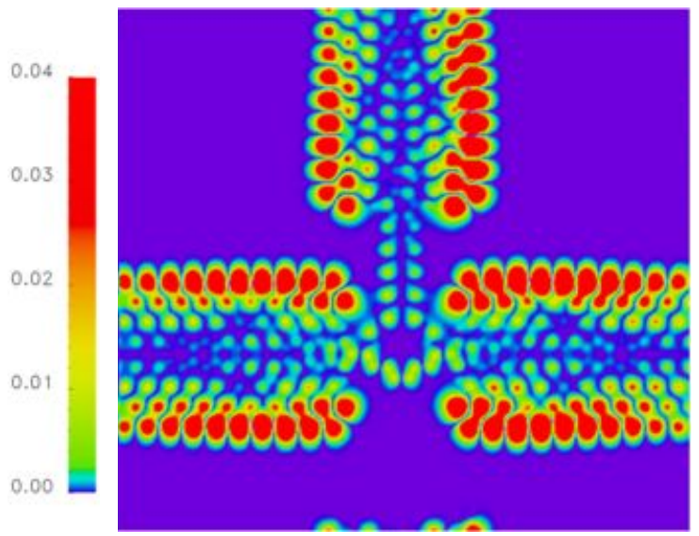
RIBBON AND ORGANIC RING STATES CAN BE EFFECTIVELY COUPLED TO YIELD TRANSISTOR OPERATIONS





Large ON/OFF ratio is mediated by the top gate

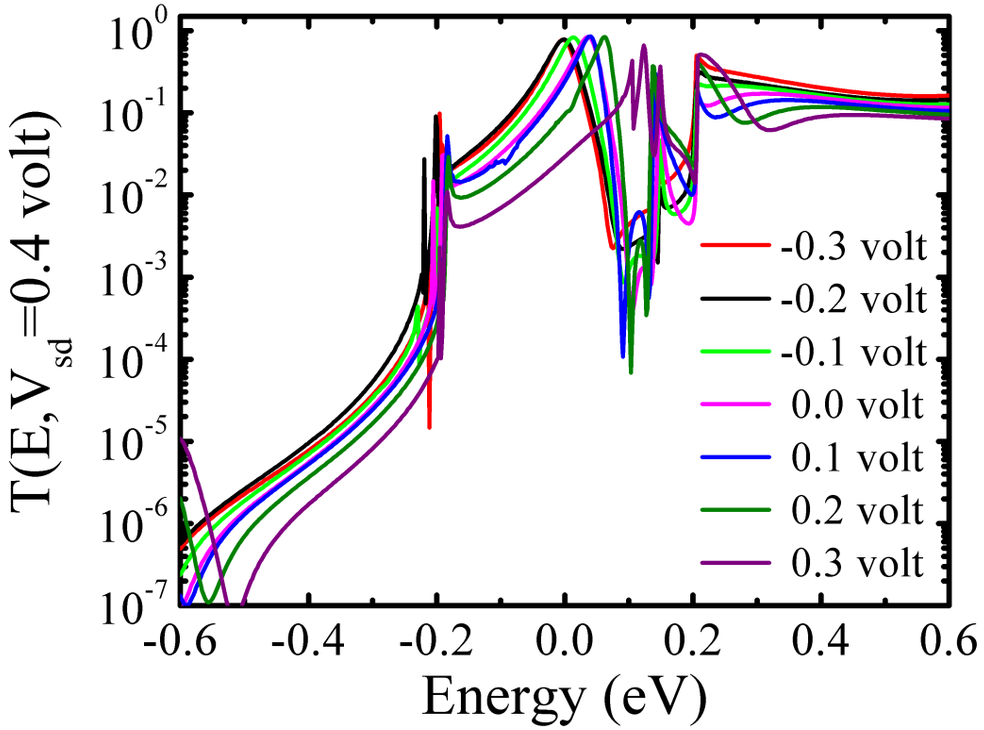


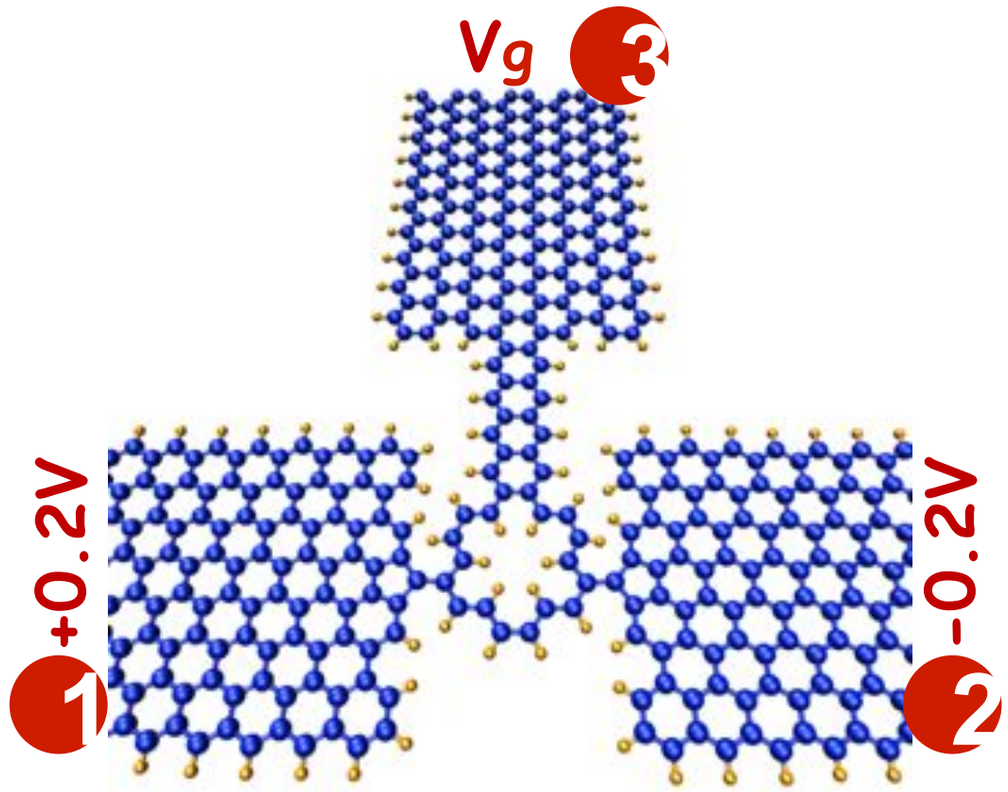


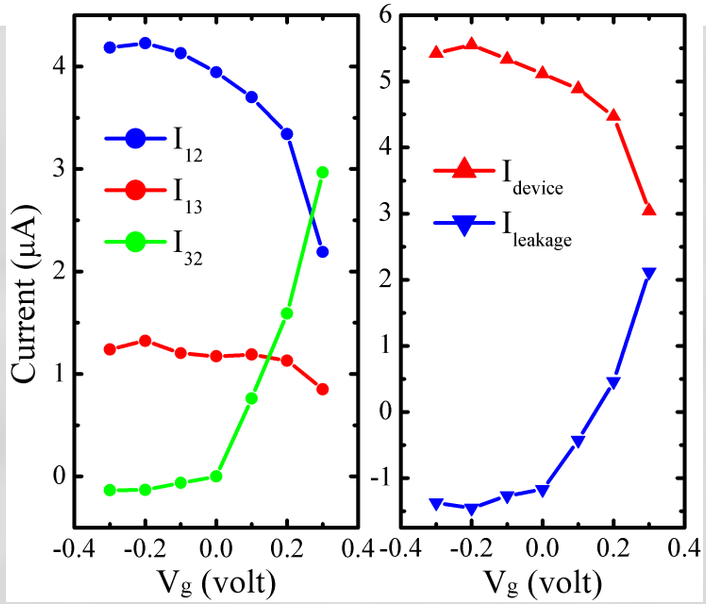
Phys. Rev. Lett., 105, 256803 (2010)

$$\tilde{T}_{21}(E) = T_{\text{coherent}}(E) + T_{\text{incoherent}}(E) = T_{21}(E) + \frac{T_{23}(E)T_{31}(E)}{T_{31}(E) + T_{23}(E)}$$

THE "OFF" TO "ON" CURRENT I MODULATED THROUGH DEPHASING ELECTRON PATHS WITH THE INFLUENCE OF THIRD ELECTRODE

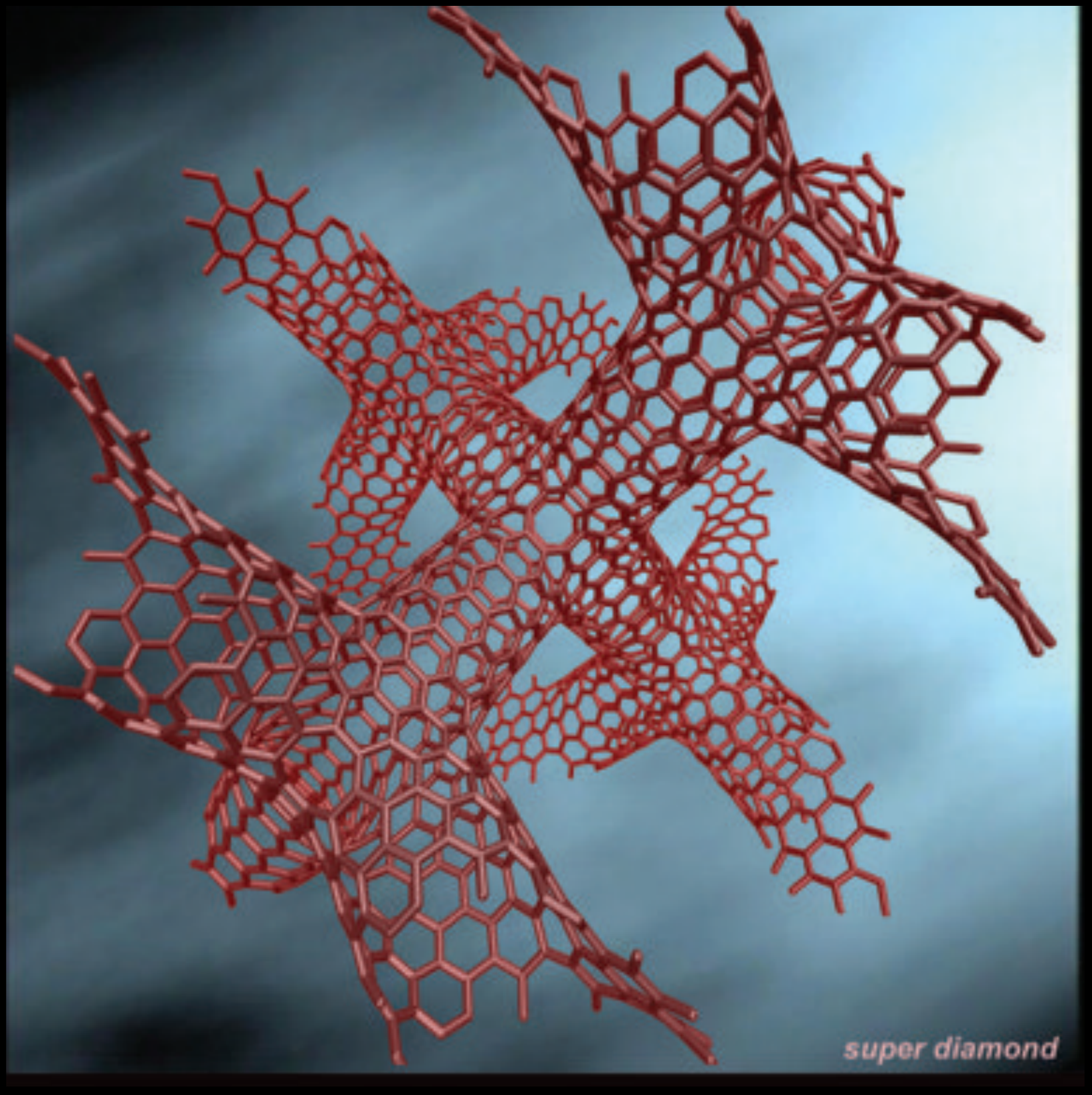






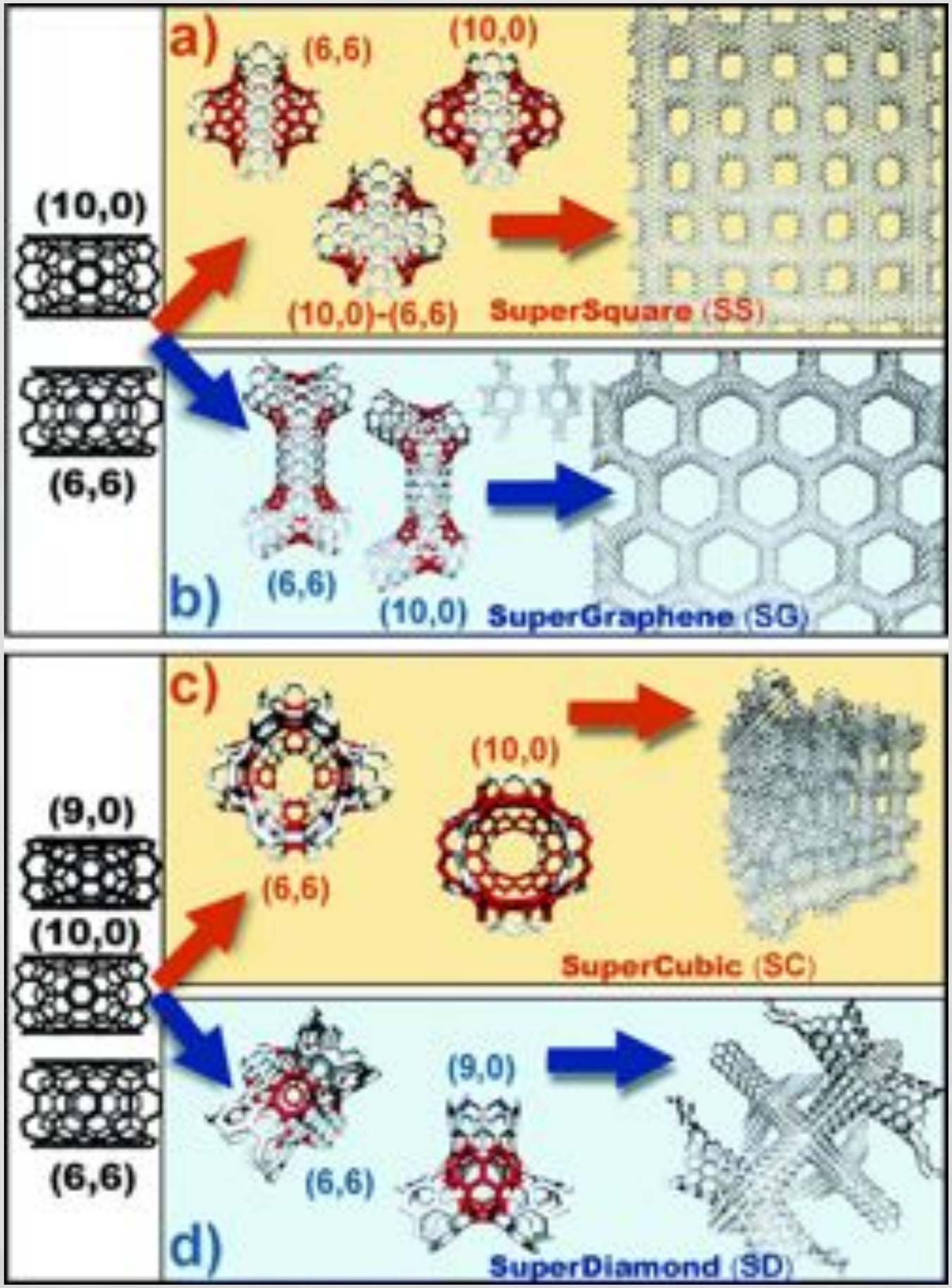
Phys. Rev. Lett., 105, 256803 (2010)

HOW CAN WE BUILD IN MORE INTERFERENCE?



