Density Functional Theory And Renormalization Techniques In Condensed Matter

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Oak Ridge National Laboratory

Personal introduction

i) Undergraduate studies at **Universidad de Madrid**, Spain.

ii) PhD. at **C.E.A.** French National Laboratory at Grenoble, France

Marie Curie individual fellowship.

- Density functional theory based methods for nanostructures.
- Electronic transport properties of one-dimensional materials.

iii) Postdoctoral Associate Researcher at **ORNL**, TN, USA.

American Recovery and Reinvestment Act fellowship.

- New materials: Boron nitride, Silicon carbide, ...
- Hybrid nanostructures to modify graphene electronic band gap.

Personal introduction

Ricky A. Kendall

@

NCCS.GOV
National Center for Computational Sciences

Bobby G. Sumpter

@

CSM Computer Science and Mathematics
Computing and Computational Sciences Directorate

Center for Nanophase Material Science

Integrated approach:
Using computational and experimental studies to explore structure-function-transport relations of materials

The central organizing concept of **CNMS** is to provide unique opportunities to understand nanoscale materials, assemblies, and phenomena, by creating a set of scientific synergies that will accelerate the process of discovery. *(http://www.cnms.ornl.gov)*

At **CNMS:**

→ We incorporate fundamental equations into efficient computer programs, to calculate the structures and properties of molecules and solids. While its results normally complement the information obtained by experiments, it can in some cases predict unobserved and emergent phenomena.

→ We attempt to understand, predict, and ultimately control matter and energy at the electronic, atomic, and molecular levels: foundations for new energy technologies, "up and to the right in performance"

Outline

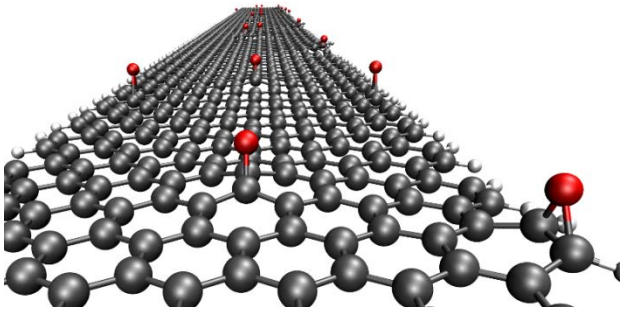
Outline of talk

→ Material modeling by design.

→ Renormalization techniques for multi-scale computer simulations.

→ Electronic transport in one-dimensional materials.

→ Density functional theory to explore the world at the nanoscale.



Challenges for Computational Sciences

size

& time scale

atoms
molecules

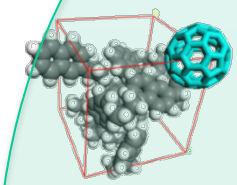
1-100
atoms

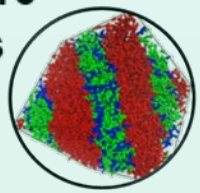
method

ab initio
method
$O(N^3)$

nanostructures

1000-10^6
atoms



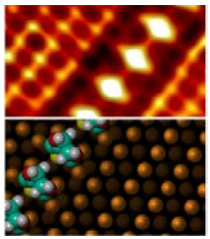


- Algorithms do not scale.

- Codes may not parallelize.

bulk

Infinite
(1-10 atoms
in a unit cell)



- *ab initio* method
- Effective mass method

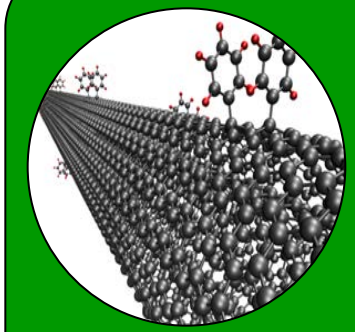
ab initio
elements
and reliability

New
algorithms

Exascale HPC

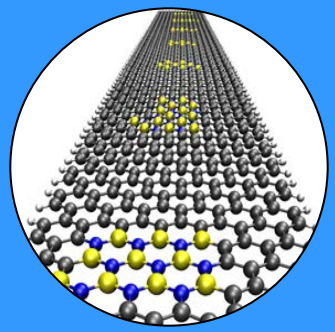
→ Growing capabilities to synthesize and characterize materials are converging with advances in simulation (theory, modeling, and computation) to create new opportunities for materials and chemistry by design.

Modeling for Innovation



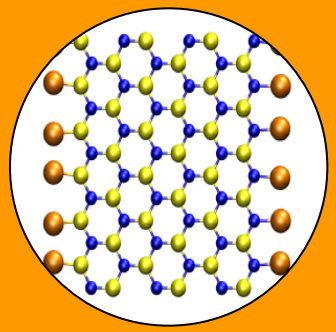
Carbon nanotubes

Chemical modification of nanotubes as an efficient approach to create electronic devices with enhanced conductivity.



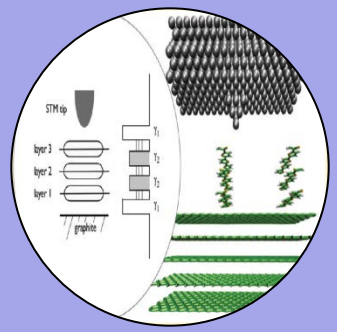
Graphene

Engineering electronic band gap in graphene with hybrid structures for next generation electronic devices.



Boron nitride

New features in boron nitride compounds: insulating materials become metallic.



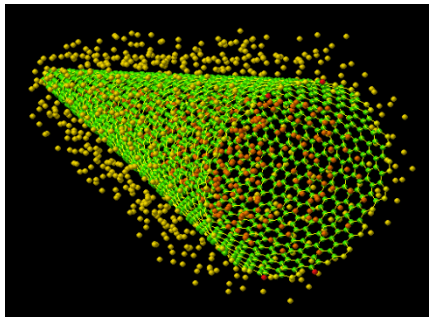
Spectroscopy

Tunneling spectroscopy modeling to improve and validate tomorrow technologies to explore the world at the nanoscale.

Prediction, Validation and Innovation

Enhance economic competitiveness by making of modeling a valuable tool to predict the features of next generation materials.

