

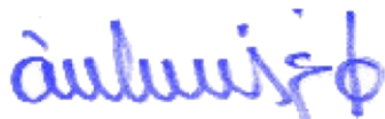


Hace constar que:

## Andrés Jaramillo Botero


Participó en el 1er Taller Anual: Del Gen al Cultivo como PONENTE -Diseño y Caracterización in-silico de primeros principios de nano-sensores (dispositivos por efecto de campo).

En constancia de lo anterior, se firma en Santiago de Cali a los siete (07) días del mes de diciembre de 2019.



---

Andrés Jaramillo Botero  
Director Científico



---

Luis Eduardo Tobón  
Subdirector Fortalecimiento Institucional

Apoyan:



El futuro  
es de todos

Gobierno  
de Colombia



COLOMBIA  
CIENTÍFICA  
Conocimiento Global para el Desarrollo





Andres Jaramillo Botero  
Director Científico



## Taller anual: Del Gen al Cultivo

**P2: Bio-Nanosensores:** Prof. Andres Jaramillo Botero y Dr. Juan Manuel Marmolejo (práctica)

**P3: Modelado Bio-Molecular:** Prof. Carlos Arango y prof. Andres Jaramillo Botero

### Parte I

Principios de Simulación Molecular

### Parte II

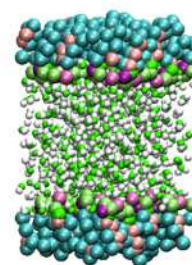
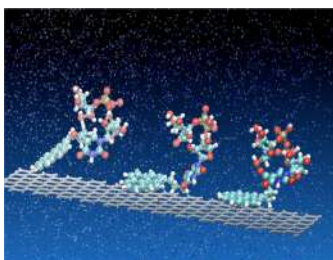
Simulación Molecular Aplicada a:

Nano Sensores Bio

Sistemas biológicos

Andres Jaramillo-Botero  
Juan Manuel Marmolejo

Carlos Arango



Nanosensores



# Taller anual: Del Gen al Cultivo

Prof. Andres Jaramillo Botero  
Dr. Juan Manuel Marmolejo (práctica)

## Taller 2: Diseño de nanosensores para biomarcadores

### Contenido:

- Fundamentos de la nano-escala
- Estructura electrónica de materiales
- Mecánica y Dinámica Molecular
- Bio-nano-sensores
- Nano-sensores (efecto de campo)
- Transporte electrónico en dispositivos
- Propiedades termodinámicas

### Nanosensores



El futuro  
es de todos

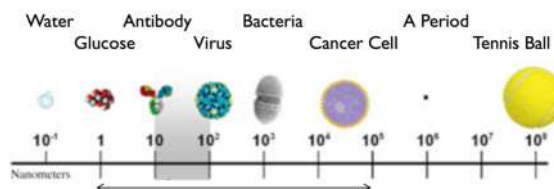
Gobierno  
de Colombia

COLOMBIA  
CIENTÍFICA



## Objective

In-silico design, characterization and screening of nano-sensor device architectures for detection of biomarkers at nM-pM/L concentrations (mM/L)