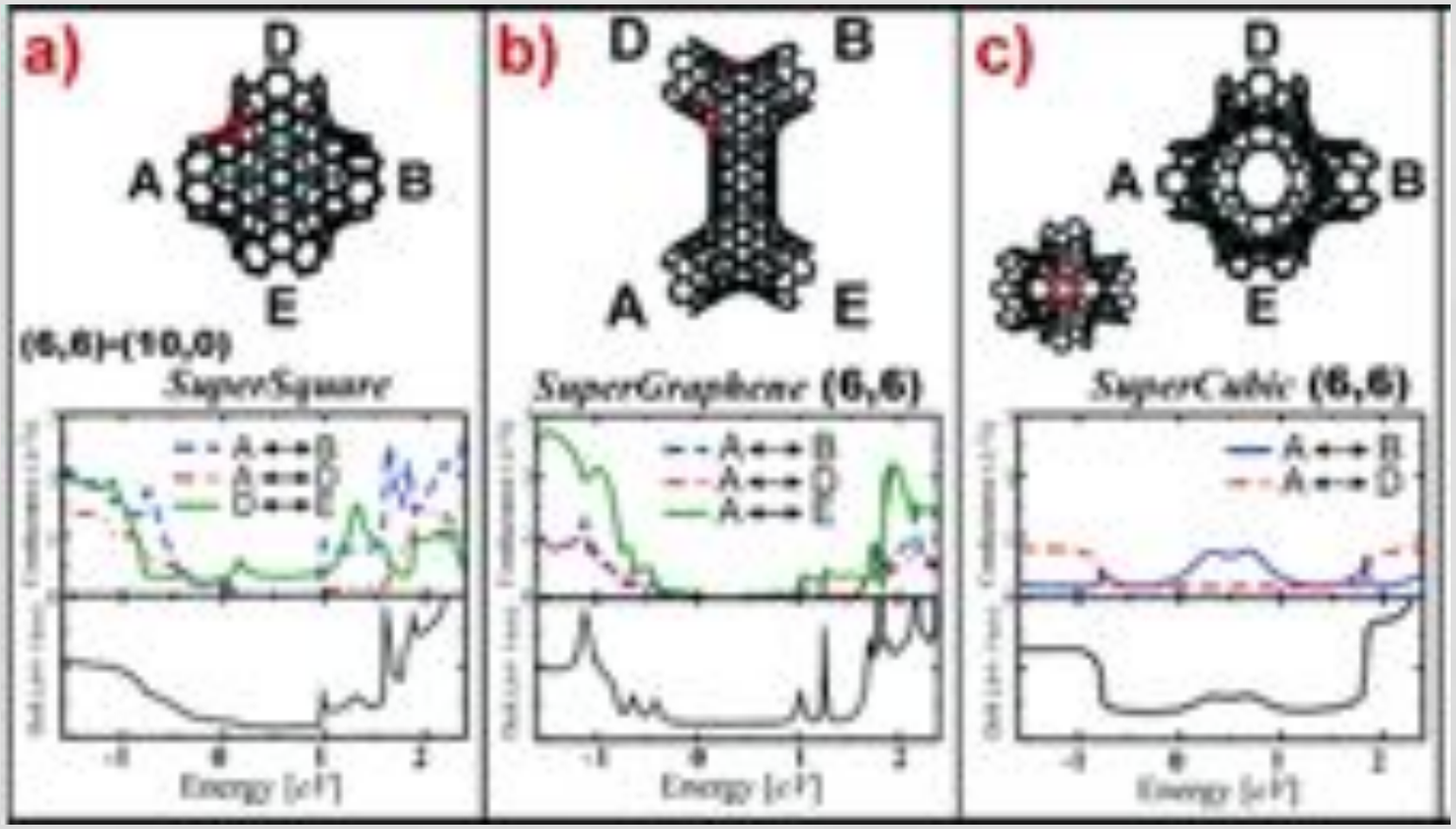
Complex NanoAssemblies; J. Romo-Herrera, V. Meunier & al., Nano Lett. 7, 570 (2007)

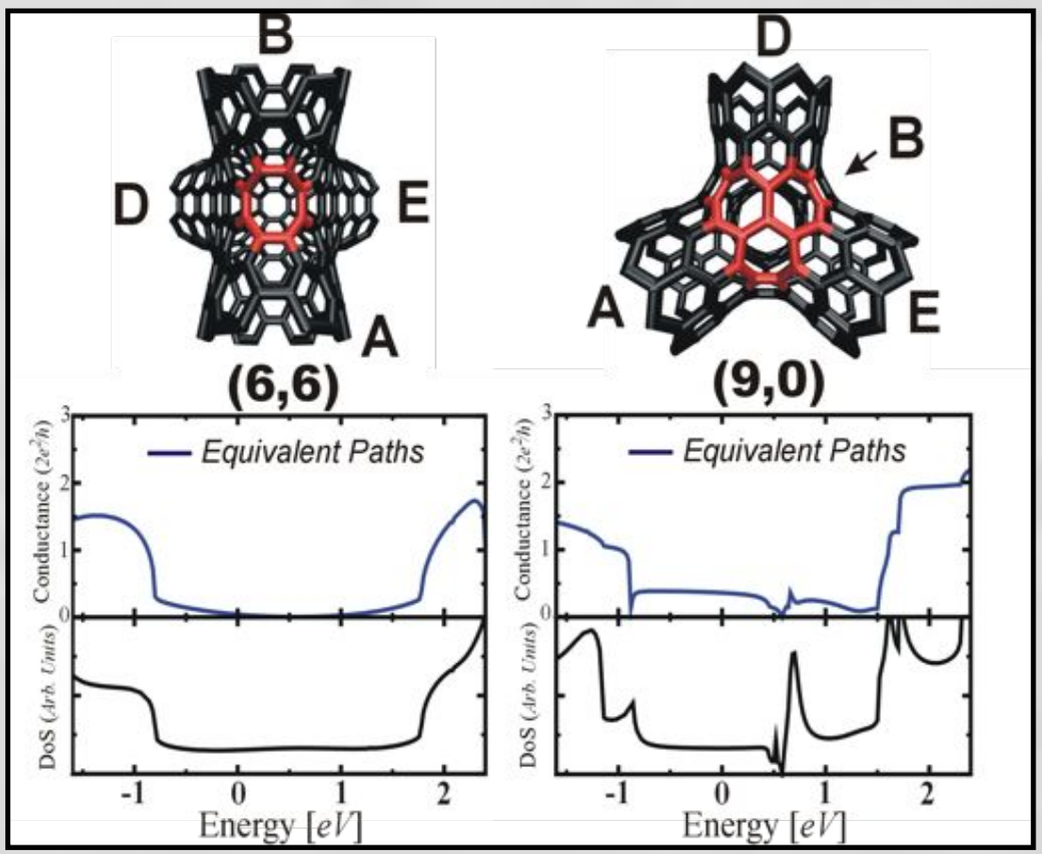
SUPERNETWORKS: POINT AND GROUP SYMMETRIES



Nano Lett. 7, 570 (2007)
Nanotechnology, 19, 315704 (2008)

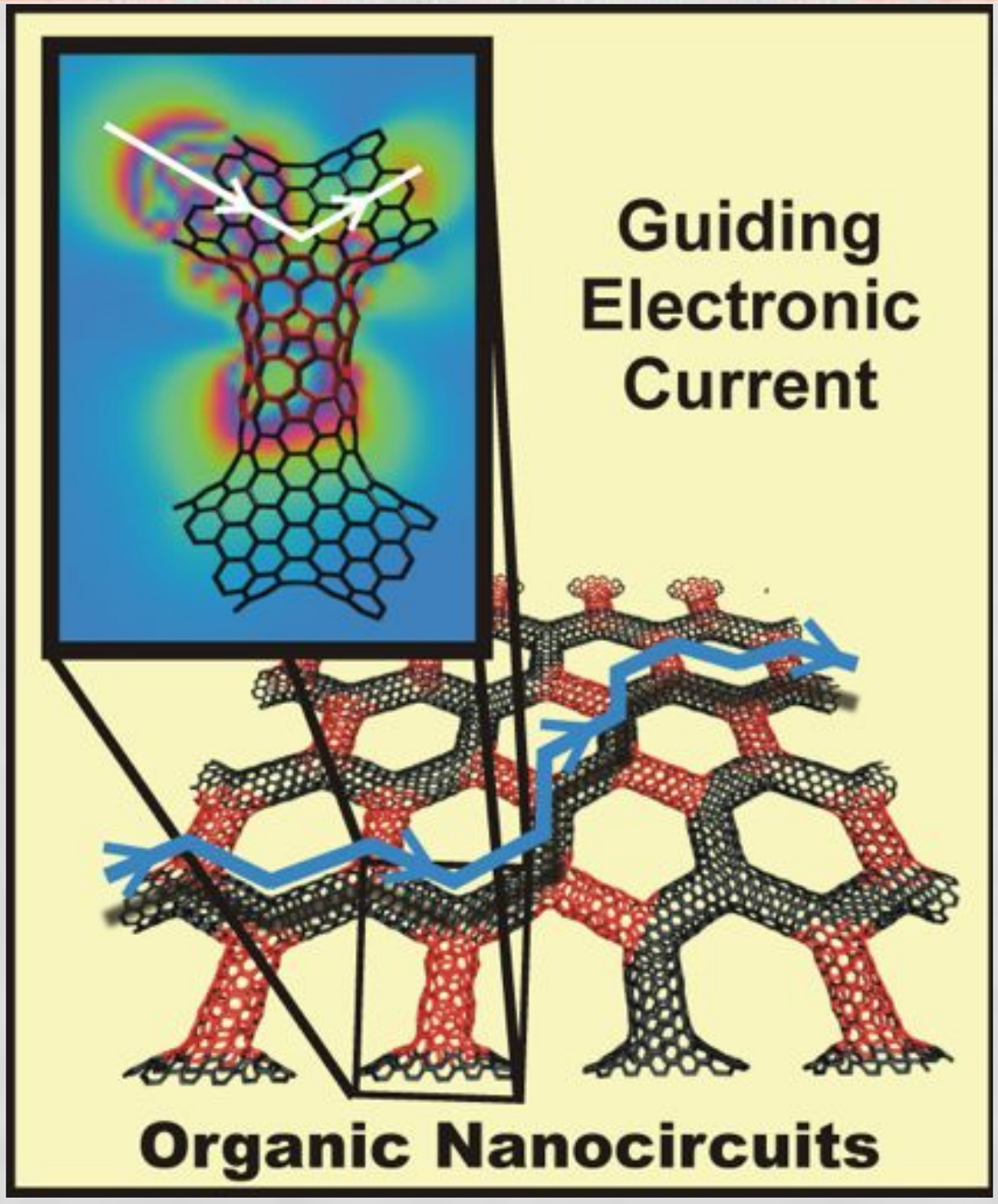
WHAT'S A GOOD CONDUCTOR ANYWAY?



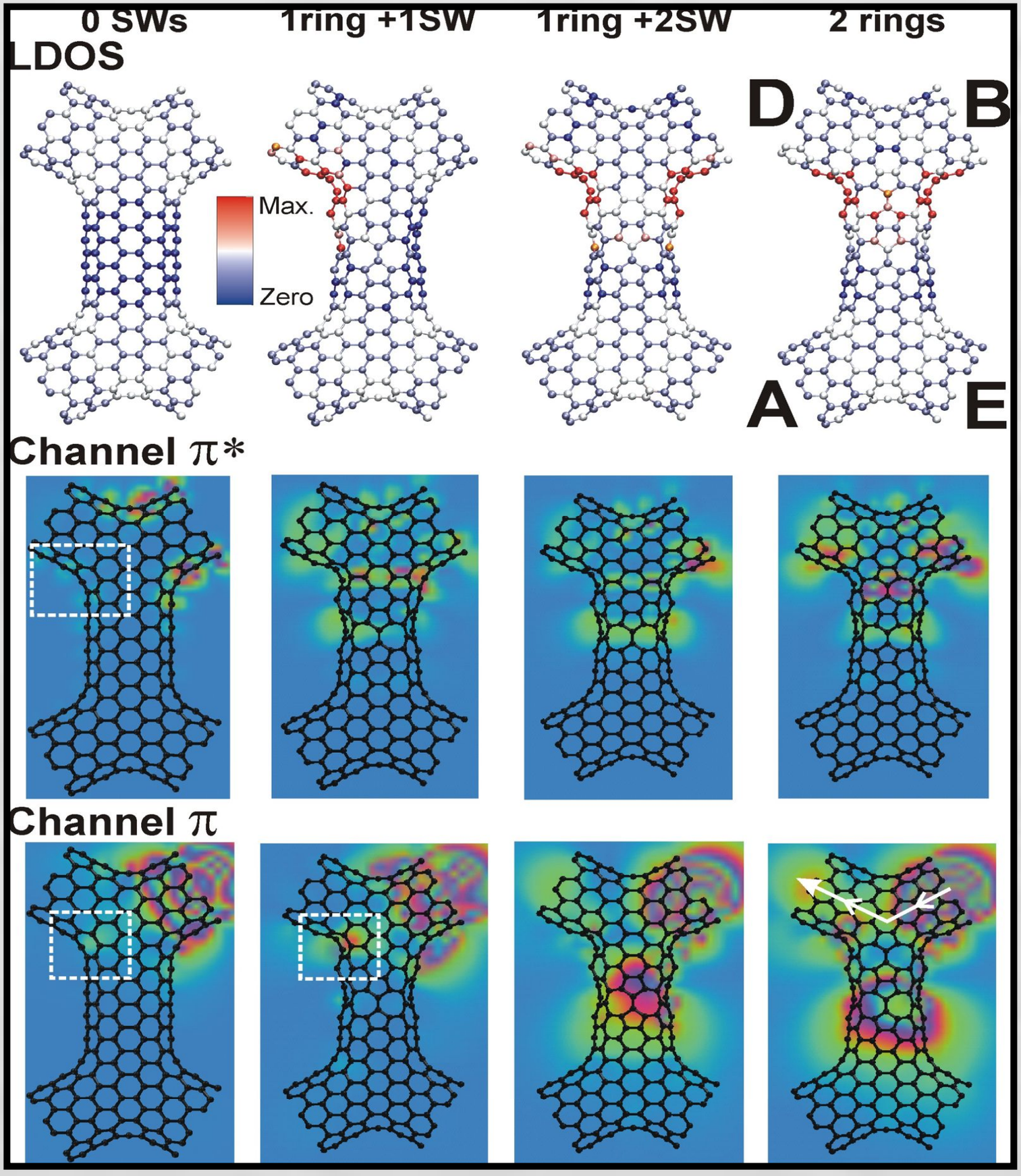


Nano Lett. 7, 570 (2007)
Nanotechnology, 19, 315704 (2008)

STRUCTURAL DEFECTS TO DIRECT ELECTRONS IN A DETERMINISTIC MANNER

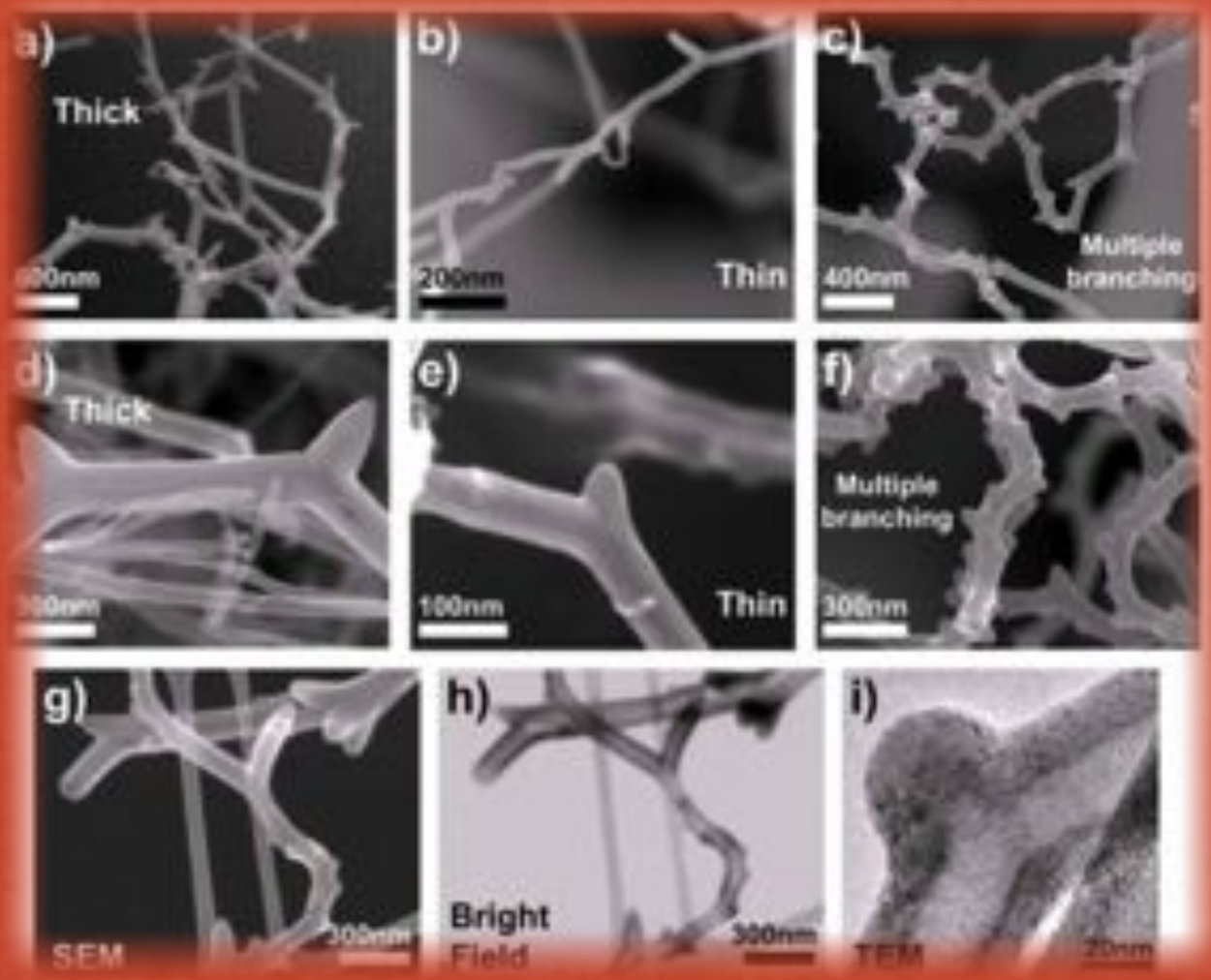


ACS Nano 2, 2585 (2008)



ACS Nano 2, 2585 (2008)