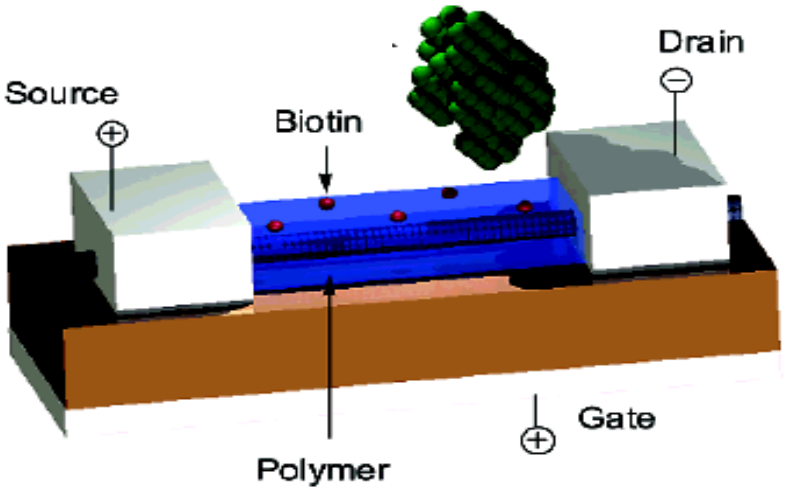
Bio-, photo-sensors

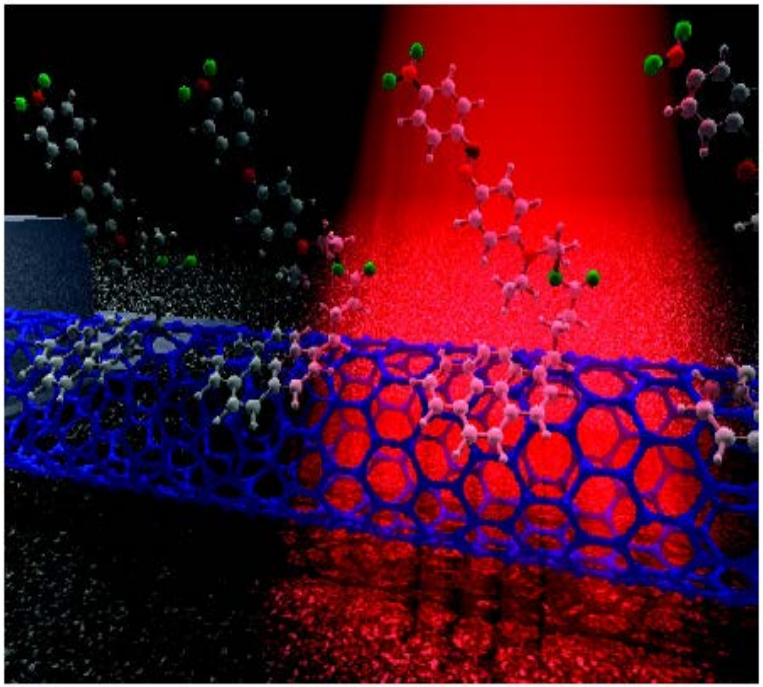


→ **Selective electrical signals of molecular adsorption events.**

→ **Protein interaction.**

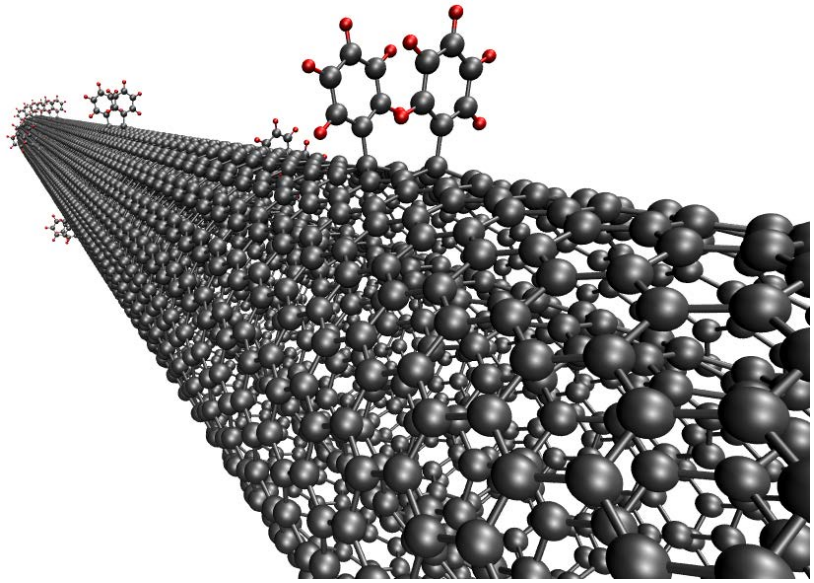
→ **Virus detection.**

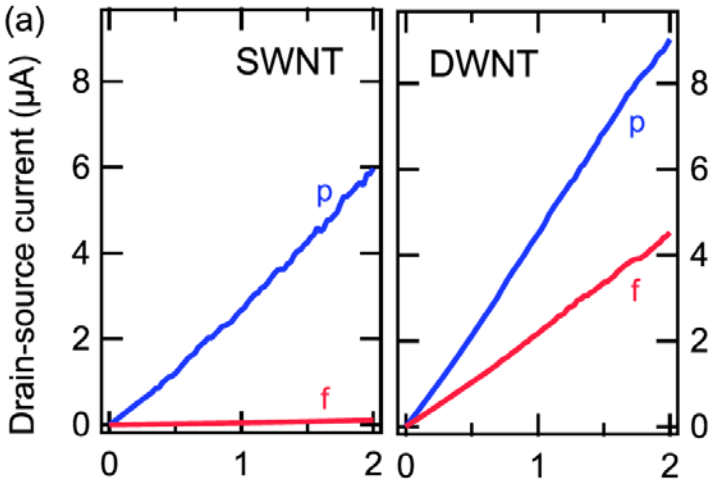




Zhou et al. Nano Letters 9, 1028 (2009)

An example



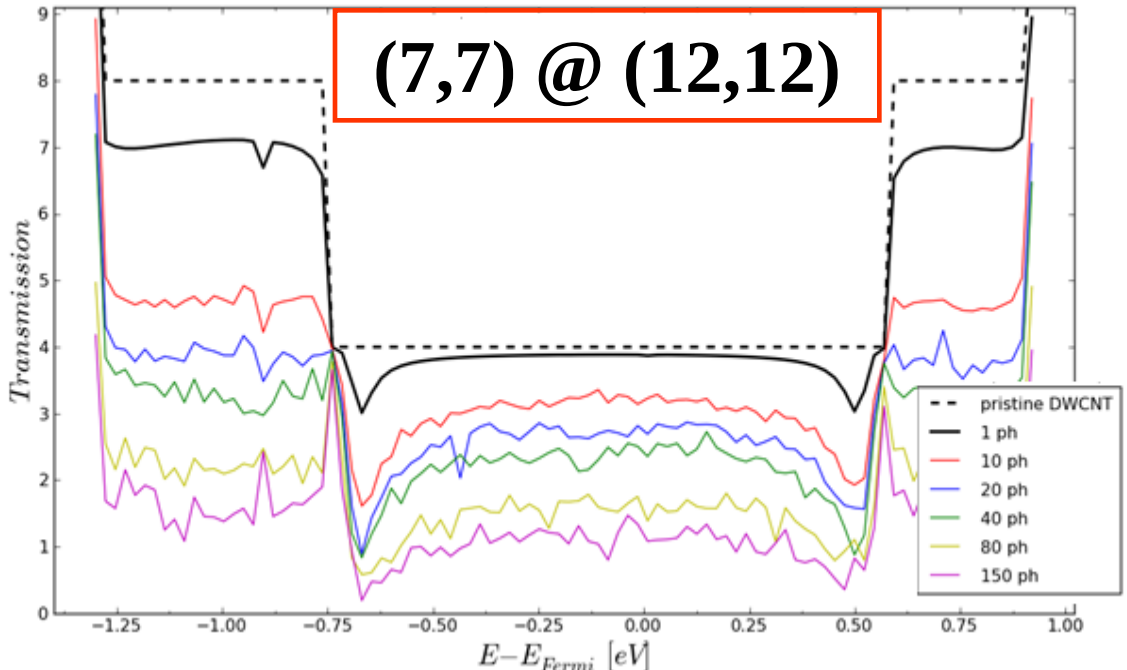


VOL. 5 ▪ NO. 6 ▪ 4927–4934 ▪ 2011 ACSNANO www.acsnano.org

→ Covalent functionalization in DWCNTs as an efficient approach to create electronic devices with enhanced conductivity.