**Very low concentration single and multi-analyte sensing!!**  
Single grain of salt in several Olympic-sized pools!

### Nanosensores

Jaramillo-Botero y Marmolejo, 2019



El futuro  
es de todos

Gobierno  
de Colombia

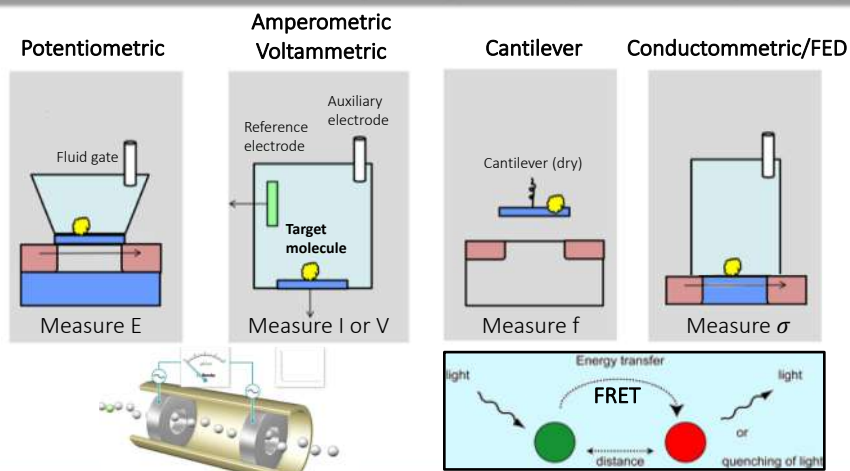
COLOMBIA  
CIENTÍFICA





# Nano-bio-sensing mechanisms

Surface functionalization, key to improve target selectivity/affinity



Nanosensores

Jaramillo-Botero y Marmolejo

2019

Estado de todos

Gobierno de Colombia

COLOMBIA CIENTIFICA

ÓMICA

## Indirect Sucrose Sensors

1. NP FRET

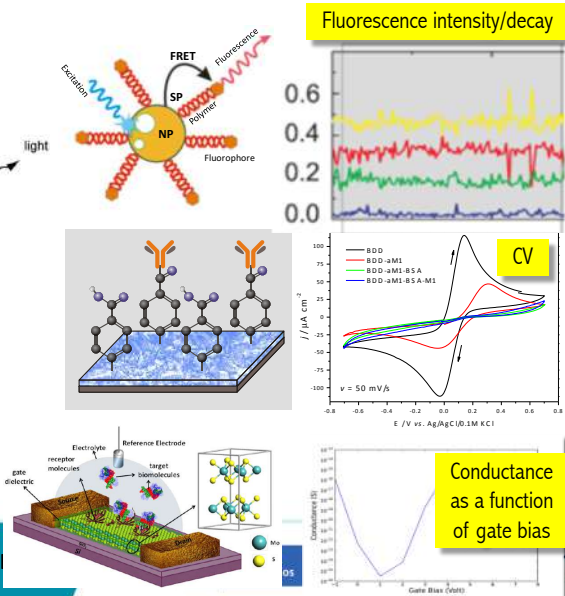
2. Electrochemical

3. FEDs

Focus on cytoplasmic sensing

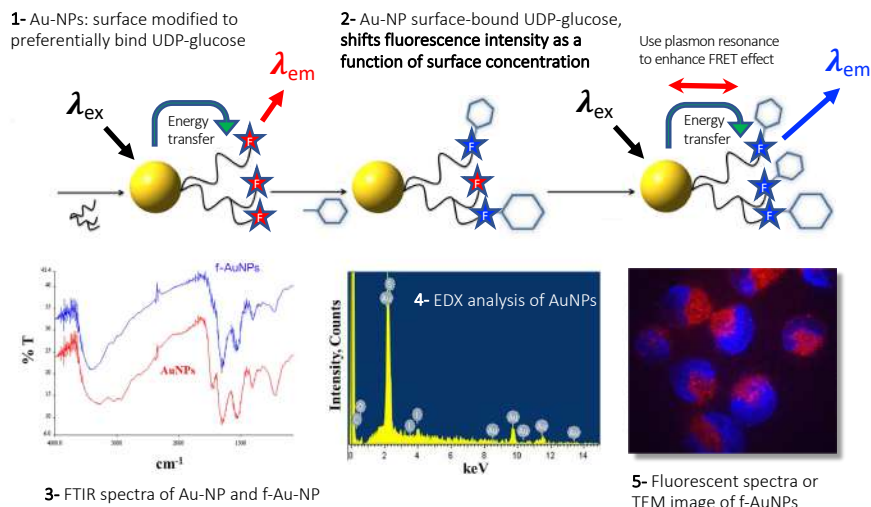
Nanosensores

Jaramillo-Botero y Marmolejo



ÓMICA

## In-Vivo Gold-nanoparticle-based Sucrose/Starch FRET sensors



Nanosensores

Jaramillo-Botero y Marmolejo, 2019

El futuro es de todos

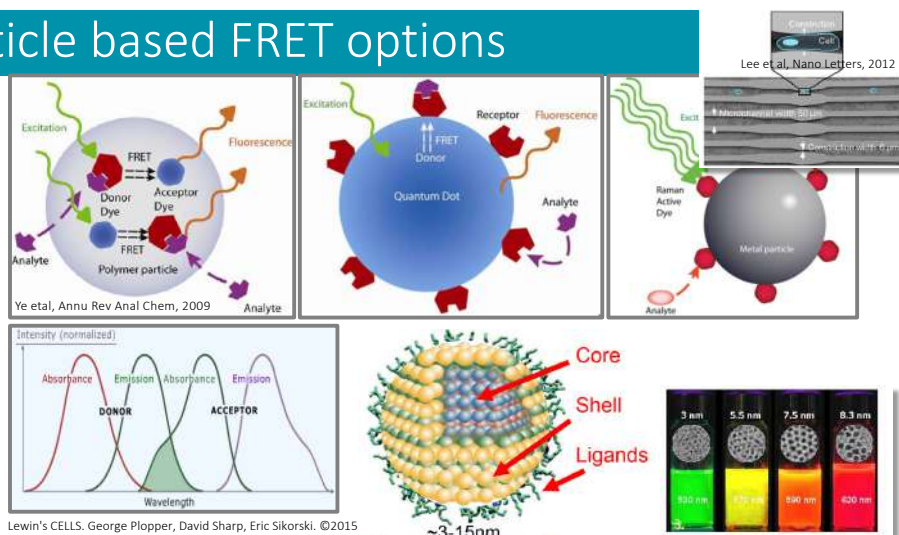
GOBIERNO DE COLOMBIA

COLOMBIA CIENTÍFICA



Jaramillo-Botero y Marmolejo, 2019

## Nanoparticle based FRET options



**Challenges:** cytosolic delivery of QDs and NPs to target, environment (autofluorescence of intracellular compar

The smaller the QD, the larger the energy gap between the energy levels and hence the higher the frequency of light emitted