SULFUR DOPING



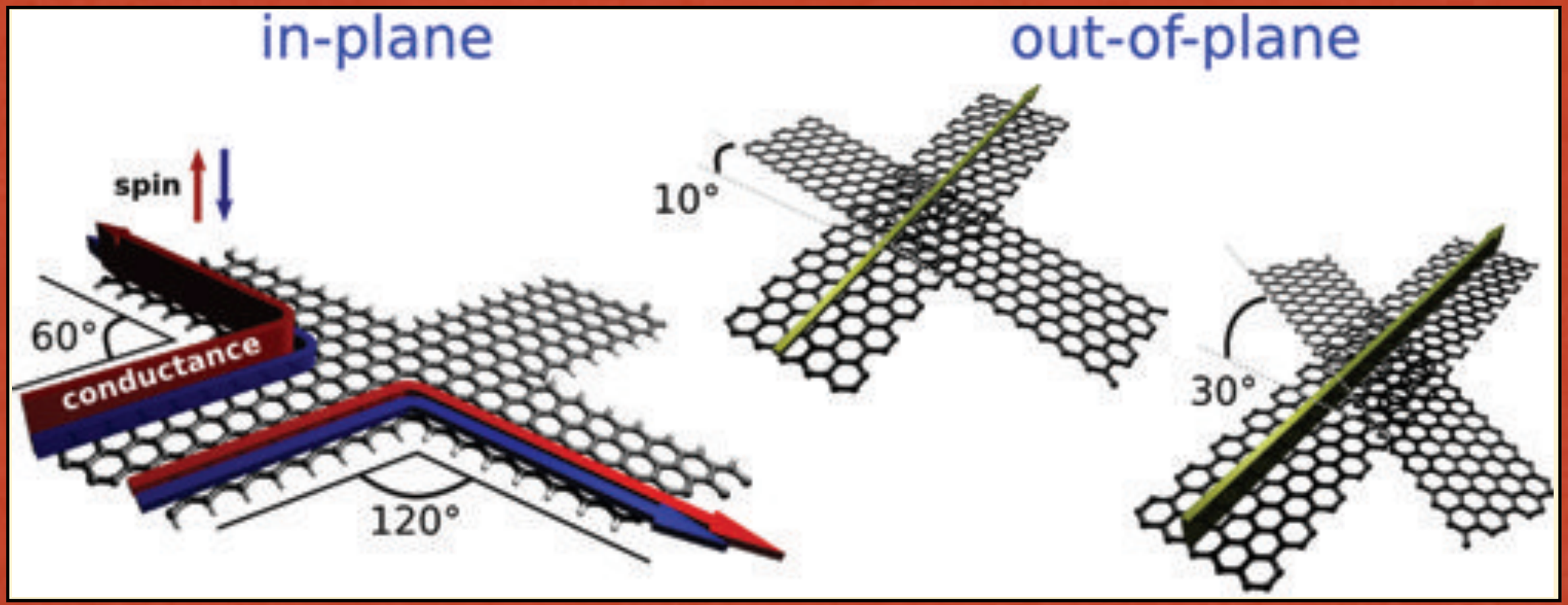
	Sulfur
Pentagon	-0.44 eV
Heptagon	-0.28 eV

Promotes both curvatures

Angewandte Chemie-International Edition 47, 2948 (2008)
Advanced Functional Materials 19, 1193 (2009)

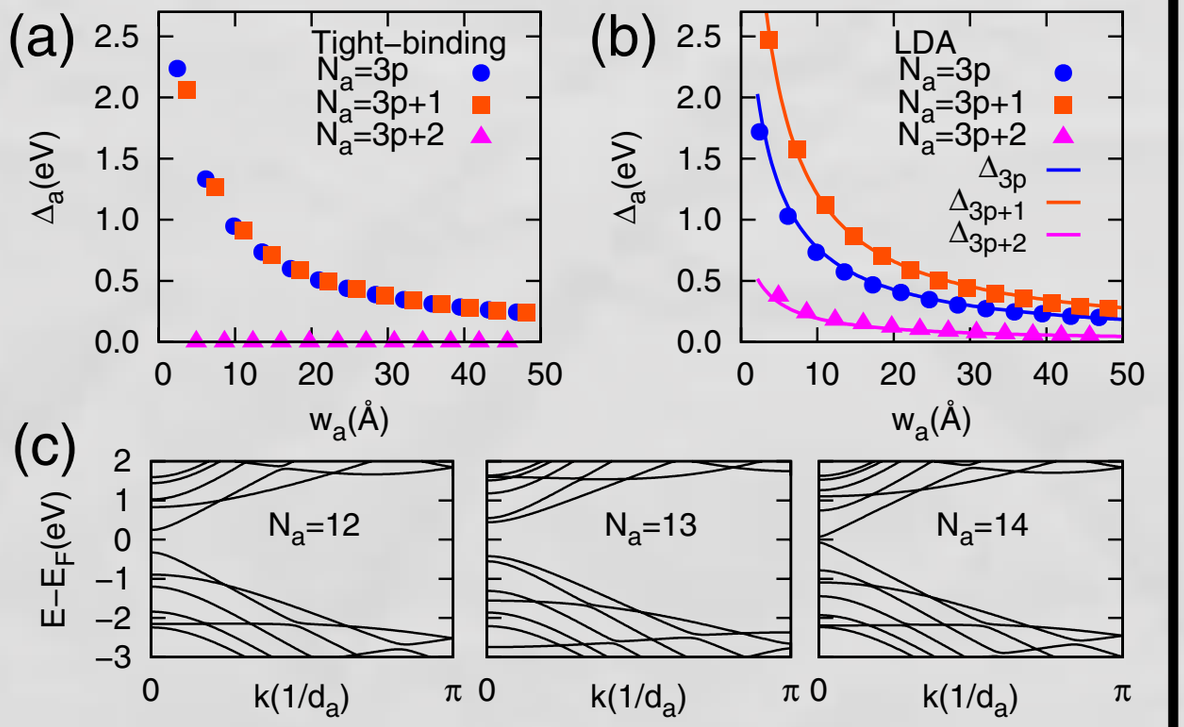
INTERFERENCE IN ASSEMBLED GNRS

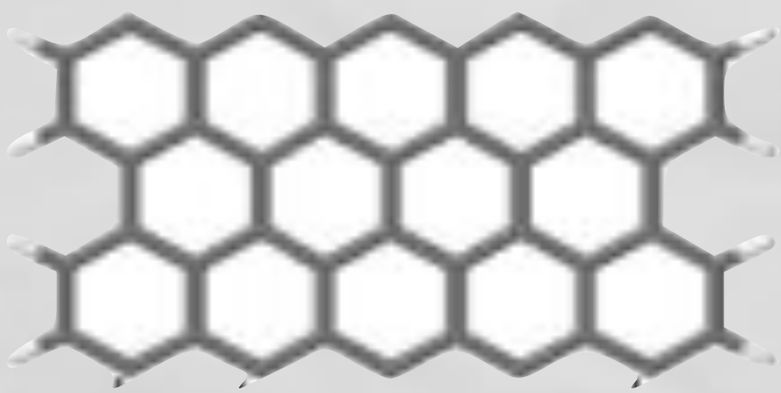
QUANTUM TRANSPORT IN GRAPHENE NANONETWORKS

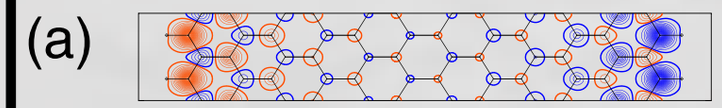


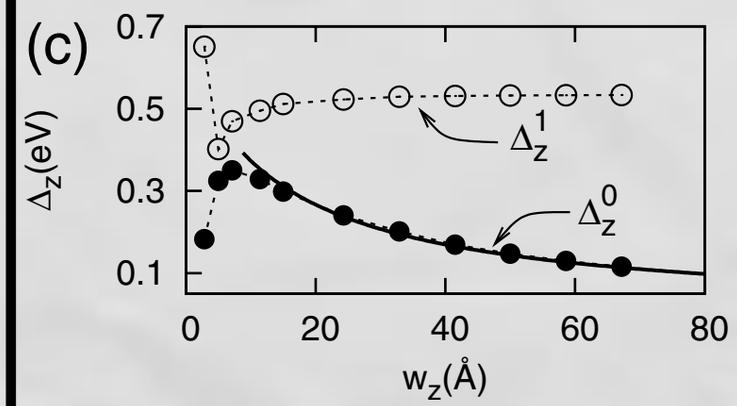
Nano Lett., 11, 3058 (2011)

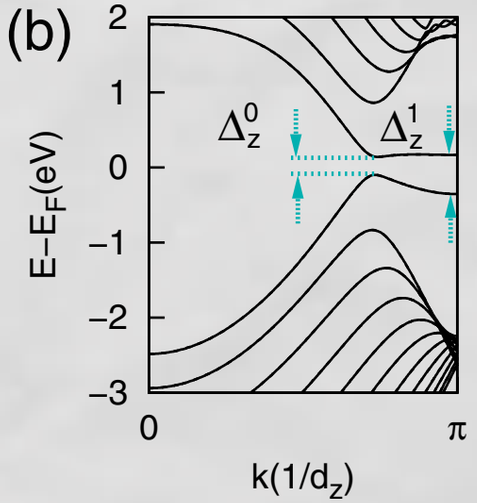
GNR ELECTRONIC PROPERTIES

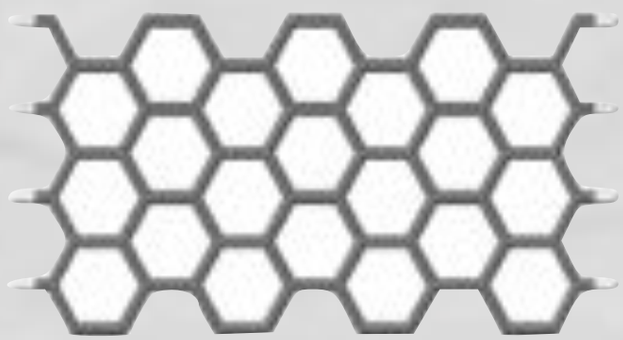






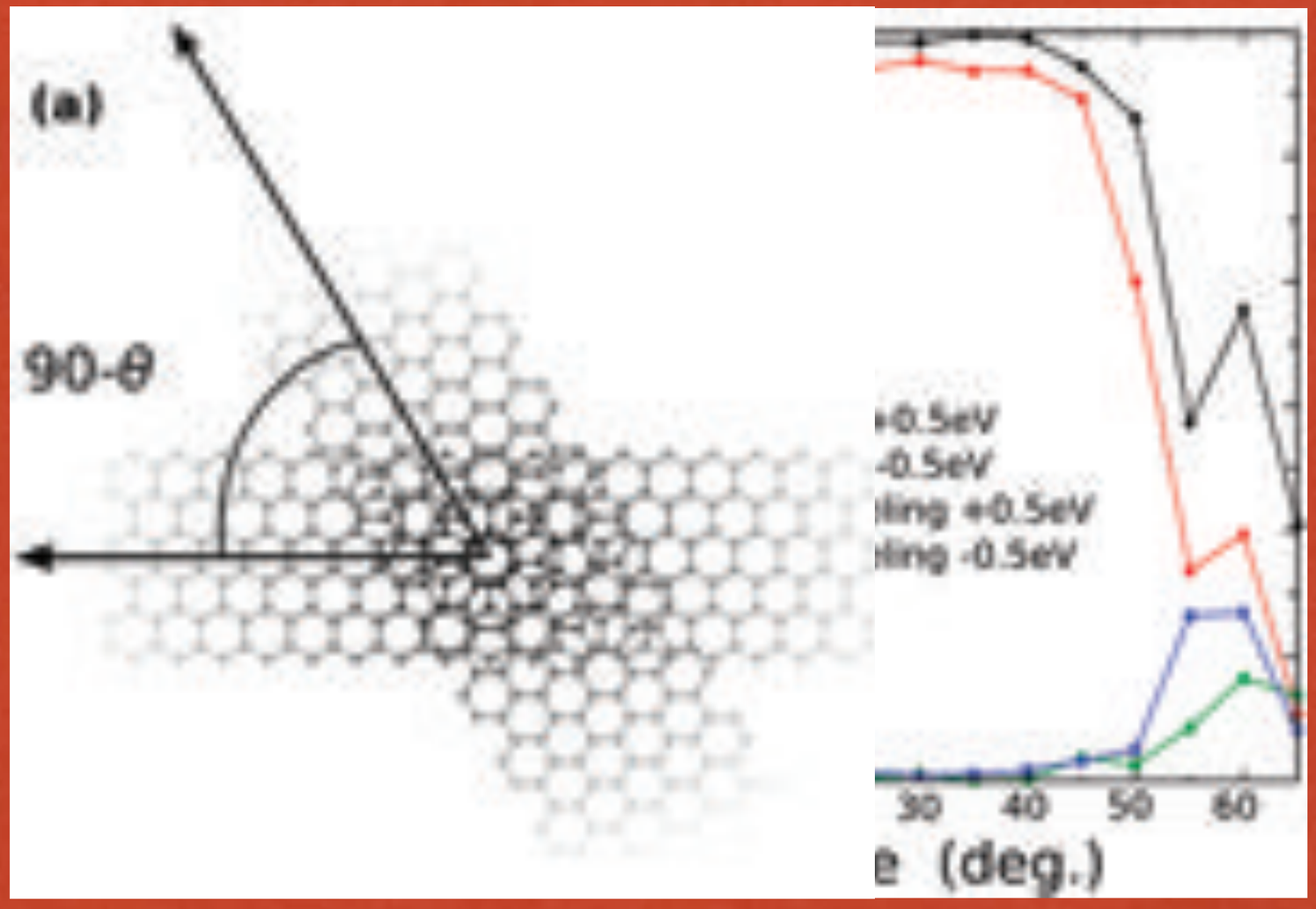






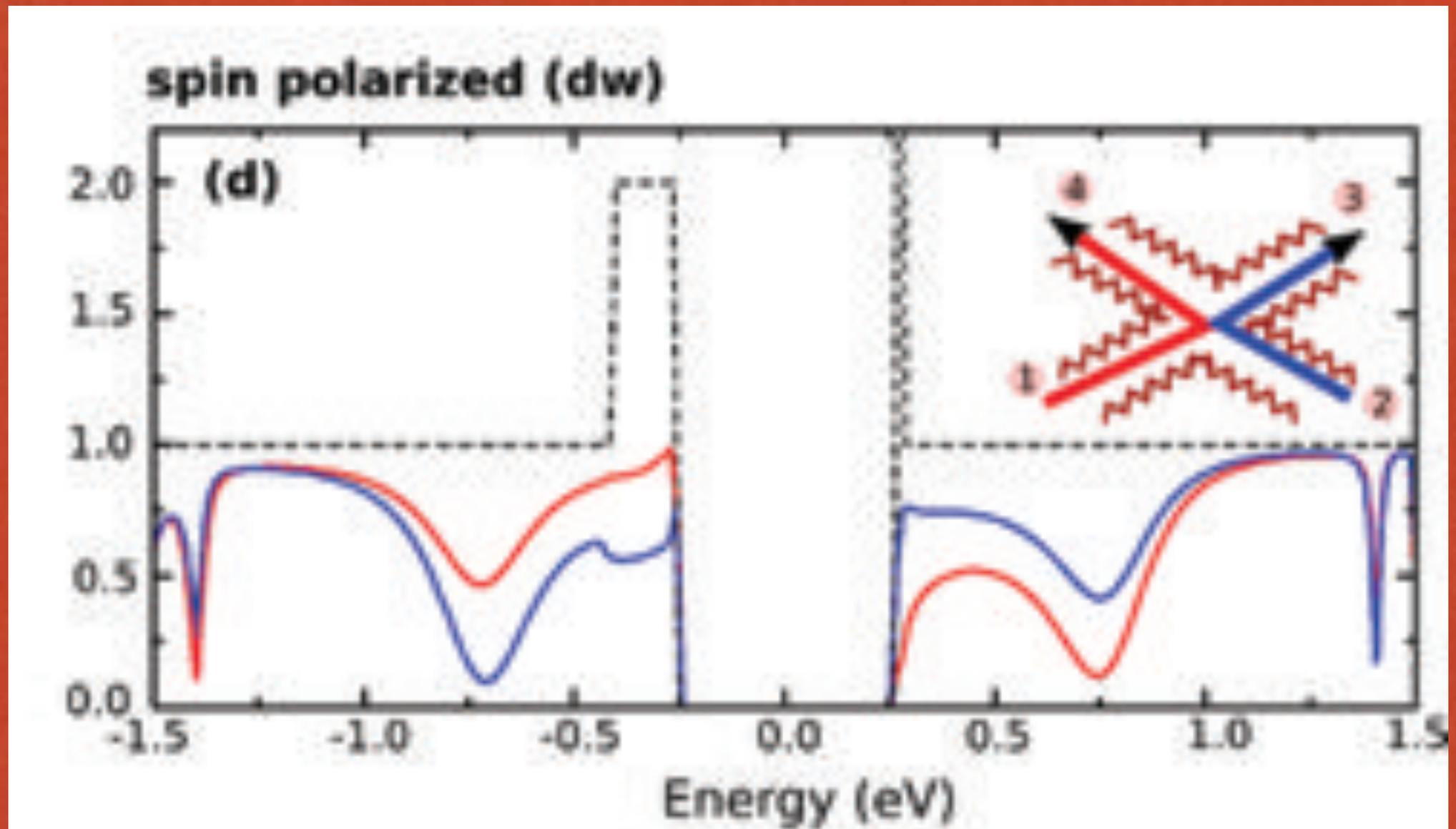
PHYS. REV. LETT. 97 (2) 16803 (2006)