→ DWCNT based transistors show that the current is carried by the inner tube.

→ How the inner tube is affected by the chemically modified outer tube?



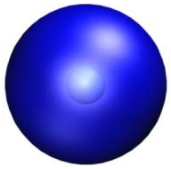
A two-step procedure

1st step

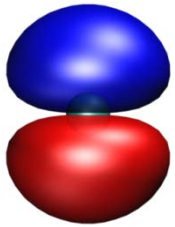
→ Efficient tool for *ab initio* **electronic structure** calculations.

→ We need a local descripiton of the atomic orbital hybridizations involved in the interaction between subsystems.

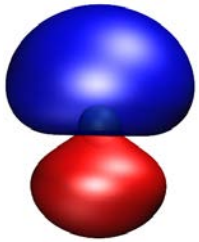
→ The overall Hamiltonian is in **sparse** format for transport calculation purposes.



s-orbital



p-orbital



sp-hybrid orbital

2nd step

→ **Transmission** and **reflexion** probabilities.

→ method of **O(N)**: inversion of Hamiltonian limits size of systems simulations.

→ **Accuracy.**

→ We want to determine the localization length, the **conductance** or the electronic transport regime of modified nanostructured materials.

Computational tools

siesta A linear-scaling density-functional method

JOURNAL OF PHYSICS: CONDENSED MATTER
PII: S0953-8984(02)30737-9

The SIESTA method for *ab initio* order-*N* materials simulation

José M Soler[1], Emilio Artacho[2], Julian D Gale[3], Alberto García[4], Javier Junquera[1,5], Pablo Ordejón[6] and Daniel Sánchez-Portal[7]

http://www.icmab.es/dmmis/leem/siesta/

$$\sum_{\substack{\text{atomic} \\ \text{site},\, j}} \sum_{\text{orbital},\alpha} [H_{i\alpha,j\beta} - E \cdot S_{i\alpha,j\beta}] C_{j\beta} = 0$$

$$H_{i\alpha,j\beta} = \langle \phi_{i\alpha} \mid H \mid \phi_{j\beta} \rangle$$

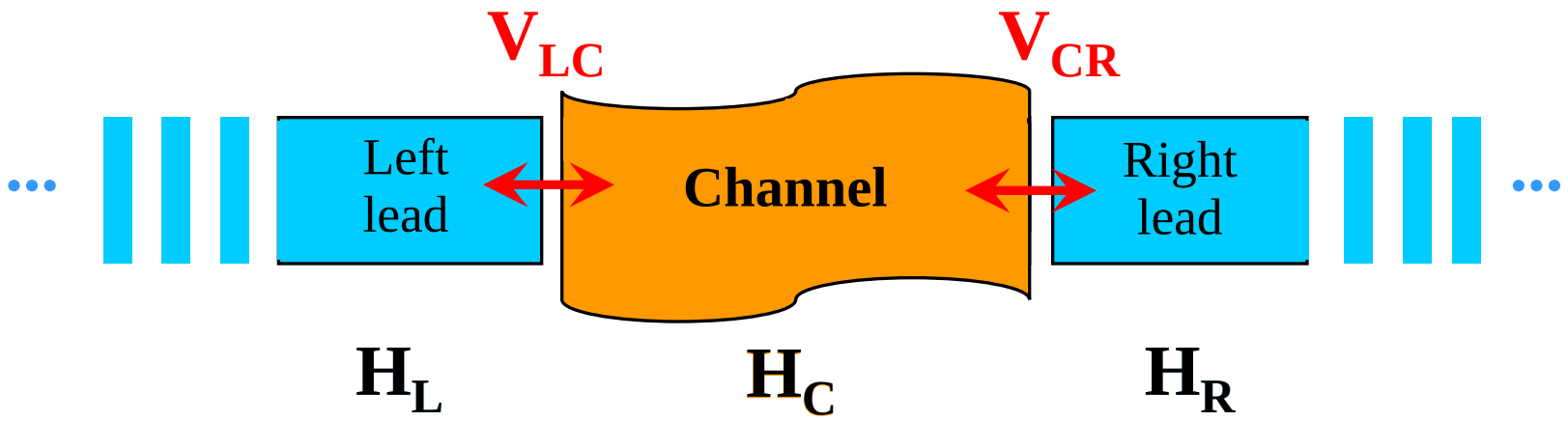
$$S_{i\alpha,j\beta} = \langle \phi_{i\alpha} \mid \phi_{j\beta} \rangle$$

→ SIESTA performs efficient *ab initio* electronic structure calculations of solids. Its efficiency stems from the use of strictly localized basis sets and from the implementation of **linear-scaling** algorithms.

→ Suitable approach for electronic **transport calculations**.

→ The SIESTA program is **distributed freely** to academics.

Mathematical approach



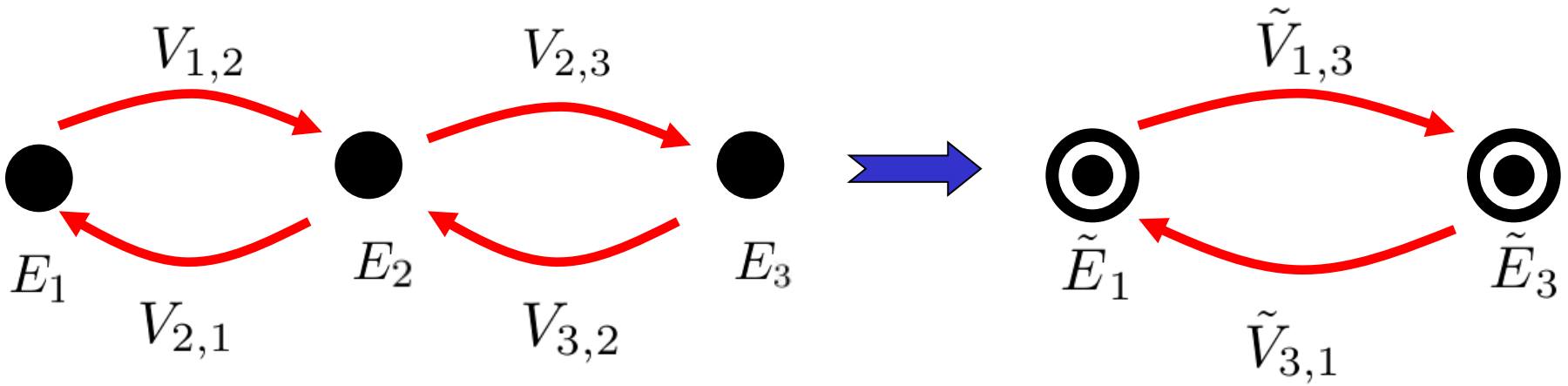
$$H = \begin{bmatrix} H_L & V_{LC} & 0 \\ V_{CL} & H_C & V_{CR} \\ 0 & V_{RC} & H_R \end{bmatrix}$$

∞ $\quad$ $\sim N_{atoms}$ $\quad$ ∞

Very long leads + Long channel (~ 100,000 atoms)