Nanosensores

El futuro es de todos

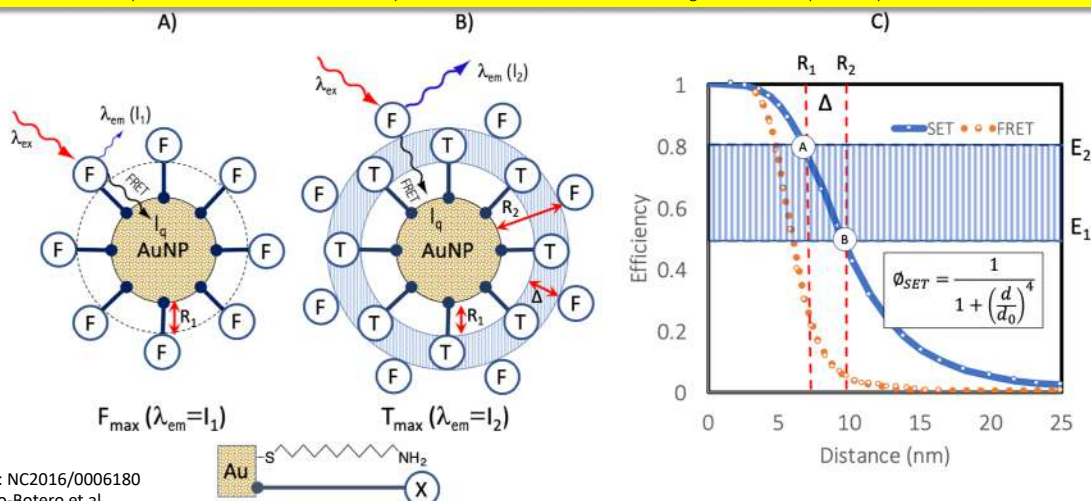
GOBIERNO DE COLOMBIA

COLOMBIA CIENTÍFICA



## SET quenching

Changes in fluorescence spectra of the nanobiosensor in the presence of different concentrations of glucose under optimal experimental conditions.



Nanosensores

Jaramillo-Botero y Marmolejo, 2019

Estado de todos

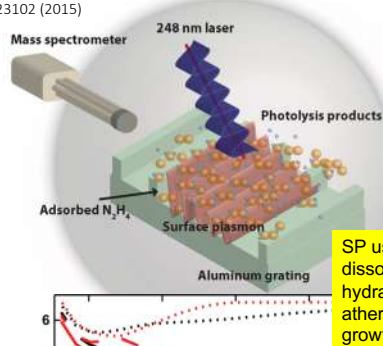
Gobierno de Colombia

COLOMBIA CIENTÍFICA

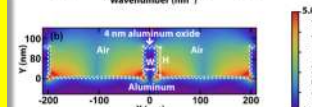
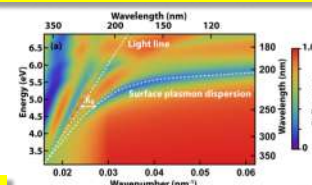
ÓMICA

## Plasmon enhanced SET/FRET

Peng, Sheldong, Jaramillo-Botero, Atwater, et al,  
Applied Physics Letters 106, 023102 (2015)



248 nm incident photons, show strong field confinement near the surface



SP used to dissociate hydrazine in athermal GaN growth

Surface Plasmons from Au coated NPs can extend FRET range to ~100nm; may amplify signal/noise and allow extra-cellular communication between donor-acceptor pair