OUT-OF-PLANE JUNCTIONS



Nano Lett. 11, 3058 (2011)

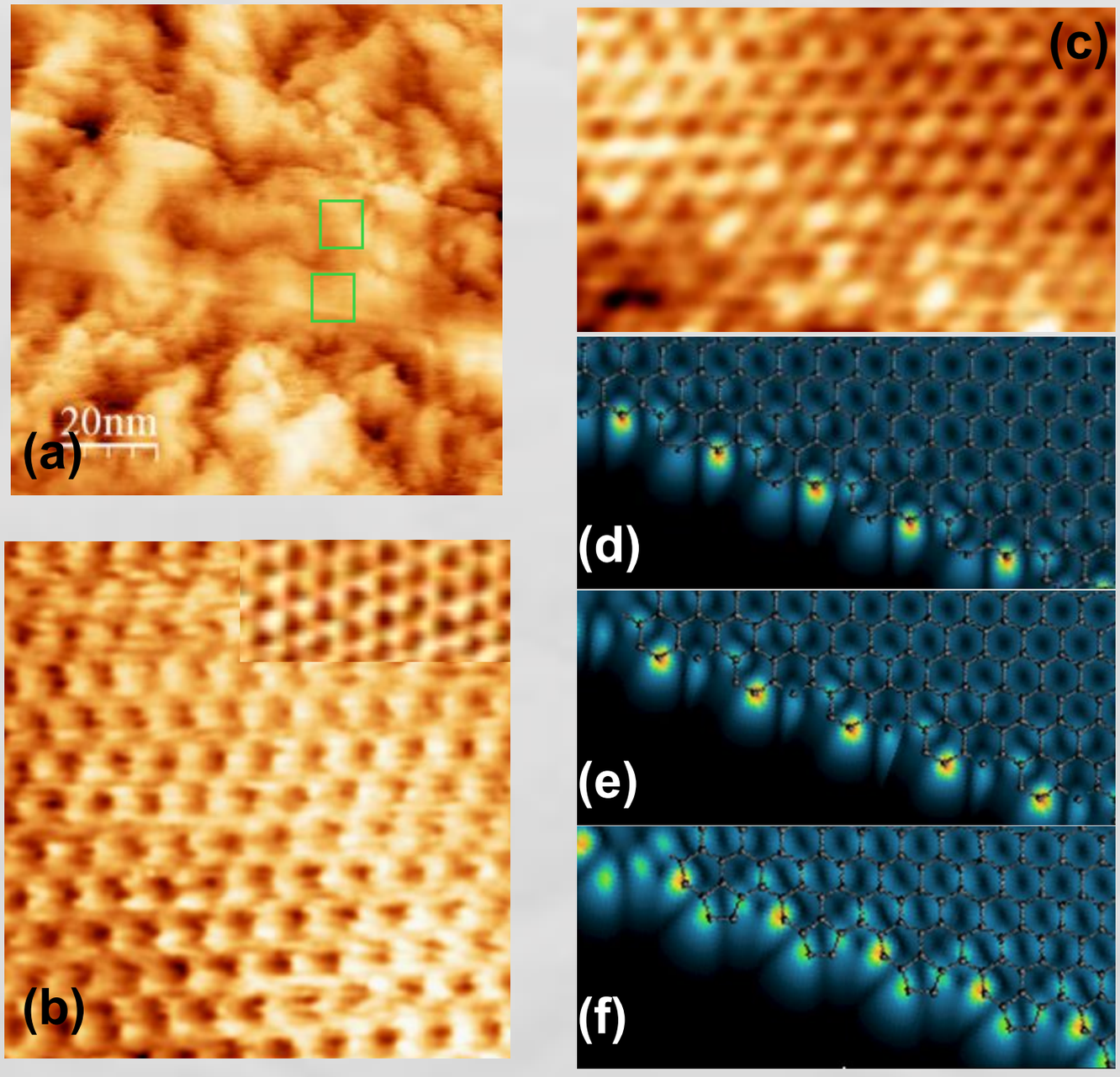
IN PLANE JUNCTIONS: ZIGZAG EDGES: SYMMETRY BREAKING DUE TO SPIN



Nano Lett. 11, 3058 (2011)

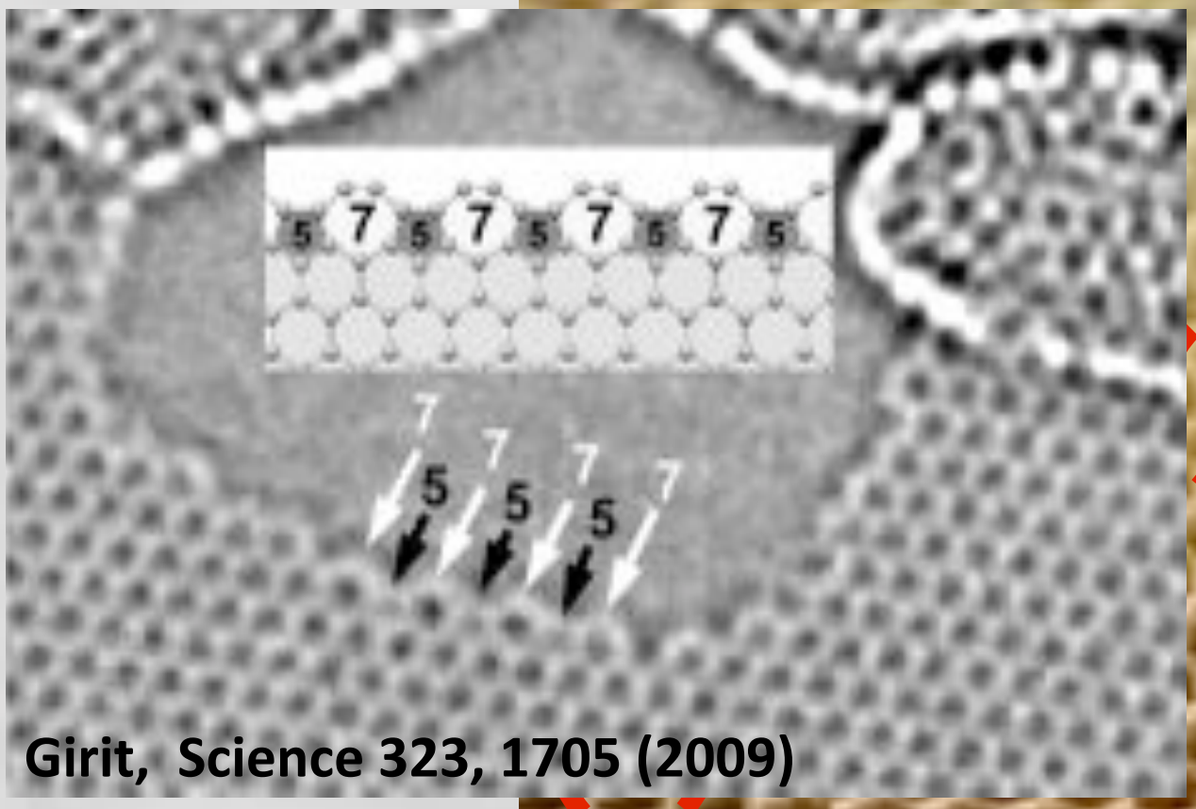
IT IS QUITE EASY TO PROPOSE SUCH HIGHLY ORDERED STRUCTURES...
WHAT ABOUT REALITY?

CVD-GROWN GNRS: ROUGH EDGES



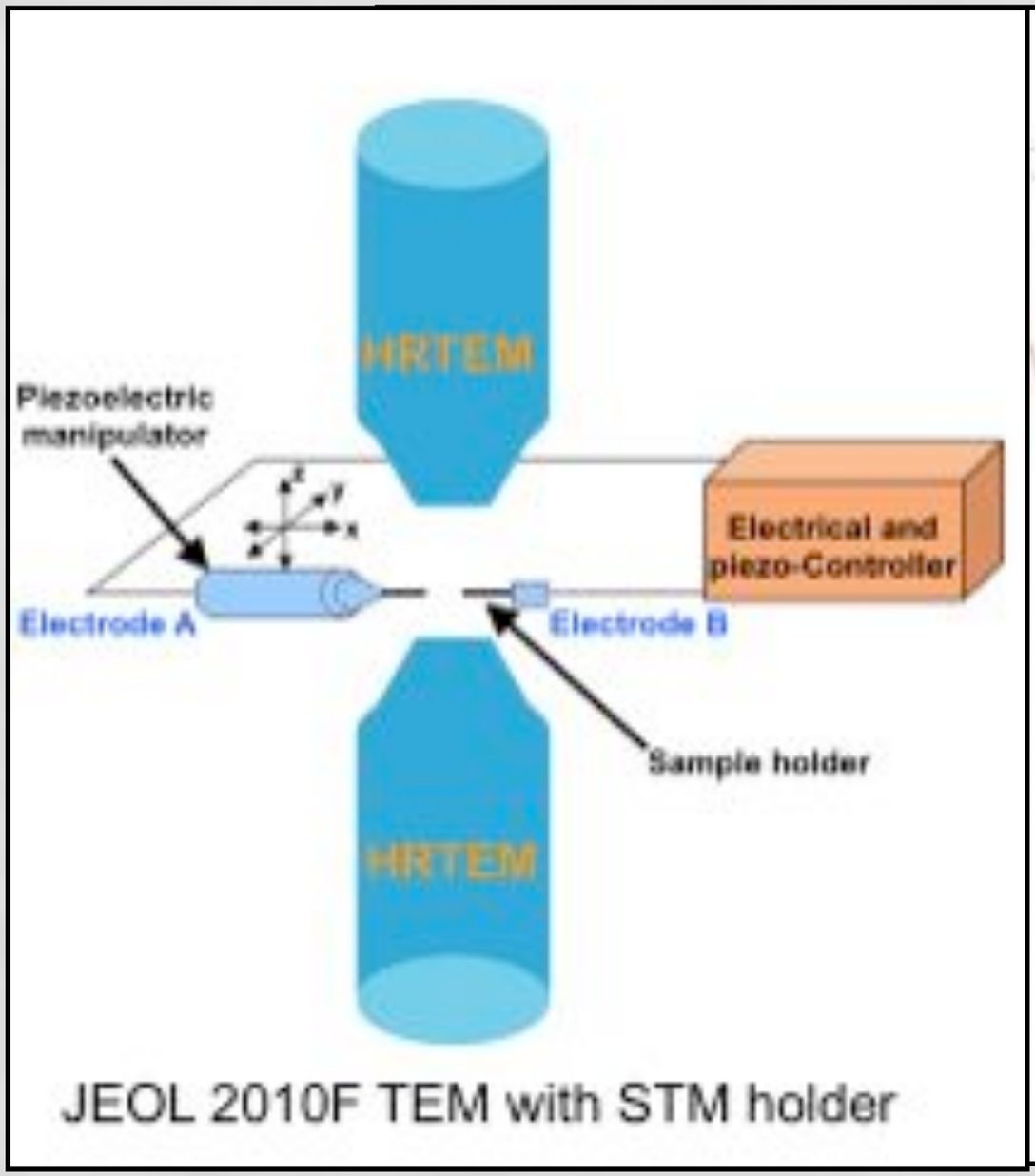
M. Pan, Meunier, Dresselhaus, under review (2011)

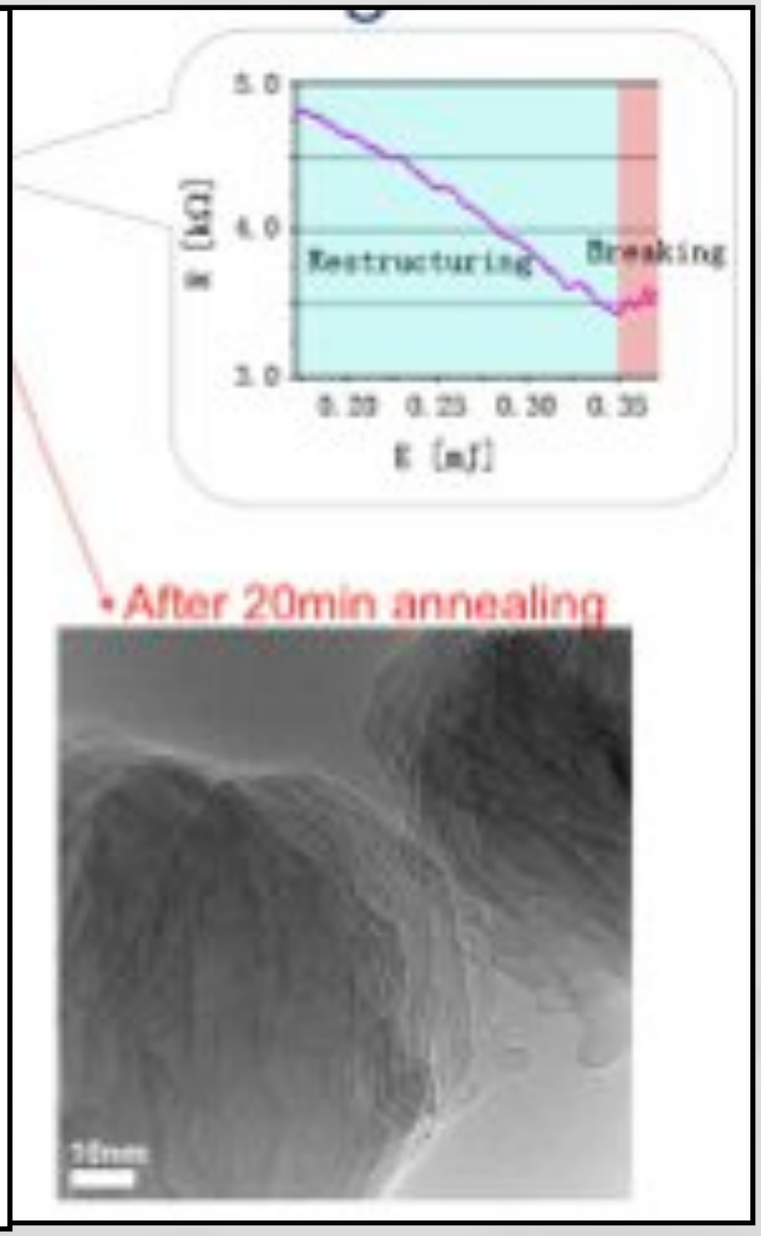
ANNEALING DEFECTS?



Girit, Science 323, 1705 (2009)