Renormalization techniques

Decimation: 3-site model



$$\begin{pmatrix} E_1 & V_{1,2} & 0 \\ V_{2,1} & E_2 & V_{2,3} \\ 0 & V_{3,2} & E_3 \end{pmatrix} \begin{pmatrix} a \\ b \\ c \end{pmatrix} = \epsilon \begin{pmatrix} a \\ b \\ c \end{pmatrix}$$

$$\begin{pmatrix} \tilde{E}_1 & \tilde{V}_{1,3} \\ \tilde{V}_{3,1} & \tilde{E}_3 \end{pmatrix} \begin{pmatrix} a \\ c \end{pmatrix} = \epsilon \begin{pmatrix} a \\ c \end{pmatrix}$$

→ A method to reduce the dimension of the Hamiltonian basis function space

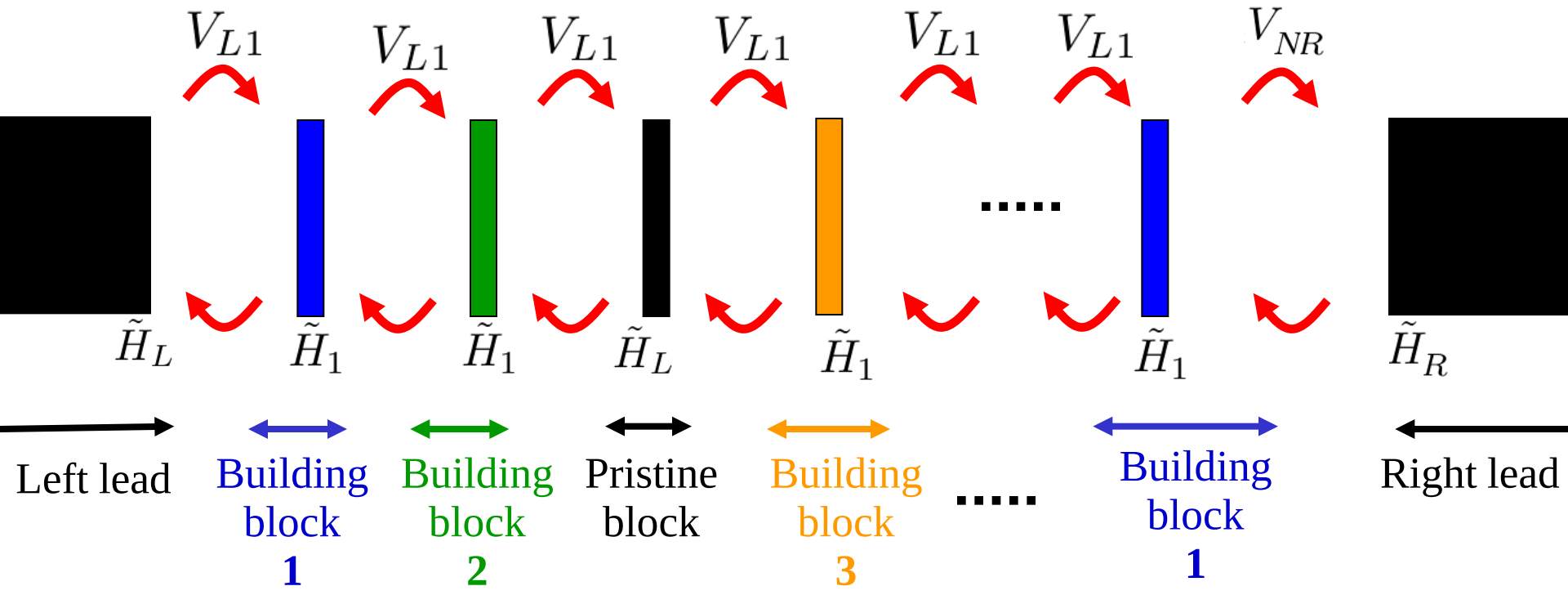
$$\tilde{E}_1(\epsilon) = E_1 + V_{1,2} \frac{1}{\epsilon - E_2} V_{2,1}$$

$$\tilde{E}_3(\epsilon) = E_3 + V_{3,2} \frac{1}{\epsilon - E_2} V_{2,3}$$

$$\tilde{V}_{1,3}(\epsilon) = V_{1,2} \frac{1}{\epsilon - E_2} V_{2,3} = \tilde{V}_{3,1}(\epsilon)$$