Nanosensores

Jaramillo-Botero y Marmolejo, 2019

Estado de todos

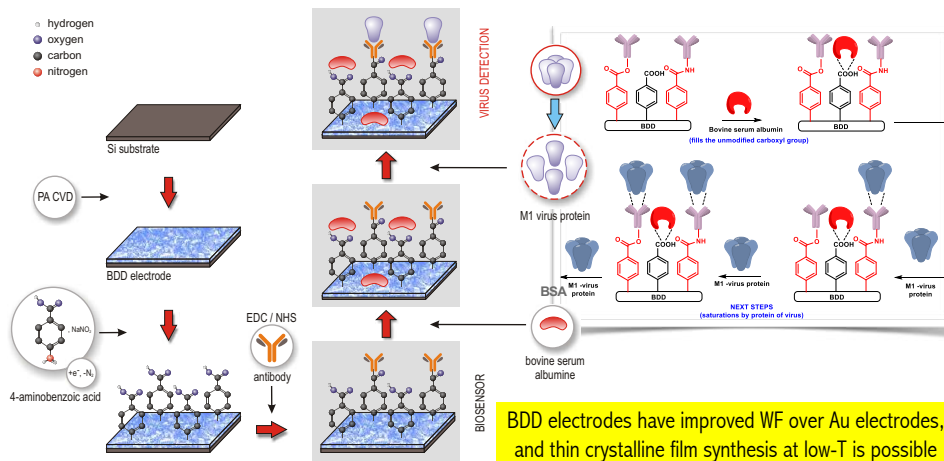
Gobierno de Colombia

COLOMBIA CIENTÍFICA

ÓMICA

## Electrochemical: influenza case

D. Nidzworski, K. Siuzdak, P. Niedziałkowski, R. Bogdanowicz, M. Sobaszek, J. Ryl, P. Weiher, M. Sawczak, E. Wnuk, W.A. Goddard, A. Jaramillo-Botero and T. Ossowski in prep for submission to Science, 2016



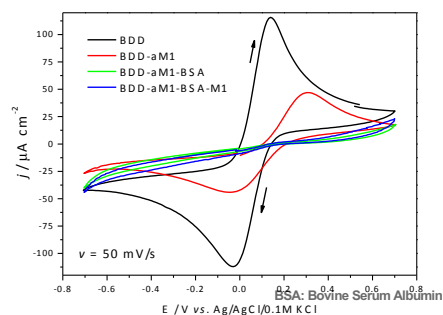
BDD electrodes have improved WF over Au electrodes, and thin crystalline film synthesis at low-T is possible

## Nanosensores

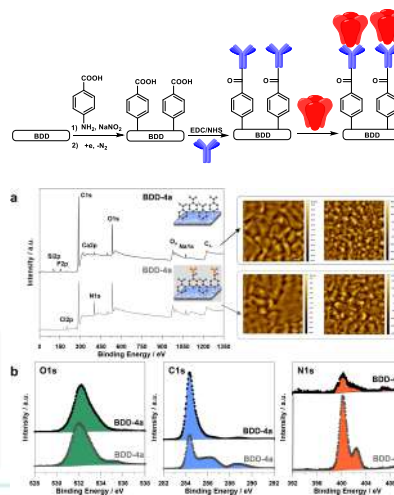


## Electrochemical: results

D. Nidzworski, K. Siuzdak, P. Niedziałkowski, R. Bogdanowicz, M. Sobaszek, J. Ryl, P. Weiher, M. Sawczak, E. Wnuk, W.A. Goddard, A. Jaramillo-Botero and T. Ossowski under submission to Nature Nanotechnology, 2016



For pristine BDD electrode the difference between oxidation and reduction potential peak equals 0.17 V, whereas when M1 antibody was bound, current decreases and potential difference grows to 0.36 V. After incubation of BDD-aM1 electrode in BSA or M1 protein solution, no oxidation or reduction peak was observed. Drastic change in CV from efficient blockage of e- transfer between electrode and redox active species

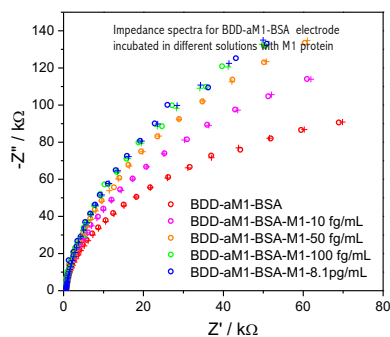


## Nanosensores

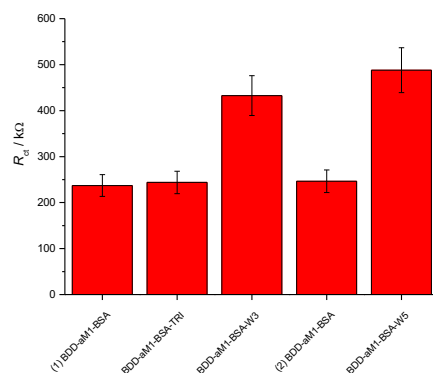


## Impedance spectra and EEQC

Impedance analyzed on the basis of an electric equivalent circuit (EEQC) using an EIS