JOULE HEATING

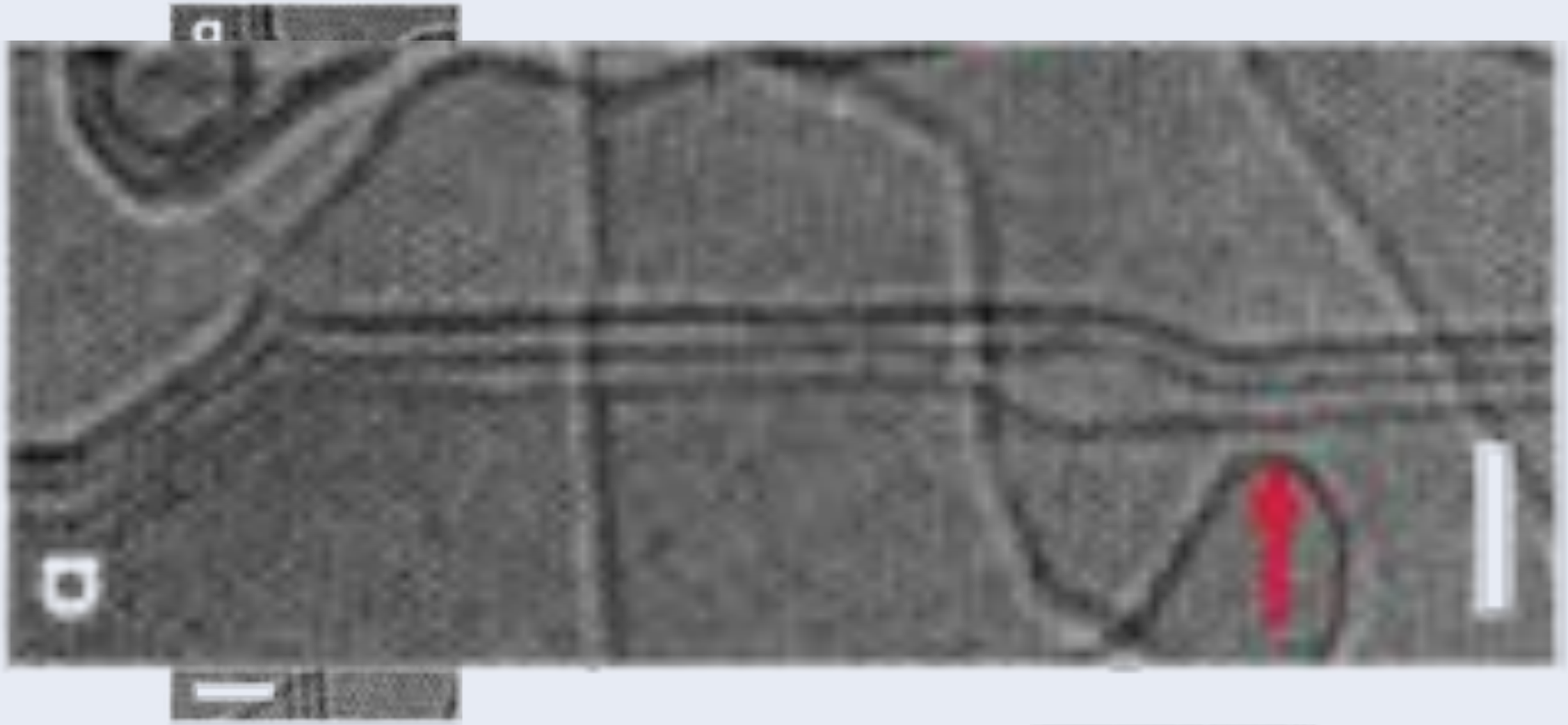




***Science* 323, 1701 (2009)**

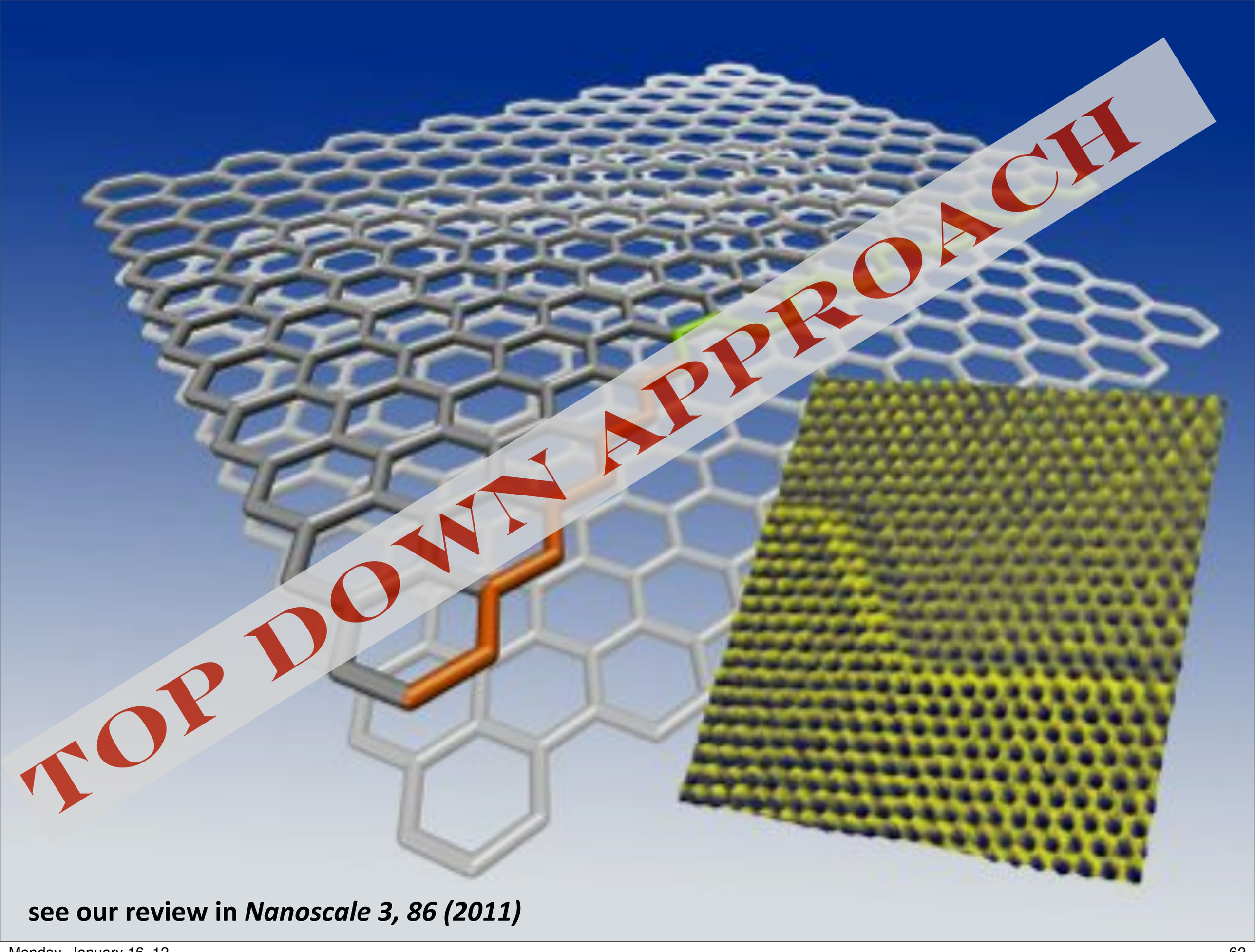
SHARP
ZIGZAG AND ARMCHAIR EDGES

***Science* 323, 1701 (2009)**



See also:

M. Engelund, J. A. Furst, A. P. Jauho, and M. Brandbyge, Phys. Rev. Lett. 104, 036807 (2010).
Meunier et al, Phys. Rev. Lett. 105, 045501 (2010)



see our review in *Nanoscale 3, 86 (2011)*

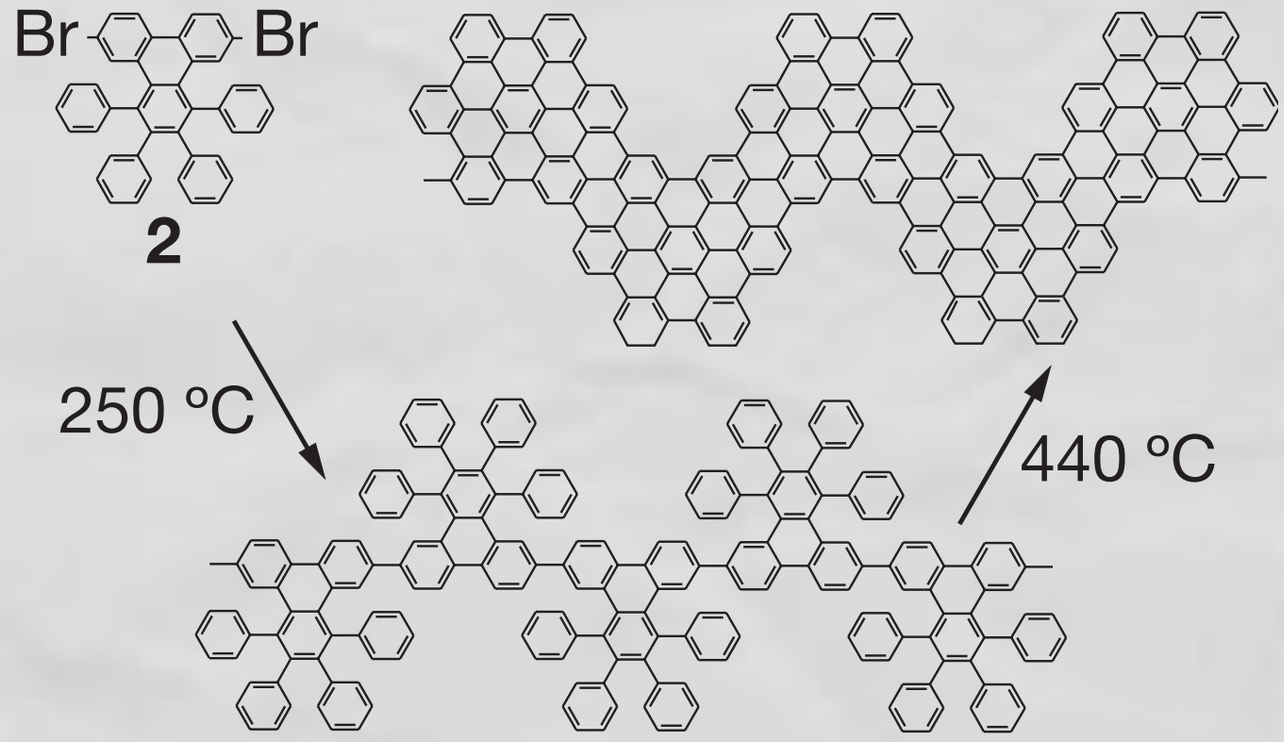
BOTTOM-UP APPROACH

nature Vol 466|22 July 2010|doi:10.1038/nature09211

LETTERS

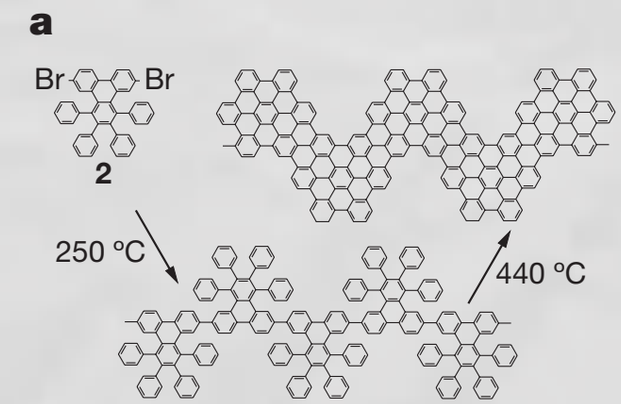
Atomically precise bottom-up fabrication of graphene nanoribbons

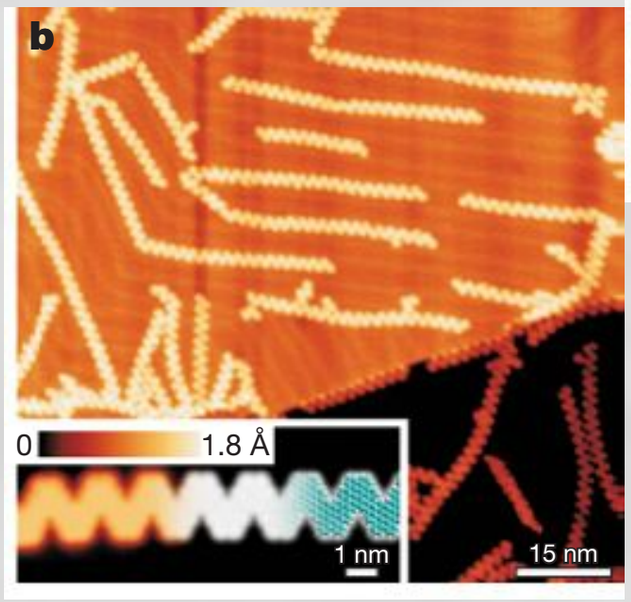
Jinming Cai[1]*, Pascal Ruffieux[1]*, Rached Jaafar[1], Marco Bieri[1], Thomas Braun[1], Stephan Blankenburg[1], Matthias Muoth[2], Ari P. Seitsonen[3,4], Moussa Saleh[5], Xinliang Feng[5], Klaus Müllen[5] & Roman Fasel[1,6]