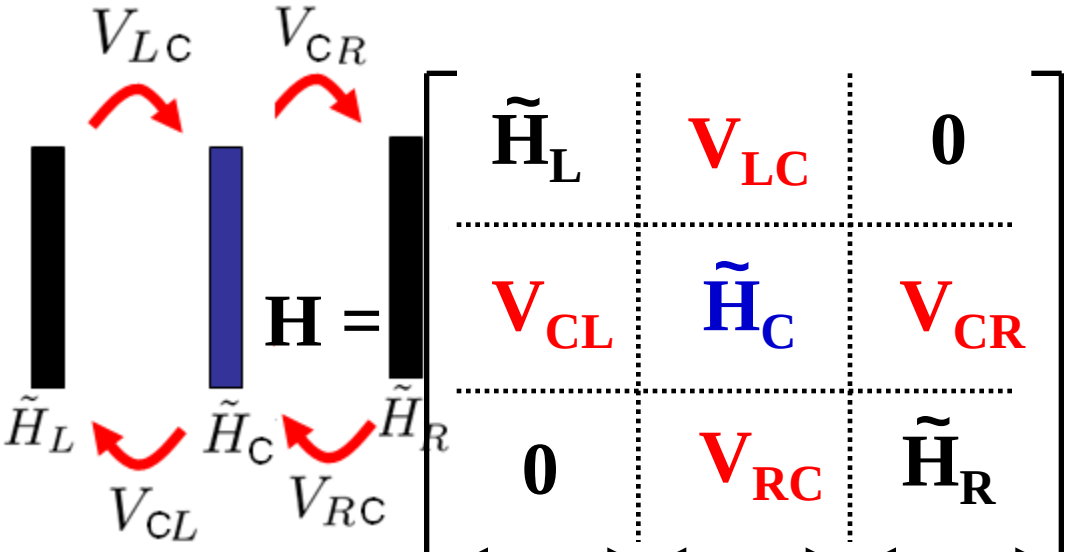
Long channel decimation

Linear scaling with length: method of N order



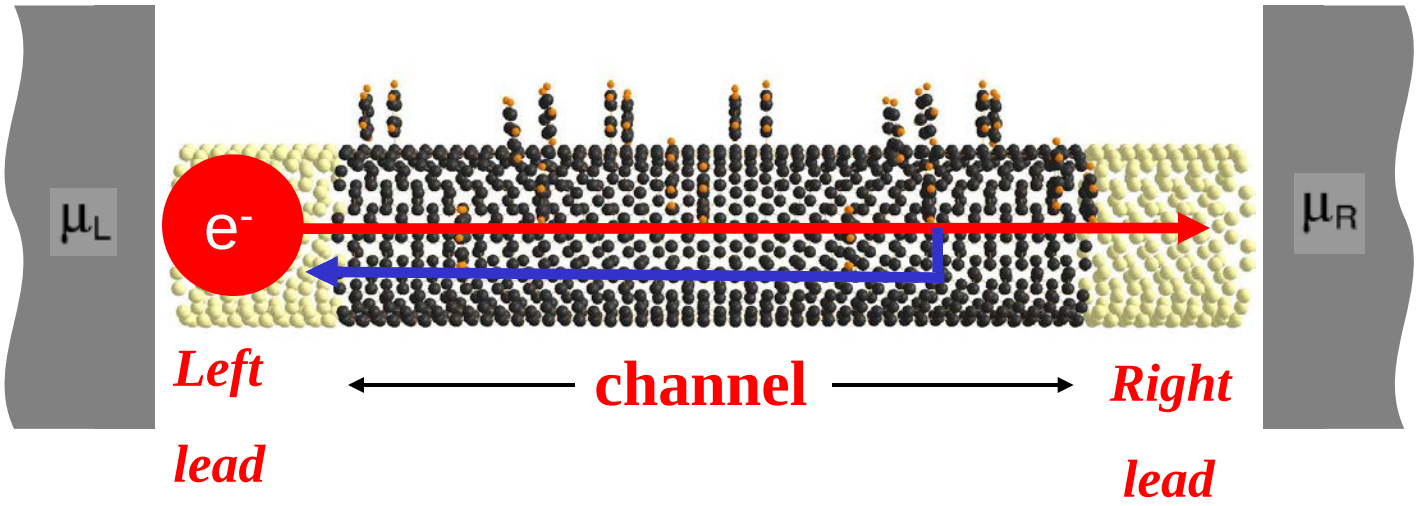
Finite system

→ Finite size Hamiltonian



Left lead Channel Right lead

Transport formalism



Conductivity :
(Landauer´s formula)

$$\mathcal{G}(E) = \frac{2e^2}{h} \sum_{m,n} T_{mn} = \frac{2e^2}{h} \mathrm{Tr}[\Gamma_L G^r \Gamma_R G^a]$$

Green´s Function :

$$G^{r,a}(E) = \frac{1}{E - \mathcal{H}_{Sys} - \left(\Sigma_L^{r,a}(E) + \Sigma_R^{r,a}(E)\right)}$$

Ab initio Hamiltonian

$\sum_{L,R}^{r,a}(E) \equiv$ ***Self-energy due to lead-channel coupling***

$$\Gamma_{L,R}(E) \equiv \mathrm{Im}\left\{\sum_{L,R}^{r,a}(E)\right\}$$

Definition and implementation

Green Function, G

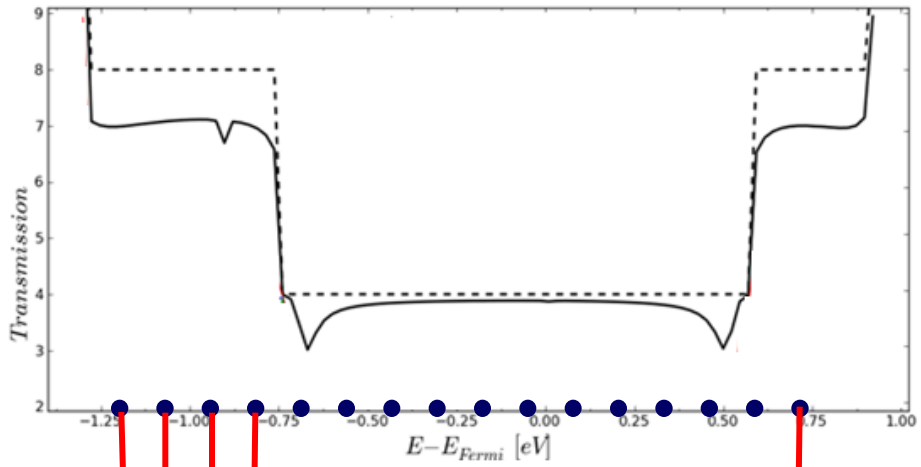
at a given energy value, E

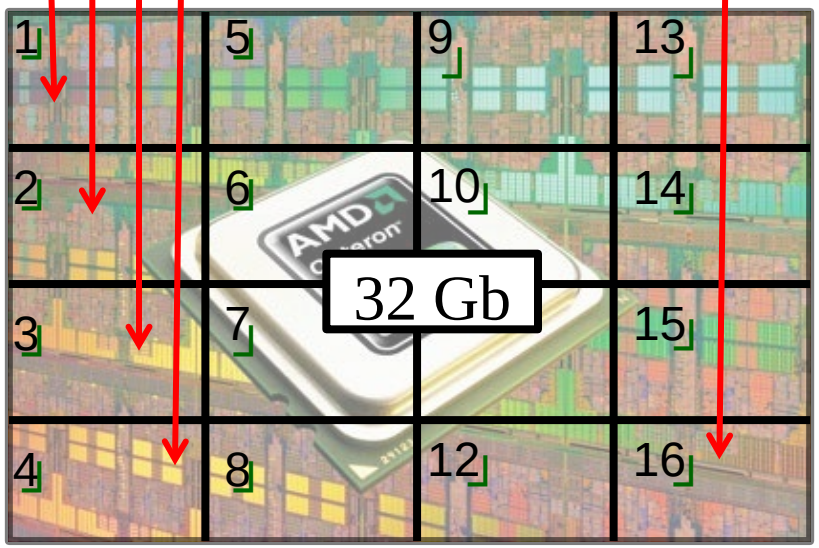
$$G(E) = \frac{1}{E \cdot S - H}$$

where:

H is the system Hamiltonian.

S is the overlap matrix.





16-core 2.2GHz AMD Opteron™ 6274 (Interlagos)

Exascale will have a broad and positive impact on U.S. industrial competitiveness.

The implementation of a formalism based on the Green Function for the exploration of new material physical properties allows for the application of a framework based on a multi-scale approach that connects the quantum-mechanically description of the material with its micrometer-level features.

Within this framework, massive and straightforward parallelization at the exascale is possible by dividing the overall problem into multiple equivalent problems of reduced complexity.

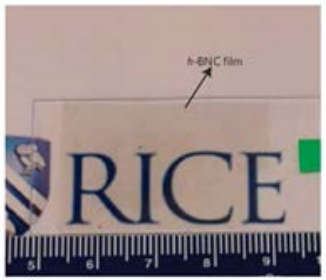
Chemically modified nanostructured materials

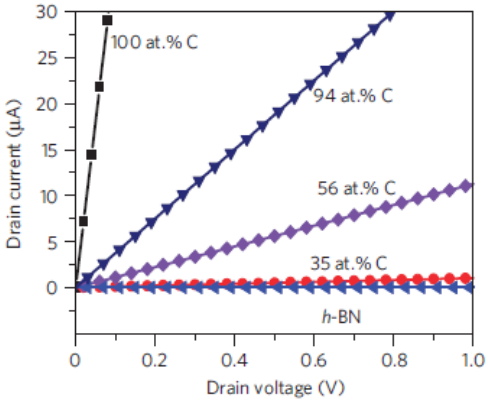
Hybrid BN-C Nanostructures

ARTICLES
PUBLISHED ONLINE: 28 FEBRUARY 2010 | DOI: 10.1038/NMAT2711
nature materials