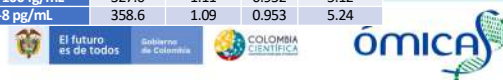


Impedance spectra of BDD-aM1-BSA electrode after incubation with different M1 concentrations recorded in 1 mM  $K_3Fe(CN)_6$  + 0.1 PBS at  $E_f = +0.13$  V vs. Ag/AgCl/0.1M KCl

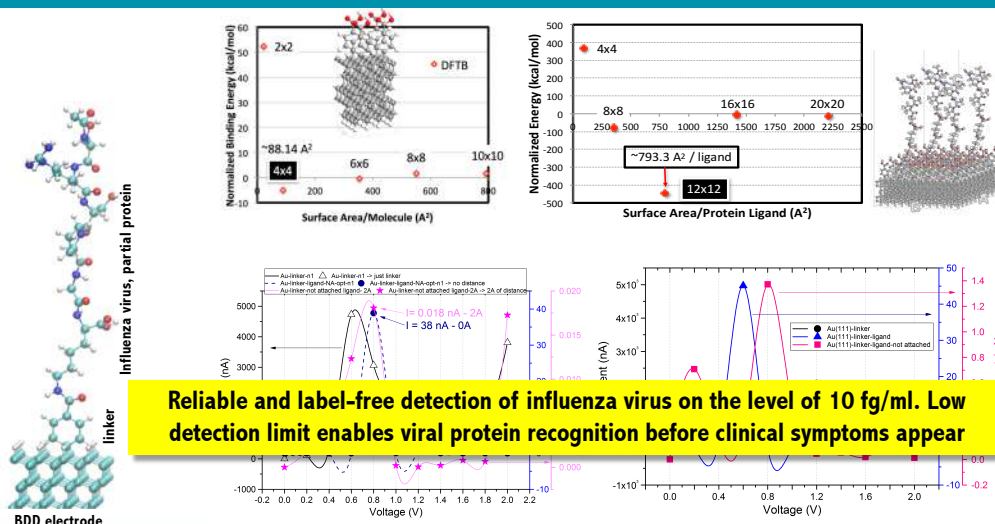


sample	$R_o / \Omega$	$Q_{ct} / \mu F \Omega^{-1} s^n$	$n$	$R_{ct} / 10^3 \Omega$
BDD-aM1-BSA	391.7	1.18	0.944	2.13
BDD-aM1-BSA-10 fg/mL	325.9	1.15	0.948	3.20
BDD-aM1-BSA-50 fg/mL	389.5	1.13	0.955	4.28
BDD-aM1-BSA-100 fg/mL	327.0	1.11	0.952	5.12
BDD-aM1-BSA-8 pg/mL	358.6	1.09	0.953	5.24

Nanosensores



## Surface coverage and IV analysis



**Reliable and label-free detection of influenza virus on the level of 10 fg/mL. Low detection limit enables viral protein recognition before clinical symptoms appear**

Nanosensores

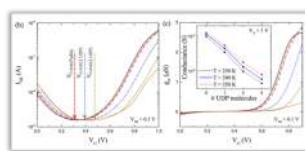




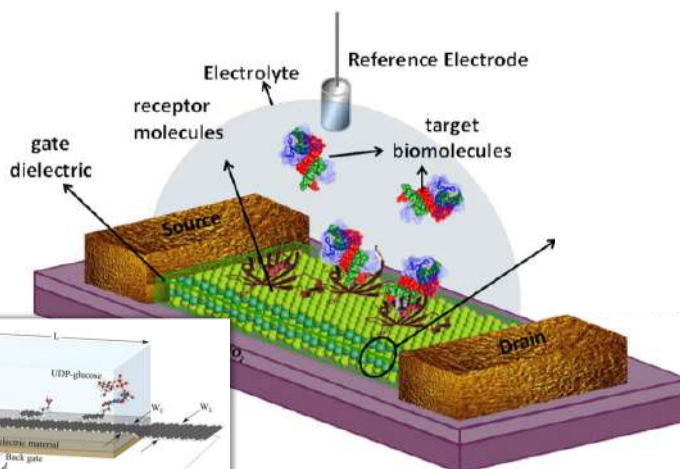
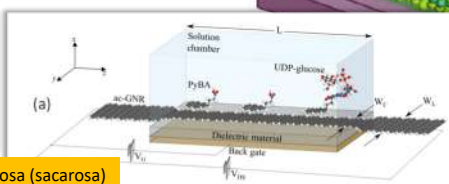
Jaramillo-Botero y Marmolejo, 2019

## Field Effect Devices (FEDs)

A. Jaramillo-Botero and Marmolejo-Tejada, IEEE Sensors, 2/2019



Nano sensor de grafeno para UDP-glucosa (sacarosa)