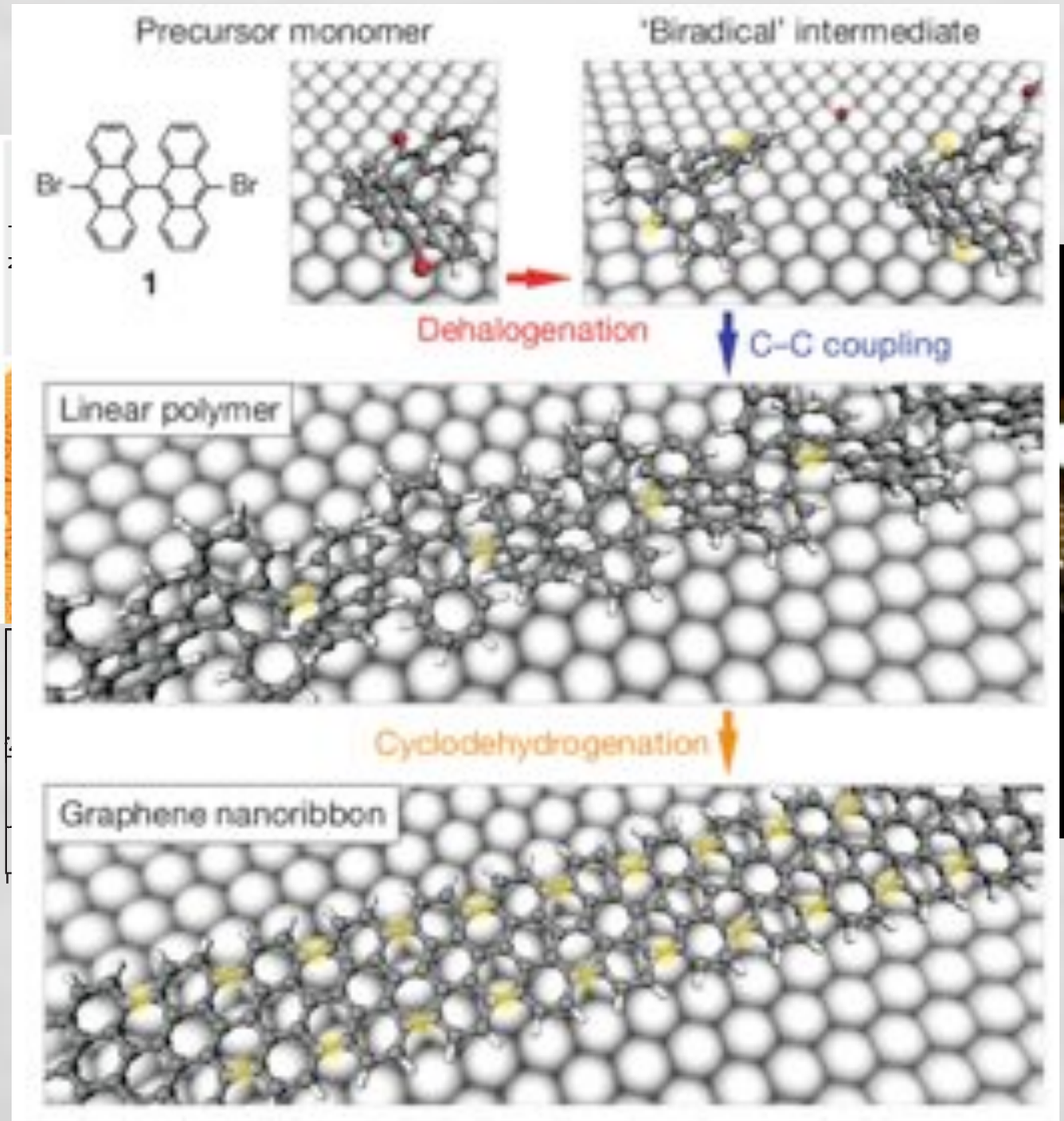


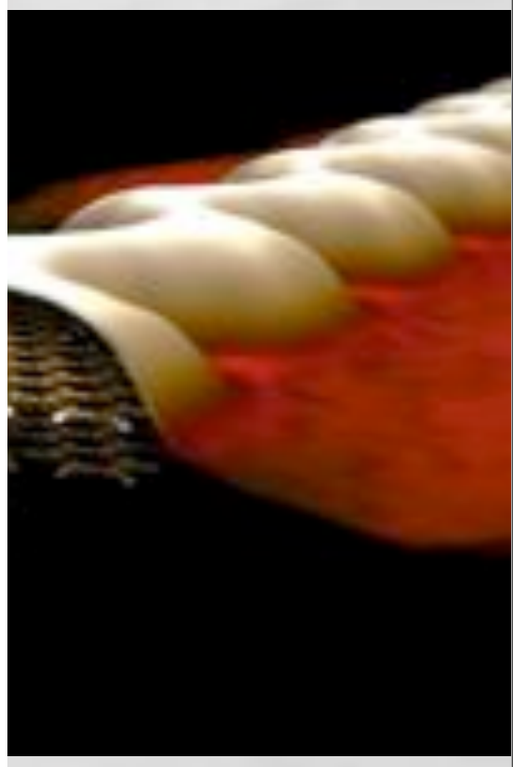
Cai et al, Nature 2010

ZIGZAGING GRAPHENE NANORIBBONS

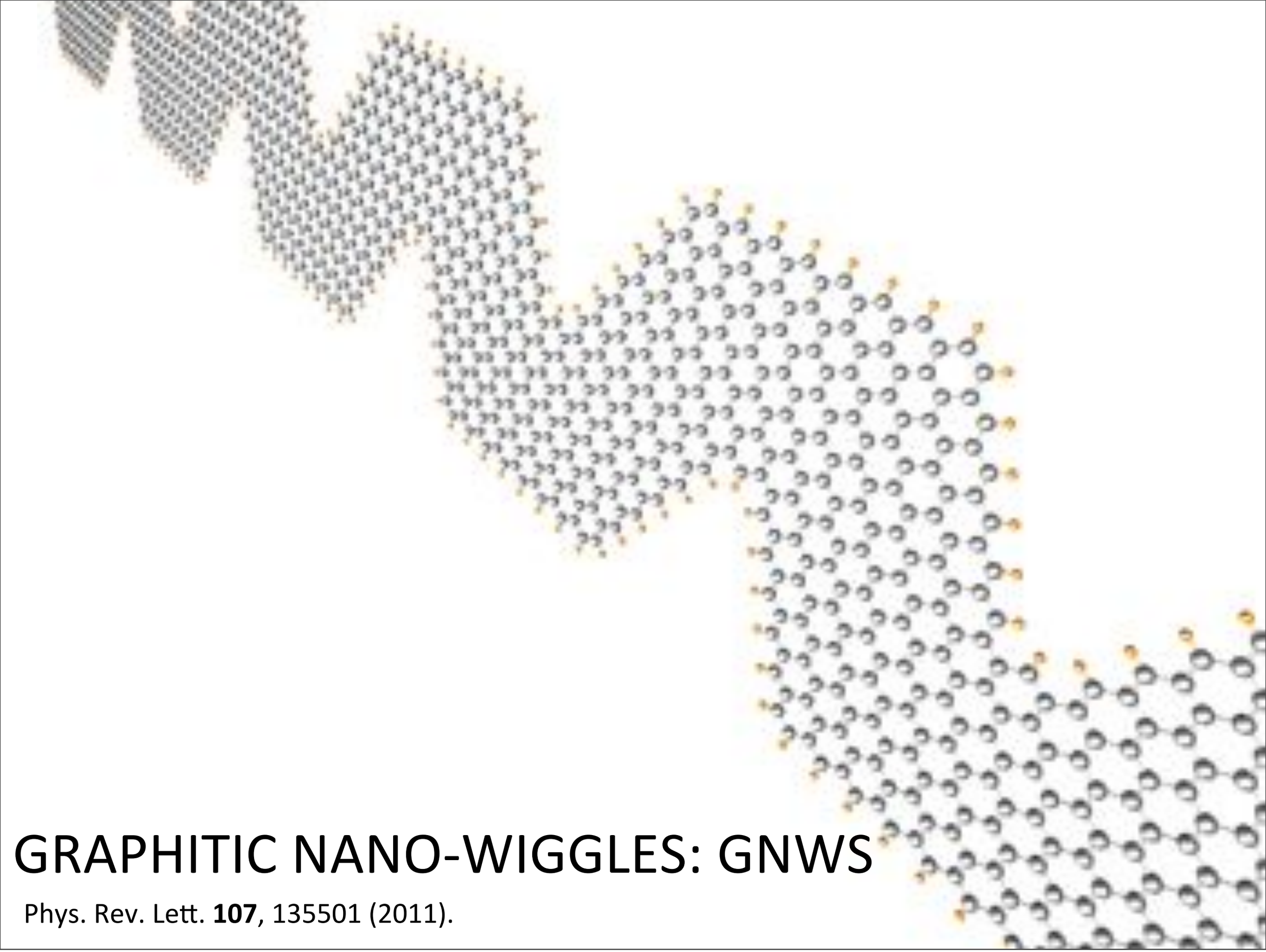








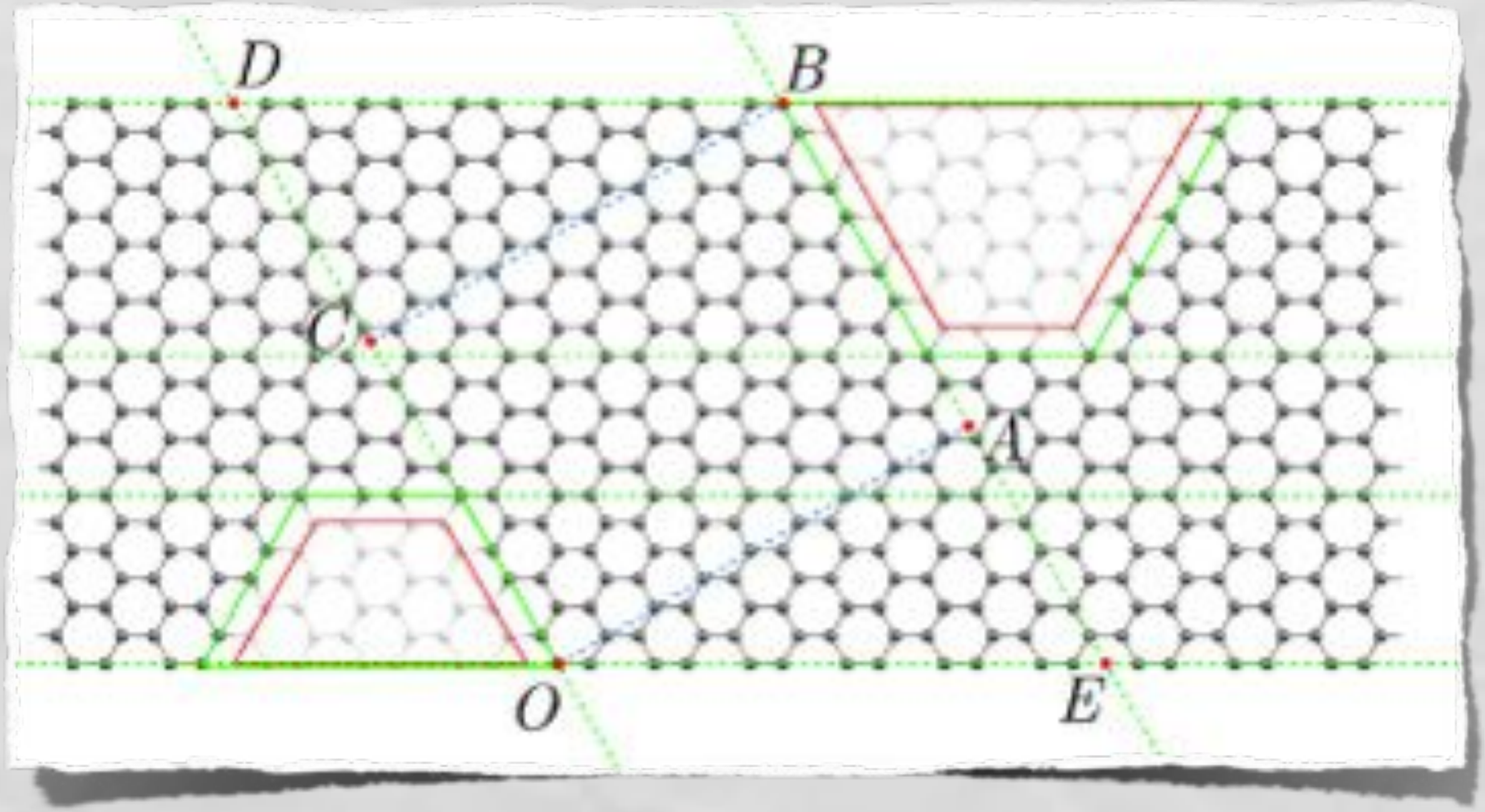
Cai et al, Nature 2010



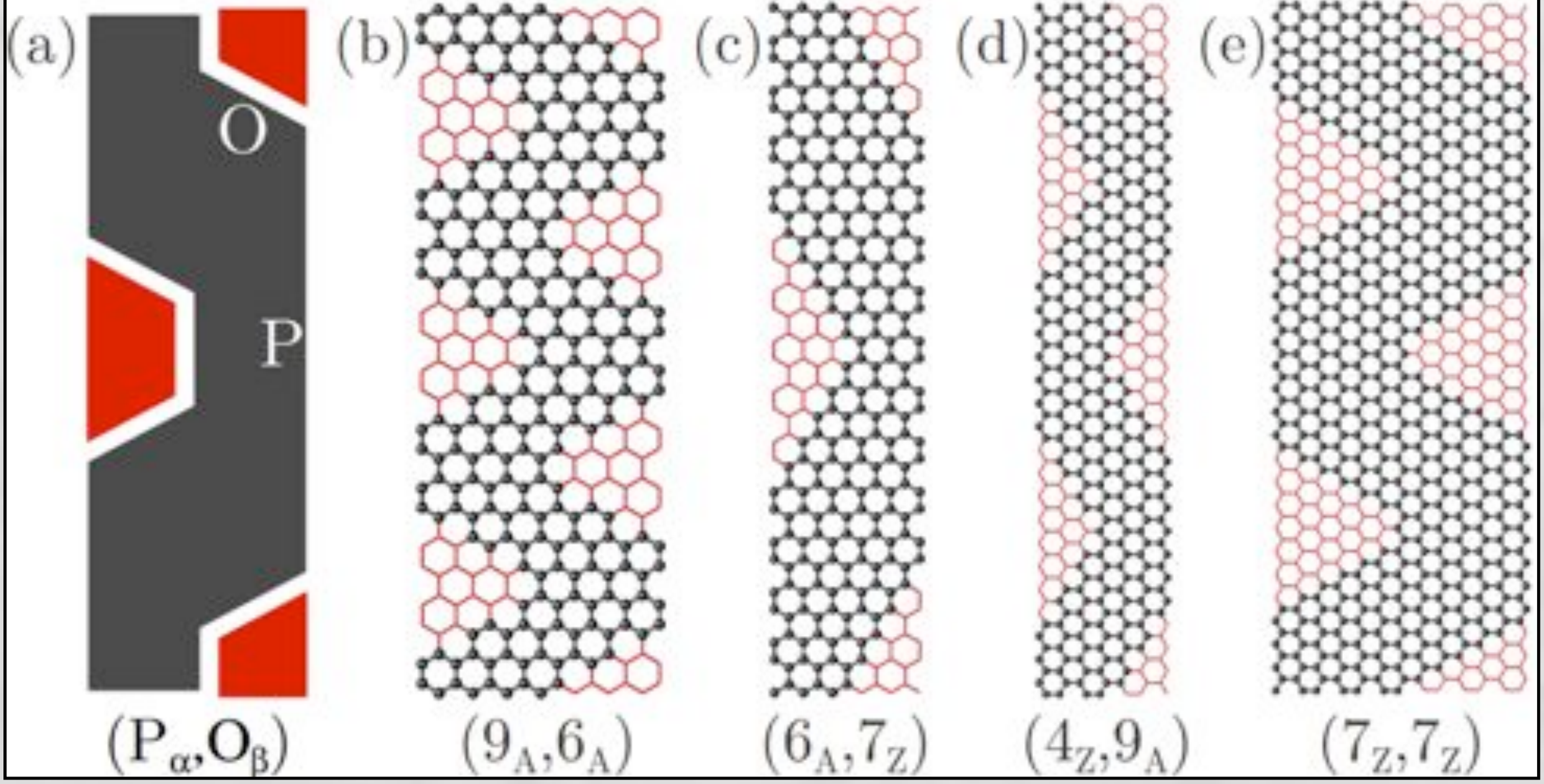
GRAPHITIC NANO-WIGGLES: GNWS

Phys. Rev. Lett. **107**, 135501 (2011).