Atomic layers of hybridized boron nitride and graphene domains

Lijie Ci[1†], Li Song[1†], Chuanhong Jin[2], Deep Jariwala[1‡], Dangxin Wu[3], Yongjie Li[1‡], Anchal Srivastava[1‡] Z. F. Wang[3], Kevin Storr[4], Luis Balicas[5], Feng Liu[3] and Pulickel M. Ajayan[1*]

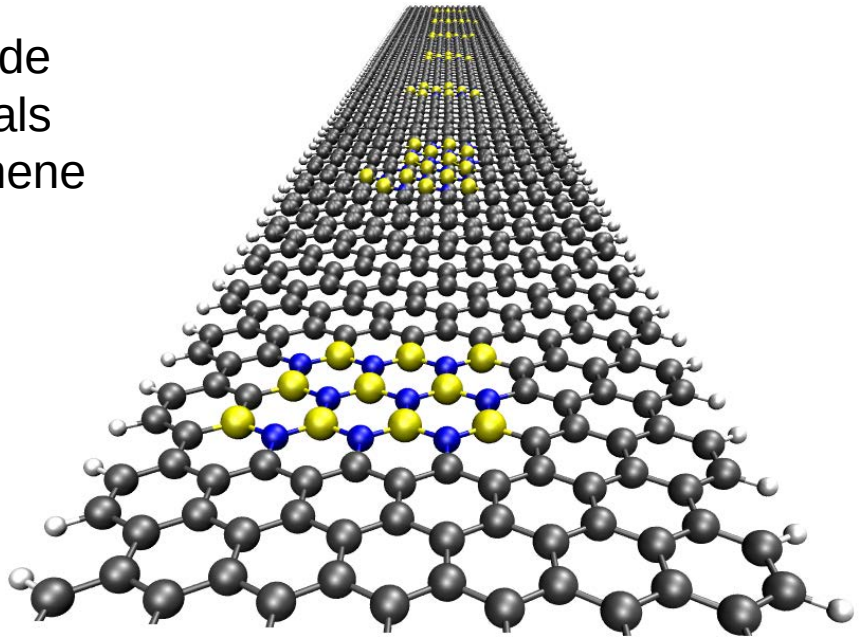




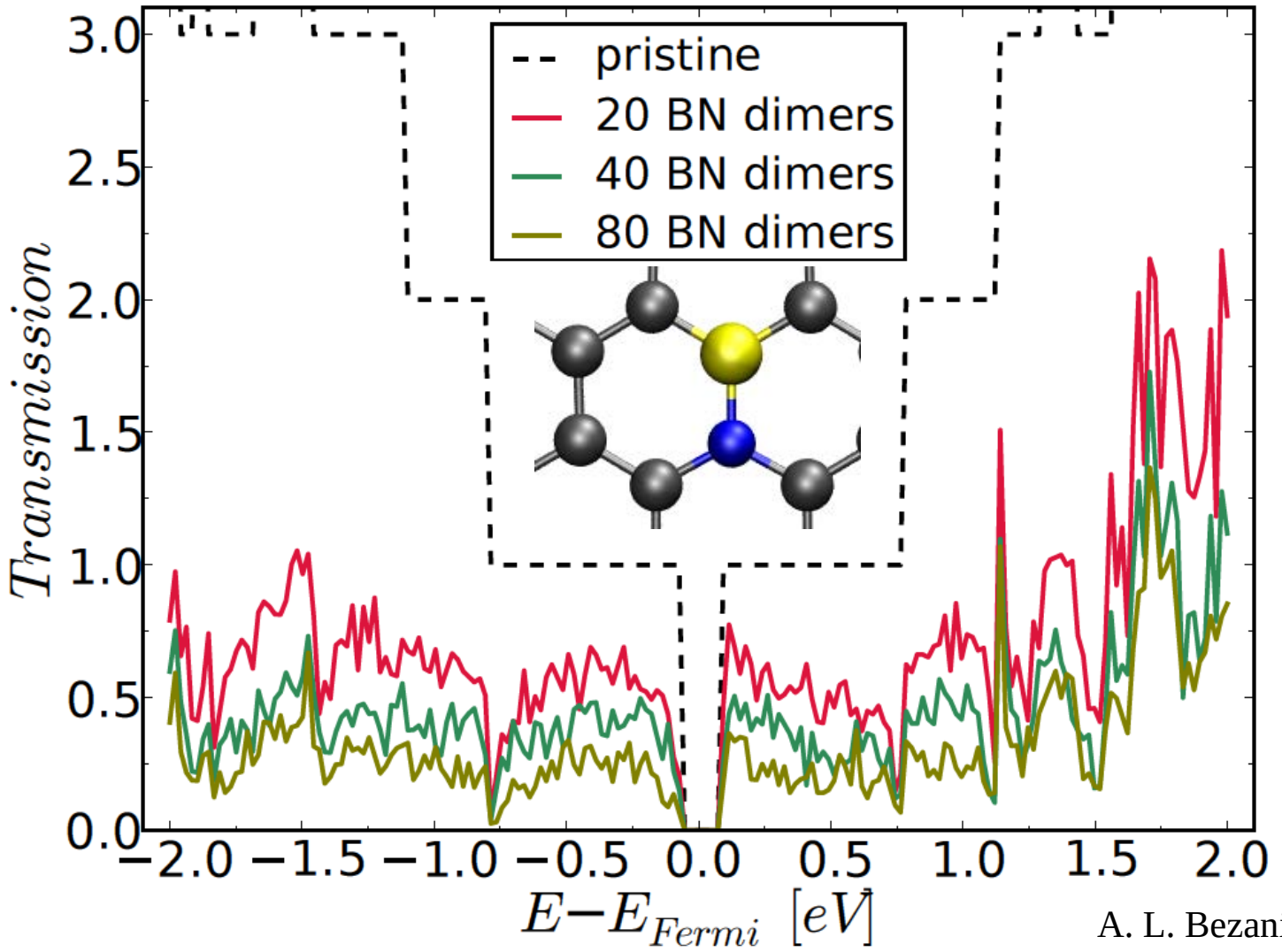
→ BN-C nanostructures for technologic applications.

→ Atomic sheets containing B, N and C over wide compositional ranges could result in new materials with properties complementary to those of graphene and *h*-BN, enabling a rich variety of electronic structures, properties and applications.

→ BN nanoscale patchworks to tackle graphene band gap.