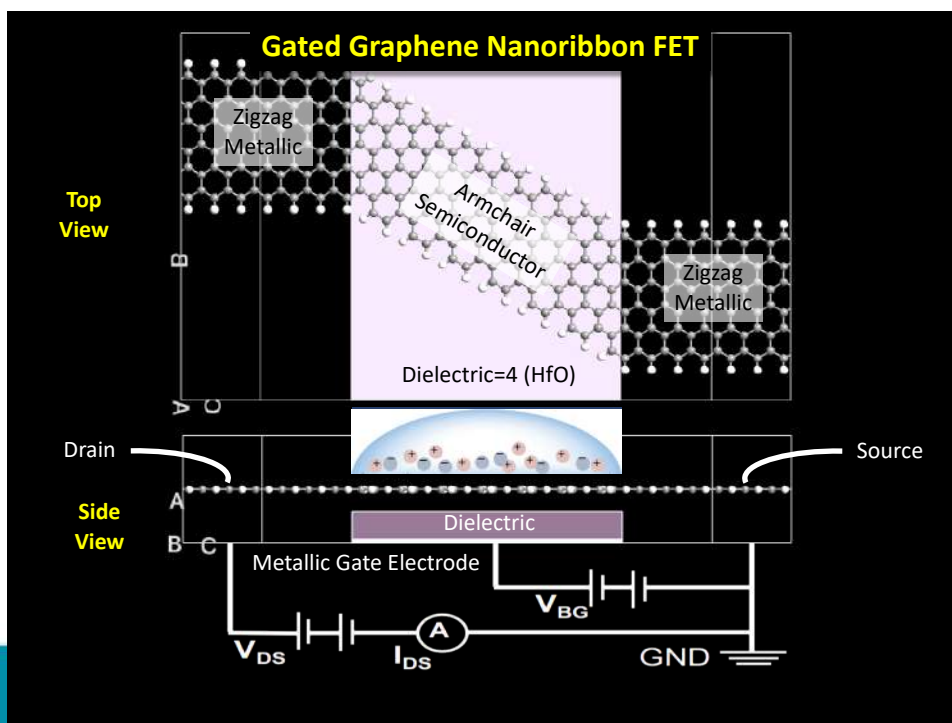
## Nanosensores



El futuro es de todos

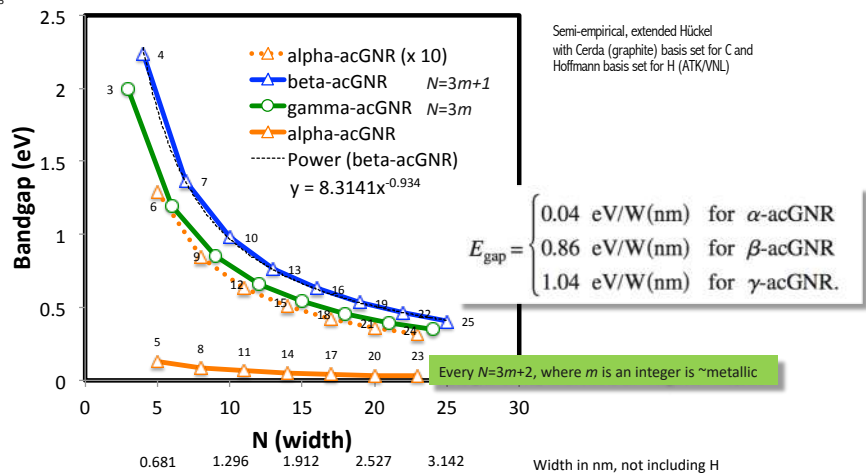
Gobierno Nacional de Colombia

COLOMBIA CIENTIFICA



## ac-GNR Bandgap

Confirmed experimentally in NATURE COMMUNICATIONS |  
DOI: 10.1038/ncomms10177, Dec. 2015



Band gaps and effective masses are inversely proportional to width, yet with a different proportionality constant