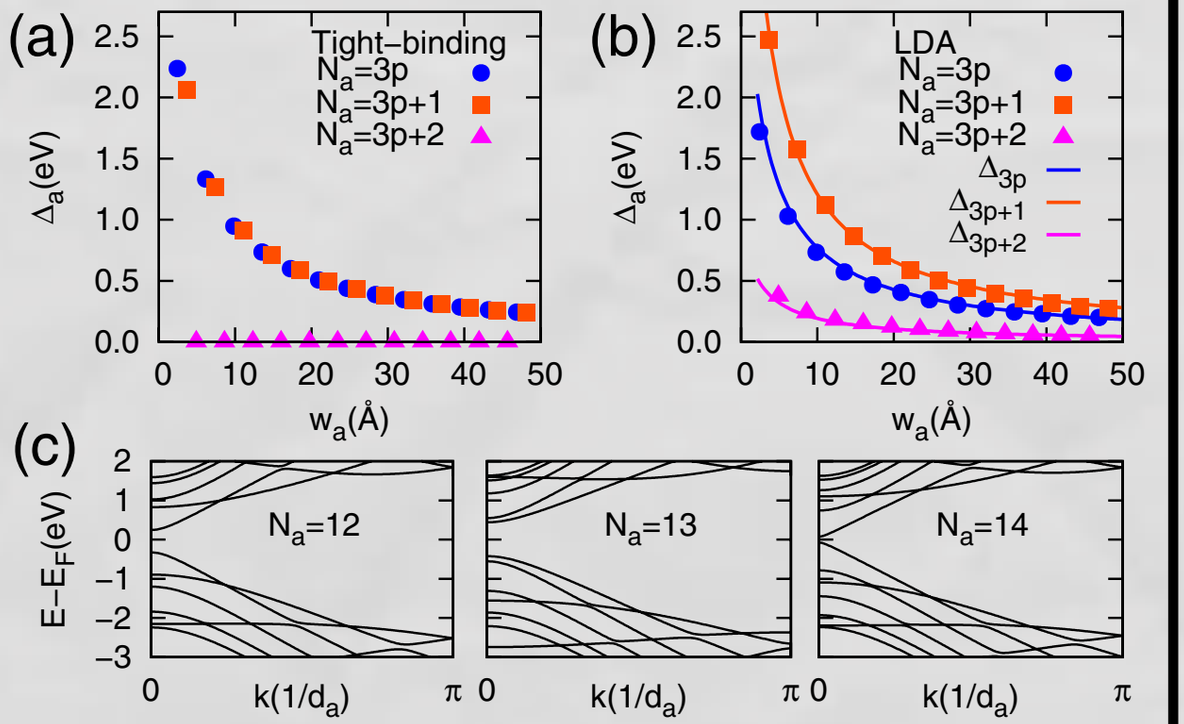
GNWS: STRUCTURAL PROPERTIES

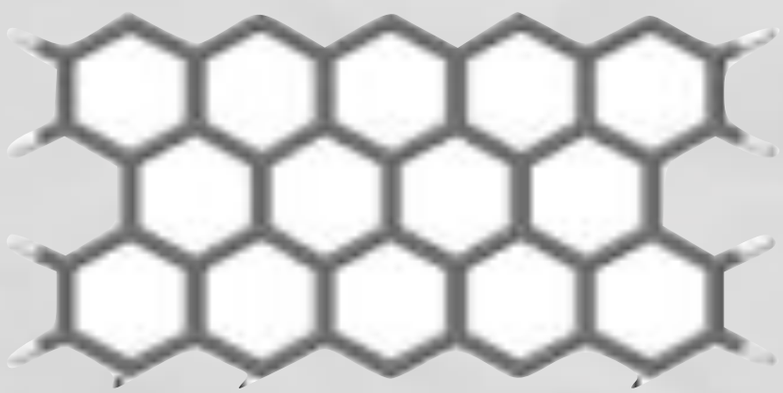


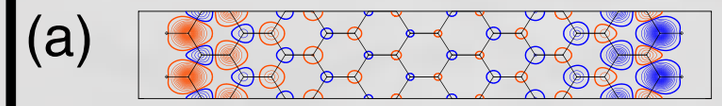
(Parallel,Oblique)=(P_α,O_β), α,β=A,Z

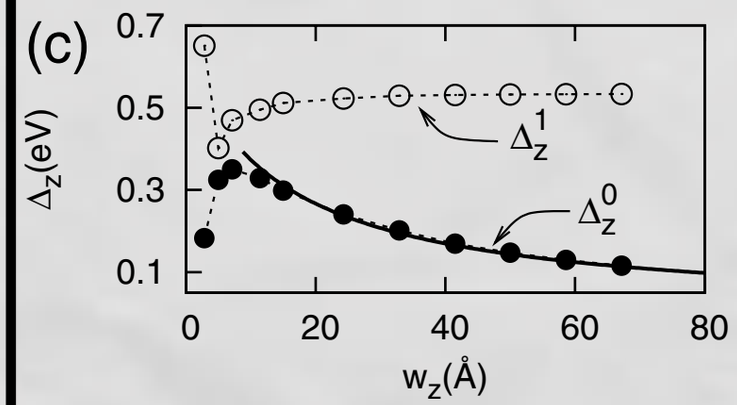


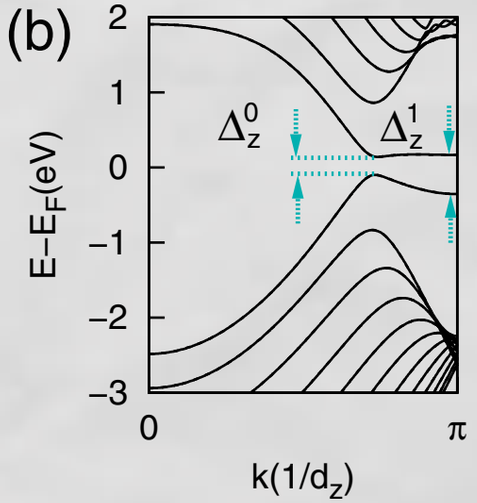
GNR ELECTRONIC PROPERTIES

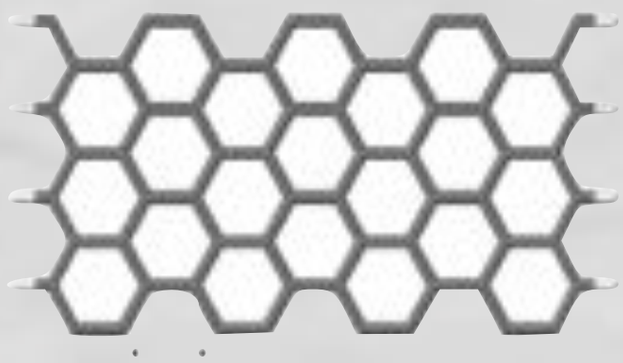






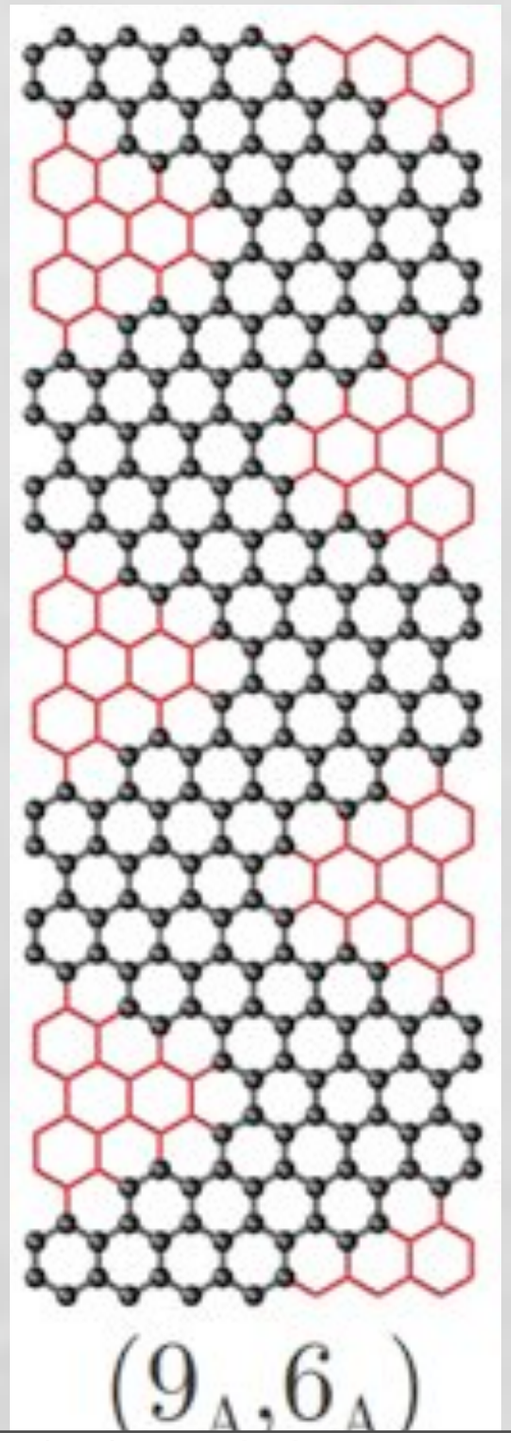


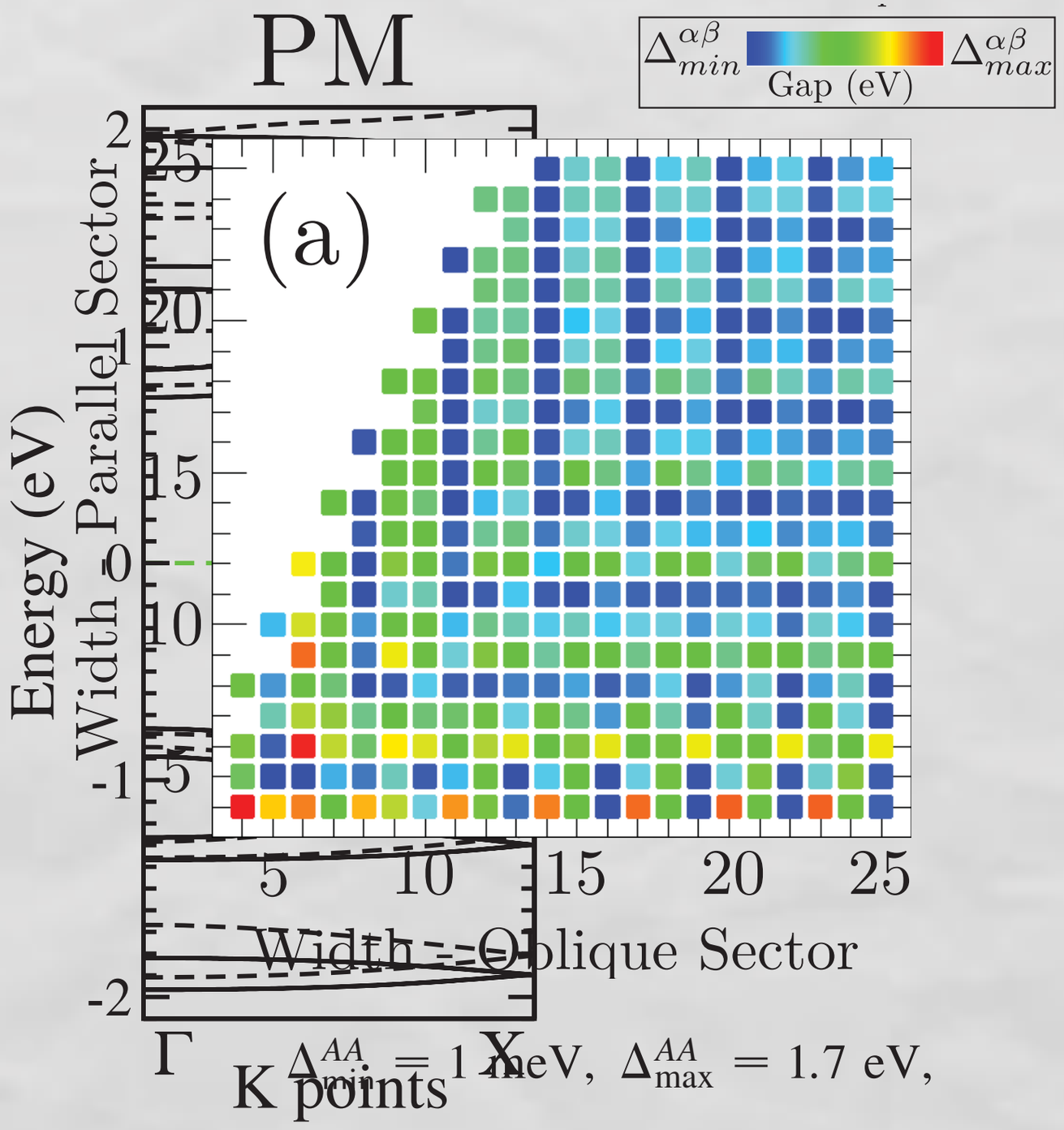




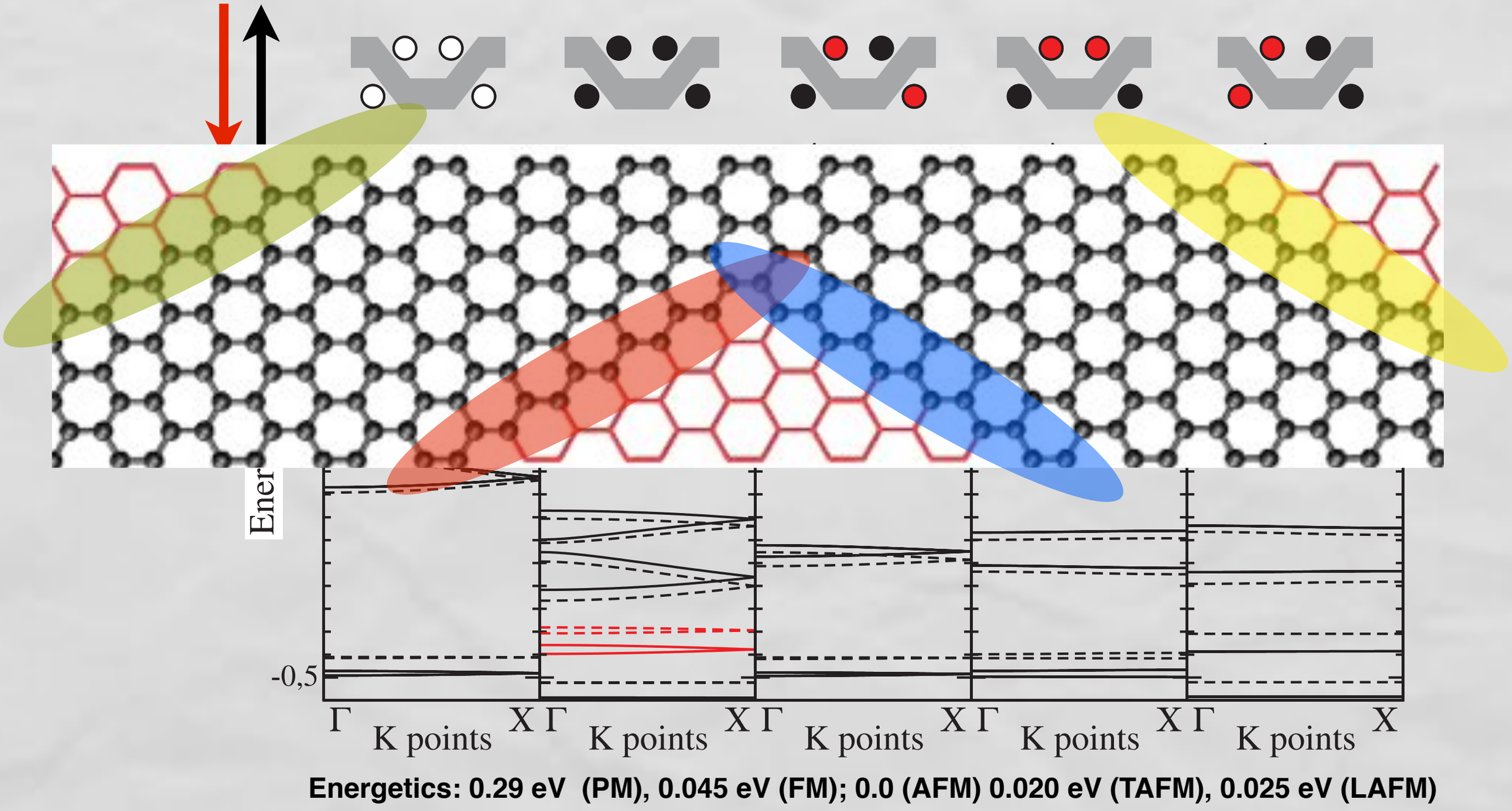
PHYS. REV. LETT. 97 (2) 16803 (2006)

ARMCHAIR-ARMCHAIR



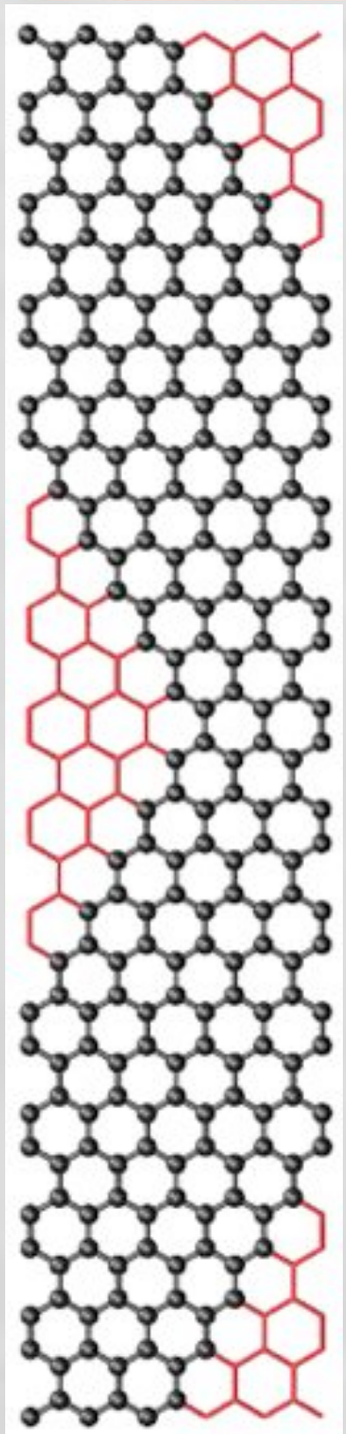


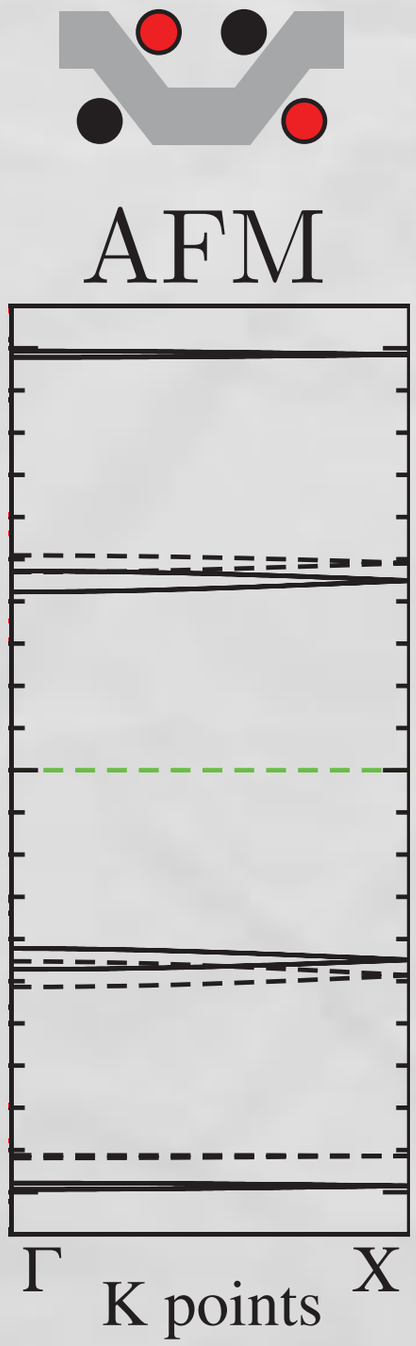
ARMCHAIR-ZIGZAG

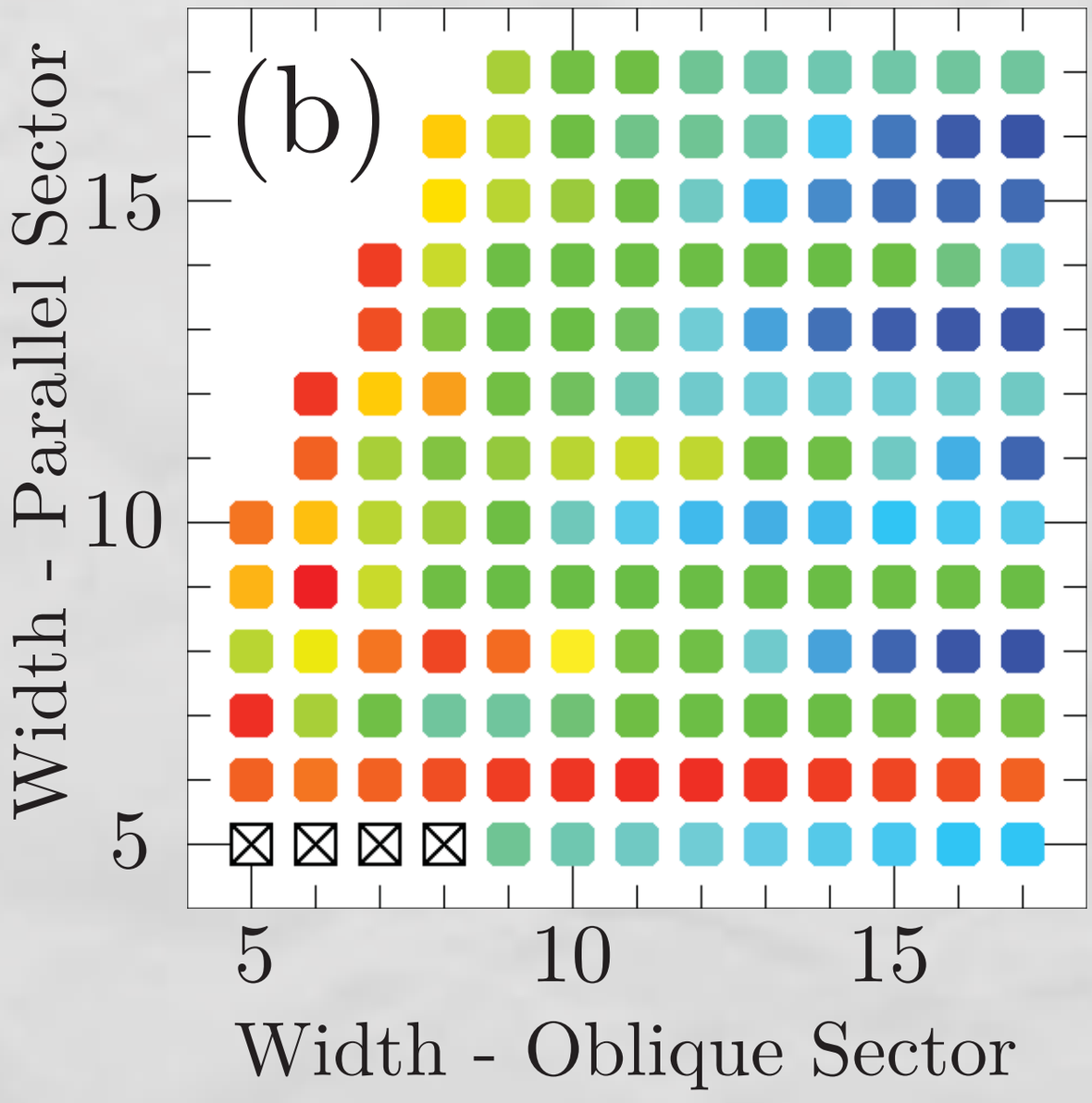


Energetics: 0.29 eV (PM), 0.045 eV (FM); 0.0 (AFM) 0.020 eV (TAFM), 0.025 eV (LAFM)