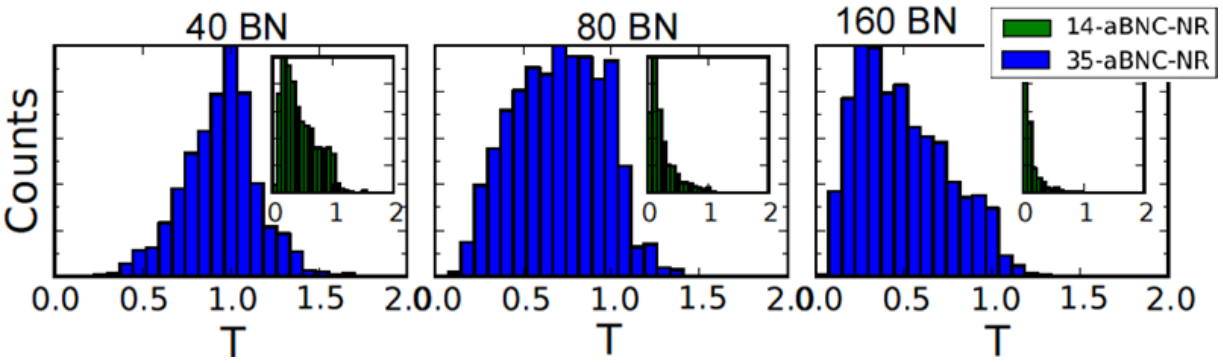
2 μm long ribbons (~ 100 configurations)

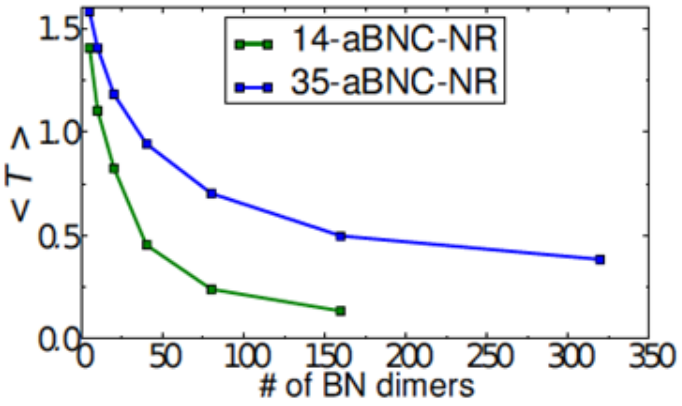


A. L. Bezanilla, S.Roche

Submitted (2012)

Exploring e$^-$ transport regimes





→ The versatility in the conduction properties offers interesting opportunities for transport gap engineering for the design of complex architectures based on this new hybrid material. From accurate first-principles calculations we can explore transport regimes, from ballistic to localize.

***Jaguar*, Cray XK6**

· For each histogram/point in the curve:

#PBS -l walltime=4:00:00,size=2560

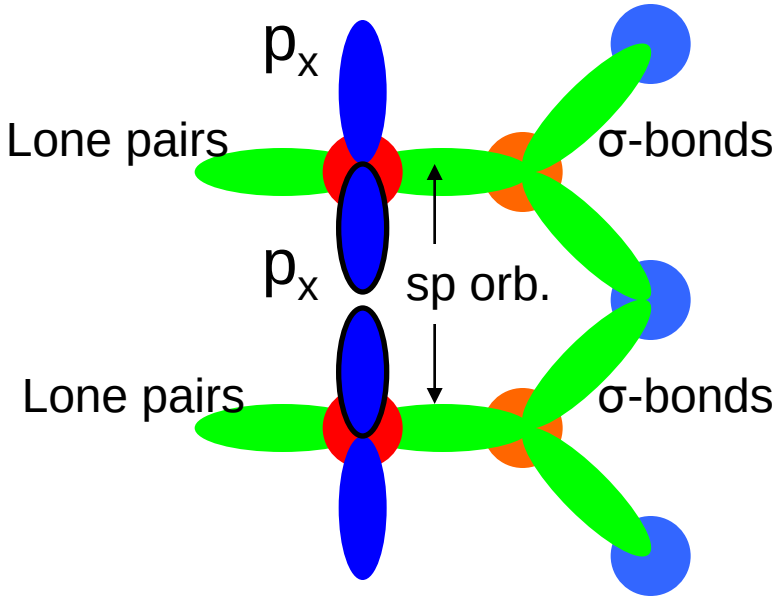
aprun -n 1280 –N 8 transmission.ex < input.dat

→ 1 type of disordered system.

→ ~10^3 of configurations.

→ x 20 different systems.

Materials by design



→ O termination yields **magnetic states**.

→ **Metallic states** related to O p_x-orbitals.

→ Enhanced electric conductivity in boron nitride material from experimental measurement.

b-initio VASP ackage ienna imulation

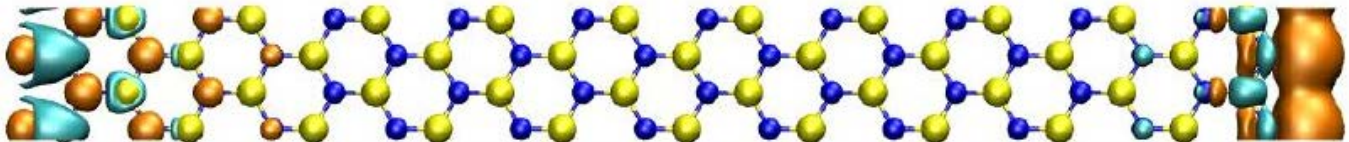
→ Exact exchange and hybrid PBE0 functional.

→In-home modification of the code.

→ Comparison with LDA yields to similar conclusions

→ Too slow for material composed over 100 atoms.

Boron Nitride Nanoribbons Become Metallic
A. López-Bezanilla, J. Huang, B. Sumpter, H. Terrones. Nano Letters 2011, 11, 3267