Nanosensores

Jaramillo-Botero y Marmolejo, 2019

Ministerio de Ciencia, Tecnología e Innovación

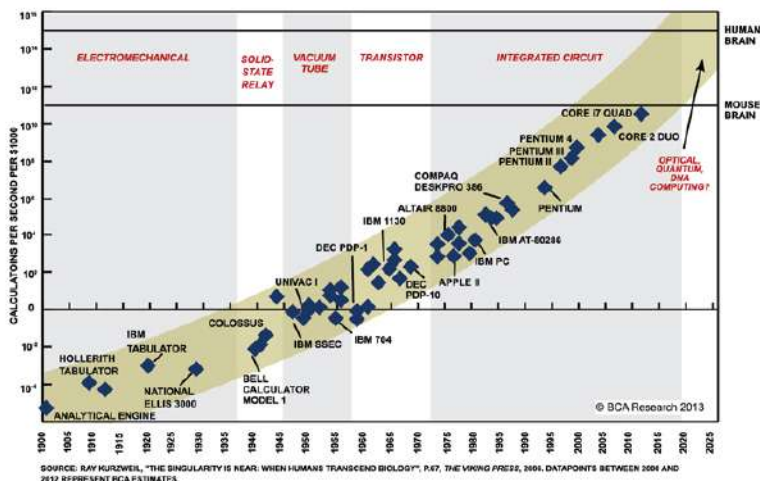
Gobernación de Cundinamarca

COLOMBIA CERTIFICADA



Computational Science

## Computers: Moore's law



## Nanosensores



El futuro  
es de todos

Gobierno  
de Colombia

COLOMBIA  
CIENTIFICA



## Computational Science: any, and all fields

- Computational:
  - Physics
  - Chemistry
  - Biology
  - Cosmology
  - Climate Modeling
  - ... and much more
- We can now simulate:
  - The (almost) exact quantum behavior of a thousand atoms
  - The approximate dynamic behavior of millions of atoms
  - Protein folding geometries during entire folding process
  - 3-dimensional, transient, turbulent reacting combustive flows
  - Global climate with 50 km resolution for next 200 years

## Nanosensores



El futuro  
es de todos

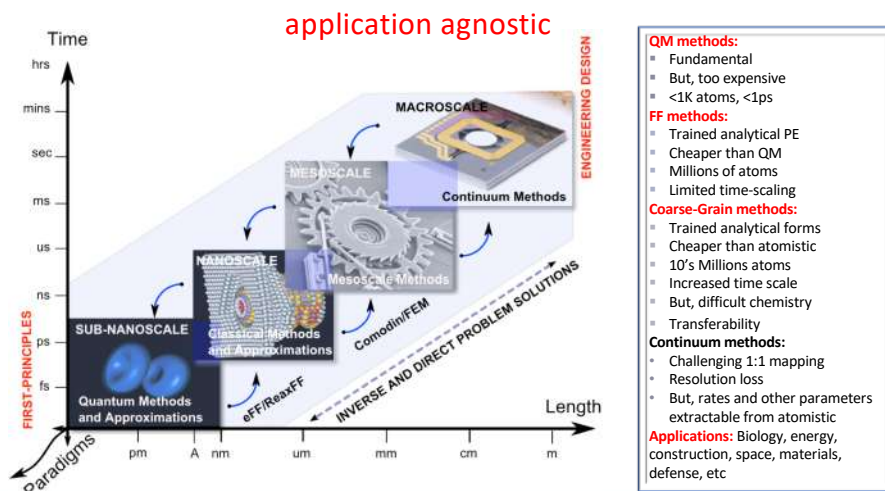
Gobierno  
de Colombia

COLOMBIA  
CIENTIFICA





# Theory, methods and tools in computational nanoscience



Nanosensores



El futuro es de todos

Gobierno de Colombia

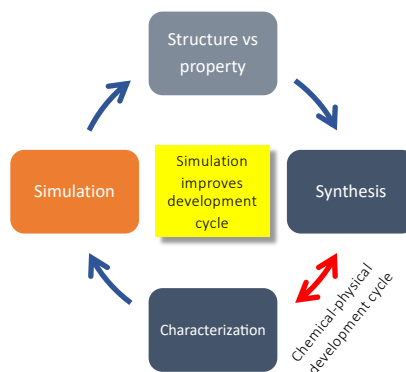
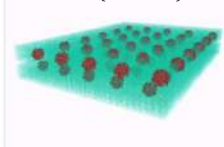
COLOMBIA CIENTIFICA



## Why Model from 1st Principles?

- Access to structural details that are difficult or impossible (e.g. In vivo versus in vitro, etc.) to explore with experiments.
- Enables predictive capabilities (as opposed to empirical models)
- Also:
  - Relatively cheap
  - Enables evaluation of design alternatives
  - Enables new application development
  - Enables intense analysis of promisory designs (thermodynamical and mechanical)
  - Reduces time to development
  - Enables development of novel engineering methods at the nanoscale

USC-Caltech (RDX+AlO<sub>2</sub>)



Nanosensores

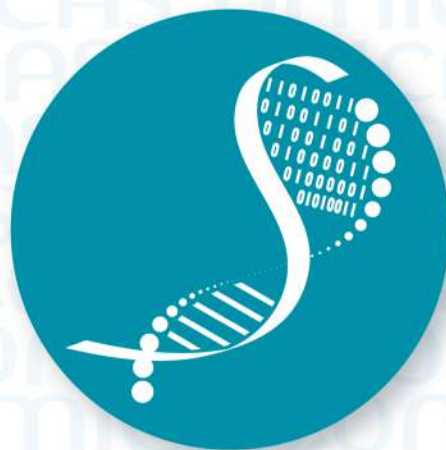


El futuro es de todos

Gobierno de Colombia

COLOMBIA CIENTIFICA





## Nanotechnology and Nanoscience

### Nanotechnology Definition

"It would be, in principle, possible (I think) for a physicist to synthesize any chemical substance that the chemist writes down. . . . Put the atoms down where the chemist says, and so you make the substance."