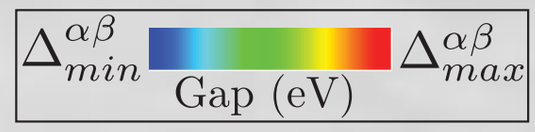
ARMCHAIR-ZIGZAG



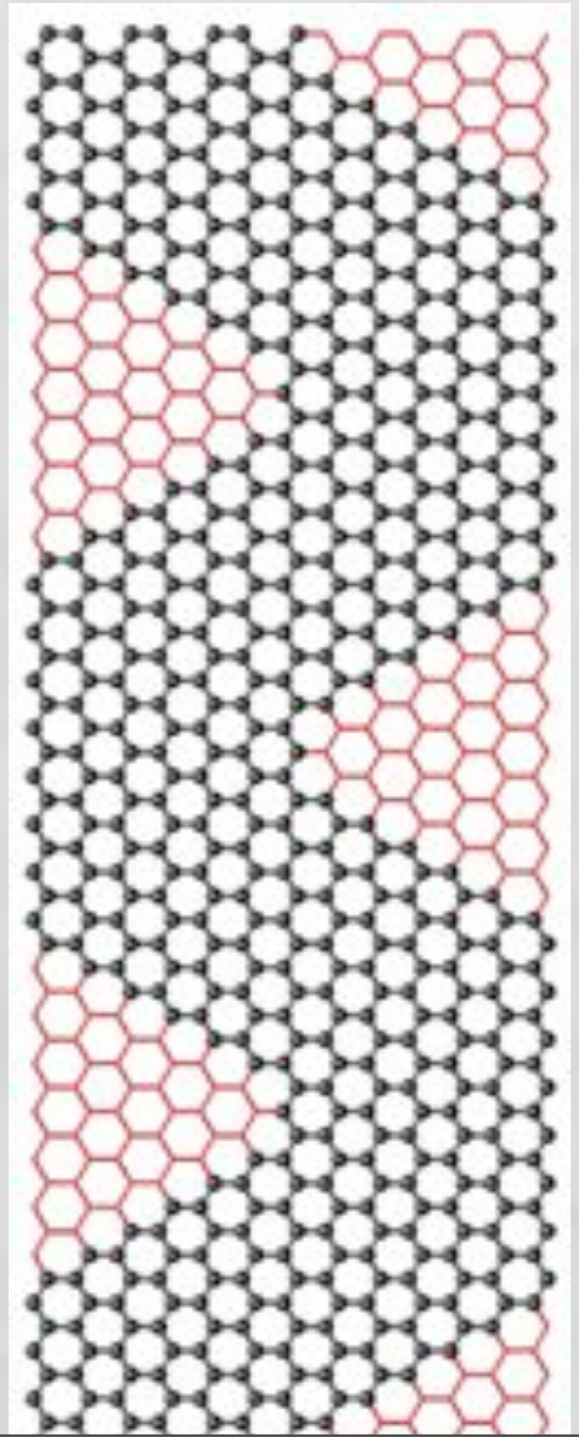


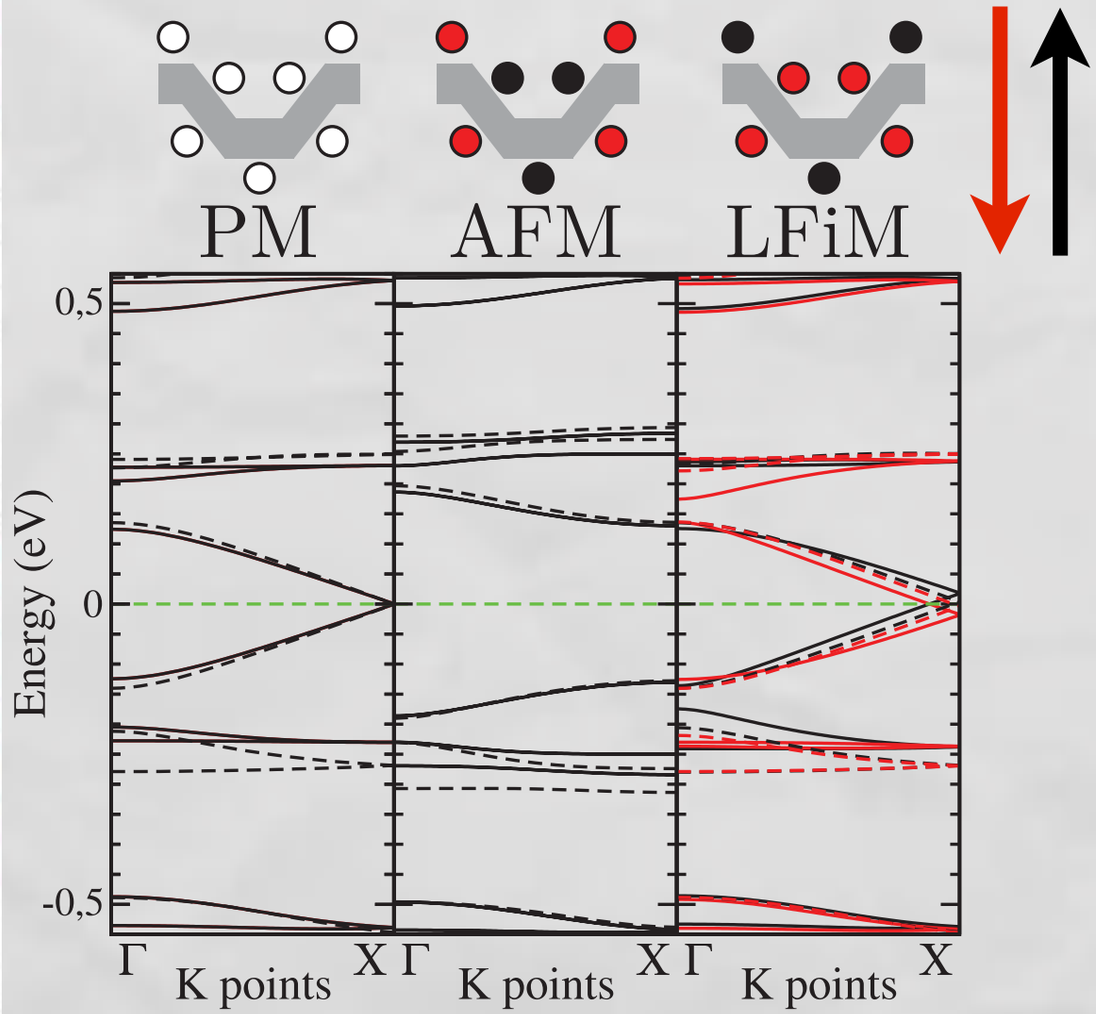


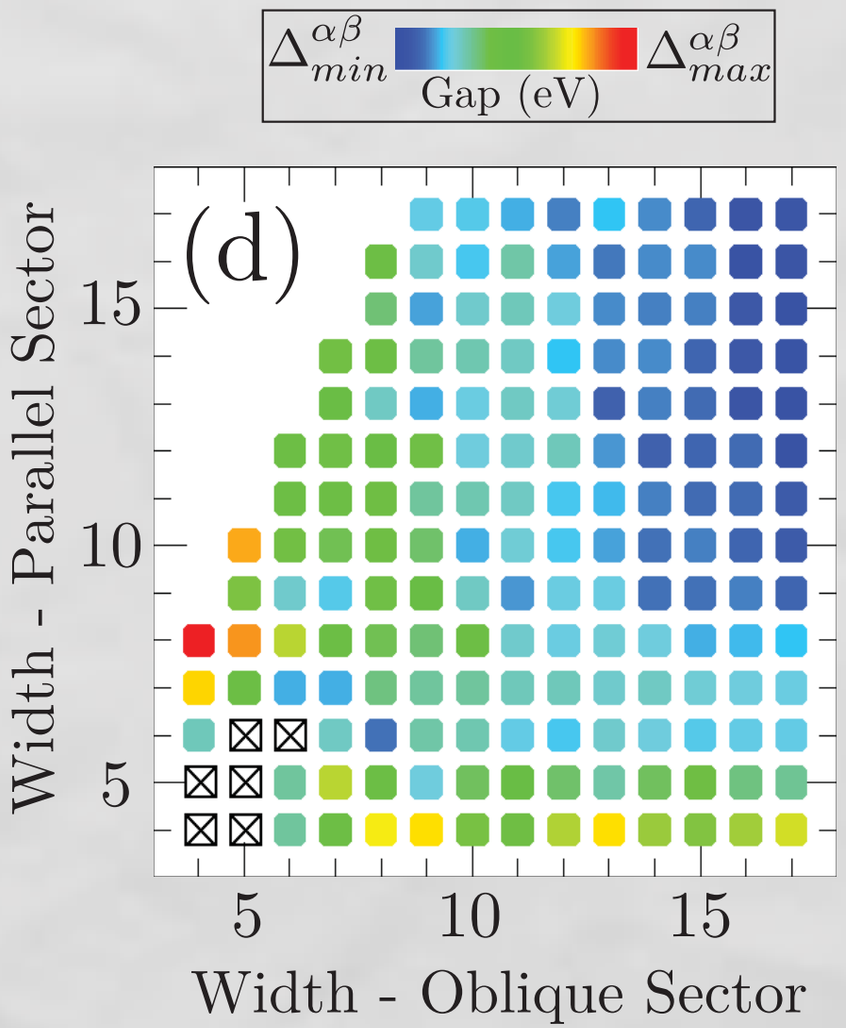
$\Delta^{AZ}_{\text{min}} = 183$ meV, $\Delta^{AZ}_{\text{max}} = 446$ meV



ZIGZAG-ZIGZAG



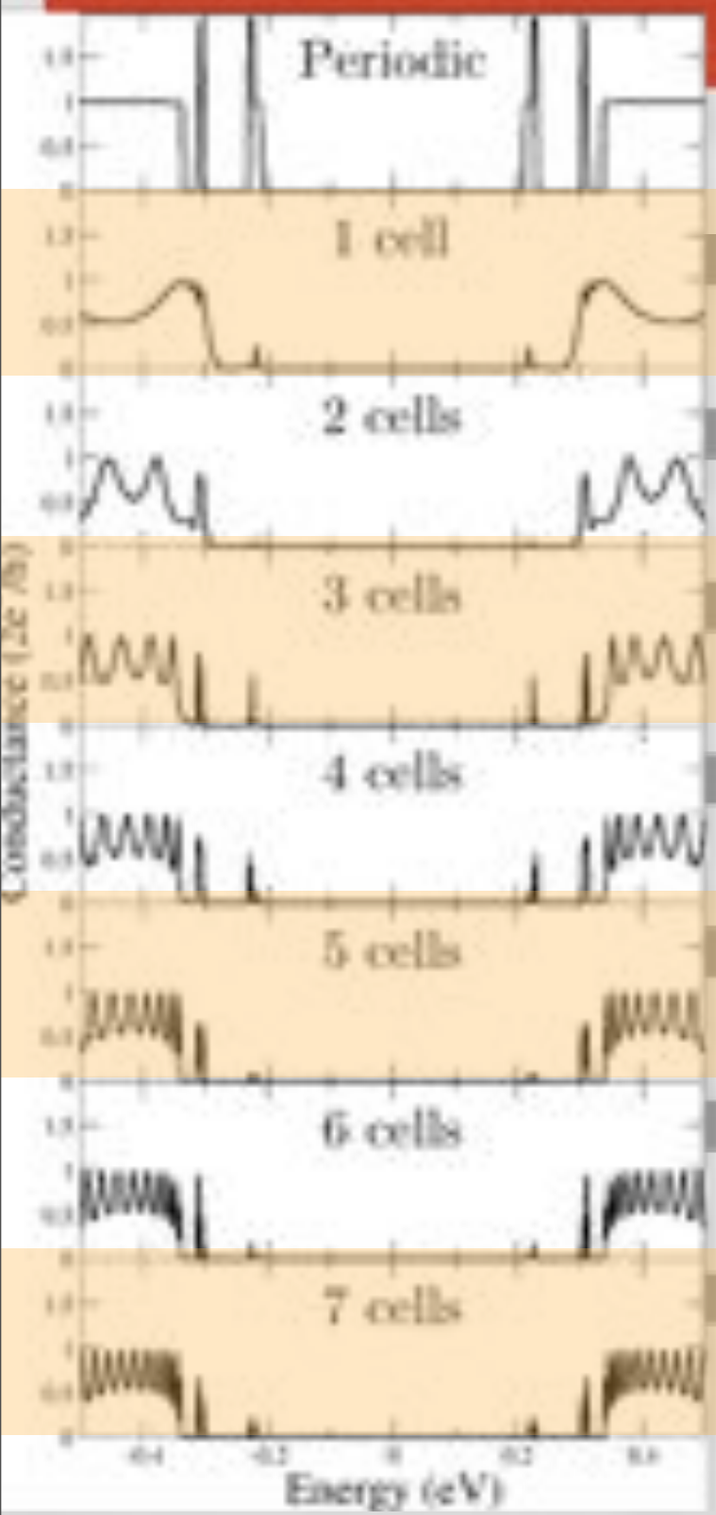


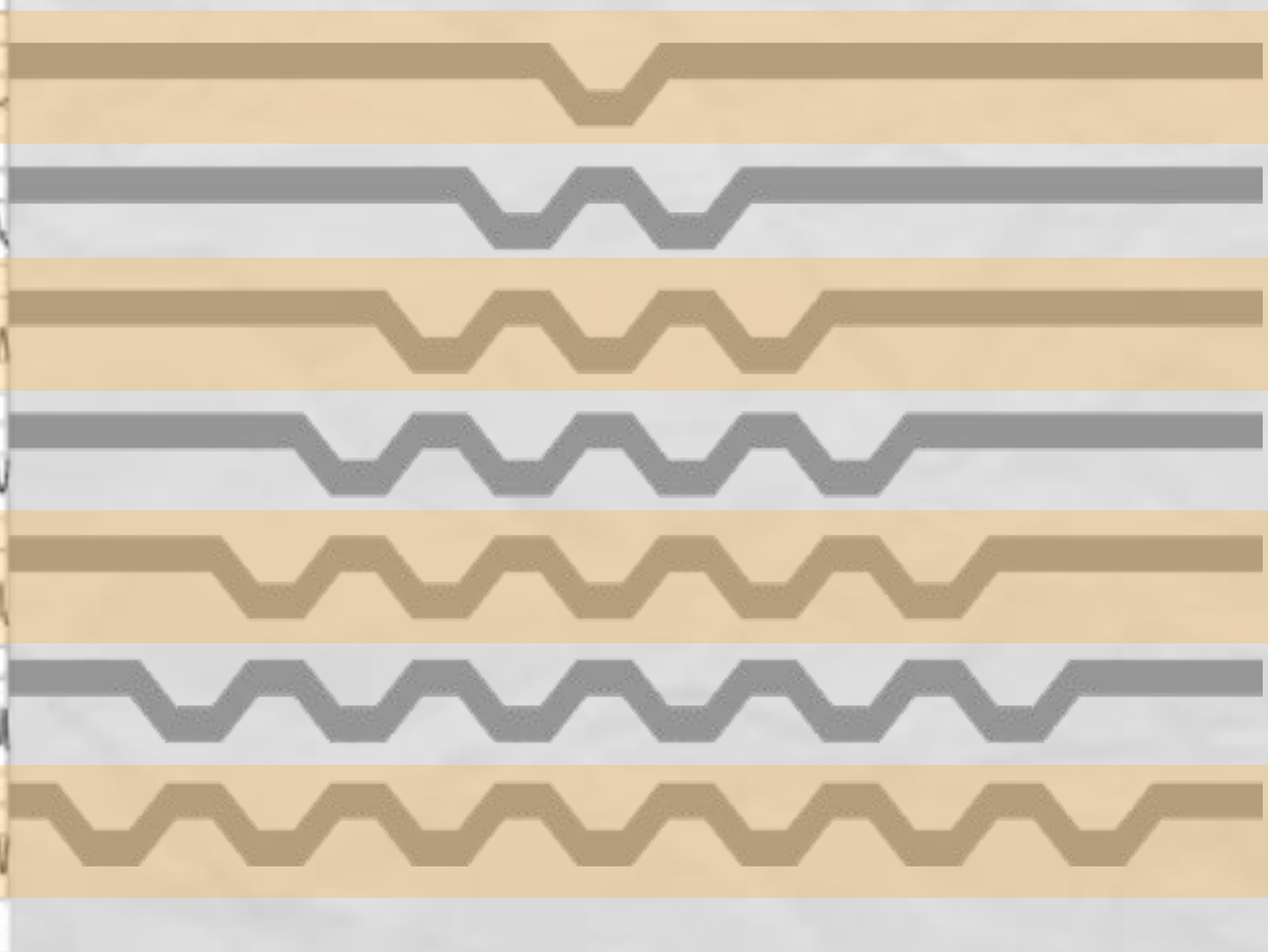


Energetics: 0.055 eV (PM), 0.056eV (LFiM)

$$\Delta^{ZZ}_{\text{min}} = 208 \text{ meV}, \Delta^{ZZ}_{\text{max}} = 491 \text{ meV}$$

TUNING RESONANCES





FOOD FOR THOUGHT

- **I've presented a broad array of examples where electronic transport is driven by quantum mechanics, far from classical regime**
- **Connections to experiment abound, yet full connection with actual experiment is still largely eluding state-of-the art**
- **What about missing QM ingredients (beyond mean field!)?**

SPECIAL THANKS

RPI: E. Costa-Girao, E. Cruz Silva, L. Liang

NCSU: J. Bernholc, W. Lu

UDel: B.K. Nikolic and Kamal Saha

ORNL: Bobby G. Sumpter, Jose Romo Herrera

PSU: M. Terrones

MIT: X. Jia, M. Dresselhaus

UCL: JC Charlier, Andres Bottello

Thank You