VASP Optimization

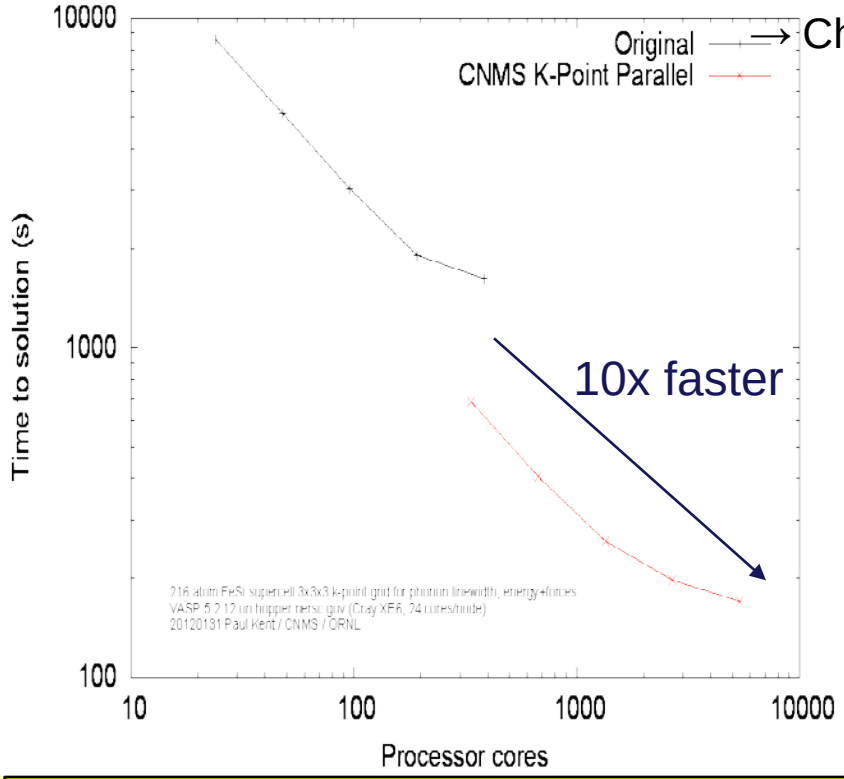
b-initio VASP ackage ienna imulation

→ Code modifications by **Paul Kent** at CNMS at ORNL

→ Ongoing collaboration between ORNL user facilities

→ Increases scalability by >>10x for science runs in this talk

→ Changes will be distributed. For now email pk7@ornl.gov

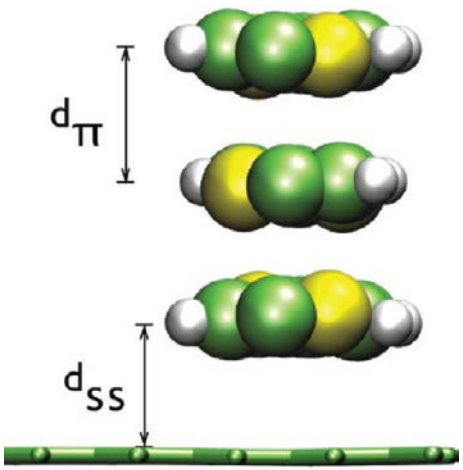


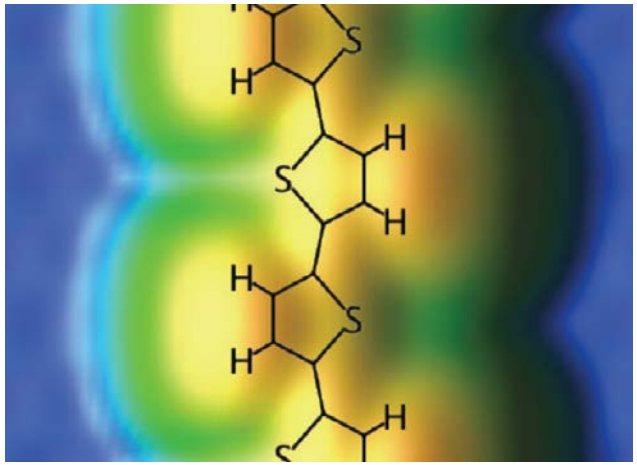
K-point parallelization of local DFT ("trivial" but mysteriously not previously implemented in VASP 5.2.12) gives linear scalability increase with # k-points.

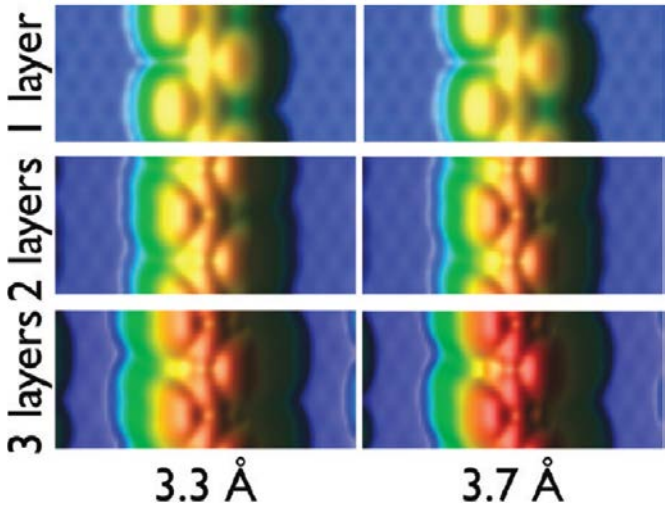
Most solid-state or surface calculations require some k-points. e.g., all "materials project" runs (Ceder@MIT)

Full k-point parallelization of hybrid DFT (not trivial) near production ready; validation ongoing March 2012. One-sided and threaded implementation to follow, allowing larger systems to be studied by overcoming memory bottlenecks + giving much faster time-to-solution.

Imaging the nanoscopic world







· The influence of p-interactions in thin layers of stacked polymers has been studied with first-principles calculations and Spectroscopy Tunneling Microscopy (STM) simulations.
Journal of Physical Chemistry C, 15, 2011

· STM constitutes a powerful technique to probe the existence of p-electron interactions in p-conjugated stacks.

· STM simulations were performed with the Strongly Parallel Adaptive Grid Solvers software at Montreal University to evaluate topographic mode images and scanning tunneling spectra (STS). The software includes several algorithmic strategies, such as parallel computation of the tunnel currents and adaptive grids that minimize the probing sites needed to obtain a high resolution image.
Bedwani, S.; Guibault, F.; Rochefort, A. «*Nanoscale adaptive meshing for rapid STM imaging*." J. Comput. Phys. 2008, 227, 6720-6726.

Publications @ ORNL

· Papers

→ **Embedded Boron Nitride Domains In Graphene Nanoribbons For Transport Gap Engineering.**

A. López-Bezanilla, S. Roche, Submitted

→ **Conductance Distributions in Doped Single Wall Carbon Nanotubes: Ab Initio Calculations Versus Macroscopic Models**

A. López-Bezanilla, L. Froufe, S. Roche, J.J. Sáenz. In preparation

→ **Structure and Electronic Properties of Edge-Functionalized Armchair Boron Nitride Nanoribbons**

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→ **Transport Gap Engineering in Graphene Nanoribbons Using Surface Functionalization**

A. Cresti, A. López-Bezanilla, P. Ordejon, S. Roche

ACS Nano, 2011, 5 (11), 9271 (link)

→ **Boron Nitride Nanoribbons Become Metallic**

A. López-Bezanilla, J. Huang, B. Sumpter, H. Terrones.
Nano Letters 2011, 11, 3267 (link)

→ **Probing π-Interactions In Stacked Polymers by STM and DFT**

A. Rochefort, S. Bedwani, A. López-Bezanilla.
Journal of Physical Chemistry C, 15, 2011 (link)

· Book and Encyclopedia Chapters

→ **Practical Aspects of Computational Chemistry II: An Overview of the Last Two Decades and Current Trends**

J. Huang, A. Beste, J. Younker, A. V. Mayagoitia, E.C.Silva, M. F.Cabrera, J. Jakowski, A.L.Bezanilla, V. Meunier, B. G. Sumpter
Chapter Book, to be published in Springer Editorial

→ **Electronic Transport in Carbon Nanomaterials**

A. López Bezanilla, S. Roche, E. Cruz-Silva, B. Sumpter, V. Meunier
Encyclopedia Chapter (to be published in Springer Editorial)

Summary

• Real space normalization mathematical procedures in combination with chemical codes for electronic structure calculations allow us to connect quantum description of new materials with typical length scales of microscopic devices.

• In the linear regime, recursive techniques allow us to calculate within O(N) the Green function matrix elements of a device channel connecting two electrodes

• Parallelization over thousands of nodes scales linearly with the number of disordered configurations.

• Several density functional theory based codes with different degrees of accuracy and applicability have been successfully ran in the exascale computing resources at ORNL.

• We have proved the validity of a multiscale approach as explaining the physical properties of micrometer-long new materials from the quantum description.

Future plans

→ Explore more advanced methodologies to reduce the computational time of the channel Green function calculation.

→ Employ a hybrid CPU/GPU algorithm that off-loads part of the matrix inversion computations to the GPU while using in sync the general-purpose CPU nodes of the platform.

→ Implement BigDFT code in hybrid architecture for large DFT calculations.

→ Incorporate to the transport description the role of lattice vibrations.

→ Keep innovating and developing next generation materials:

"*Innovation also demands basic research. Today, the discoveries taking place in our federally financed Labs and Universities could lead to new treatments that kill cancer cells but leave healthy ones untouched… Support the same kind of research and innovation that led to the computer chip and the Internet; to new American jobs and new American industries*."

President B. Obama s speech at the 2012 State of the Union Address.

Thanks for your attention