- Richard Feynman, *There's Plenty of Room at the Bottom* (Caltech, APS talk, 1959).

Not "nano by accident"

Smaller than we've ever  
manufactured

"The purposeful engineering of matter at  
scales of less than 100 nanometers to  
achieve size-dependent properties and  
functions"

Not just "small;" "small and different"

Matthew Nordan,  
Lux Research, 2005.

- o AKA: **Molecular Manufacturing**
- o **Shift in paradigm:** Bottom-up vs Top-down
- o **1 nm** = 1 billionth of a meter!

Nanosensores

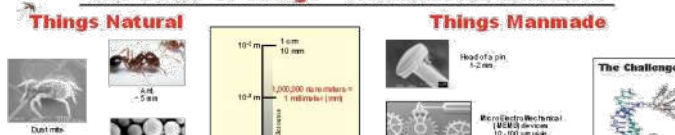


El futuro  
es de todos

Gobierno  
de Colombia

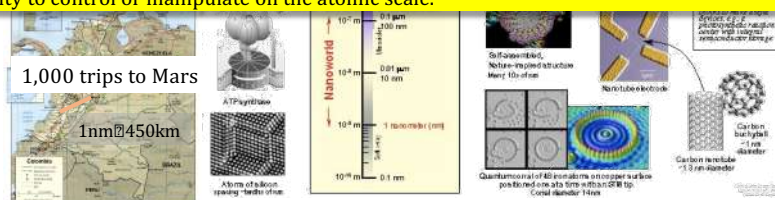


## The Scale of Things – Nanometers and More



Labeled "nanotechnology" only if it involves all of the following:

1. Research and technology development at atomic, molecular or macromolecular levels, in length scale of approximately 1 - 100 nm range.
2. Creating and using structures, devices and systems that have novel properties and functions because of their small and/or intermediate size.
3. Ability to control or manipulate on the atomic scale.



## Nanosensores



# What makes the nanoscale special?

1. Interfaces (SA/V)
2. Quantum effects
3. Thermal fluctuations
4. Discreteness of matter

Many material properties, including melting point, fluorescence, surface tension, electrical conductivity, magnetic permeability, and chemical reactivity change as a function of particle size!

These:

- Can lead to differences between nanosystems and bulk
- Can be exploited to generate whole new devices and phenomena
- Can pose challenges that require novel solutions

Jaramillo-Botero et al, Nanomedicine: A Systems Engineering Approach, Pan Stanford Publishing (World Scientific), Nov. 2008.

## Nanosensores



## Surface area (SA) to volume (V)

- A larger SA/V ratio as a function of entity size
  - Assume cube with side  $l$ ,  $V=l^3$  and  $A=6l^2$  then  $A/V=6/l$  increases for small  $l$
  - In cells: surface must allow sufficient exchange to support contents, hence ratio limits size (e.g. Eukaryotic cell  $\sim 5\text{--}100\mu\text{m}$ )
  - Higher ratio leads to more surface available for reactions (e.g. in enzymes)



Jaramillo-Botero et al, Nanomedicine: A Systems Engineering Approach, Pan Stanford Publishing (World Scientific), Nov. 2008.

## Nanosensores



## Quantum Effects

- Consider the energy levels of a metal as its size decreases
- 
- Heisenberg's Uncertainty Principle: e.g. the more an electron is confined, the greater its momentum range, and vice versa
  - Quantum effects can yield a range of exploitable phenomena, e.g.:
    - Nanoscale gold particles selectively accumulate in tumors and the motion of their electrons is confined, which changes its optical response properties, so they can enable both precise imaging and targeted destruction of tumor
    - "Tunability of properties" implies that particle size can be used to fine-tune a material property of interest (e.g., changing fluorescence color in QD)
    - "Electron tunneling" have enabled STMs and flash memories

## Nanosensores



## Quantized energy states at atomic level

- Discrete quantum levels of a nanocluster may be tuned to modulate the electron transport, normally modulated by the pH, ions, and redox centers.
- Important Quantum effects include “electron tunneling” for STM, quantum Hall effect for resistance calibration instruments, spin polarization in MRI.
- Radiation induced processes such as photoisomerization in vision and photosynthesis in plants depend on quantum yield, which depends in turn on molecular structure.
- Novel optical and magnetic properties for nanometer scale devices potentially, useful for medical diagnosis or intervention.

Nanosensores

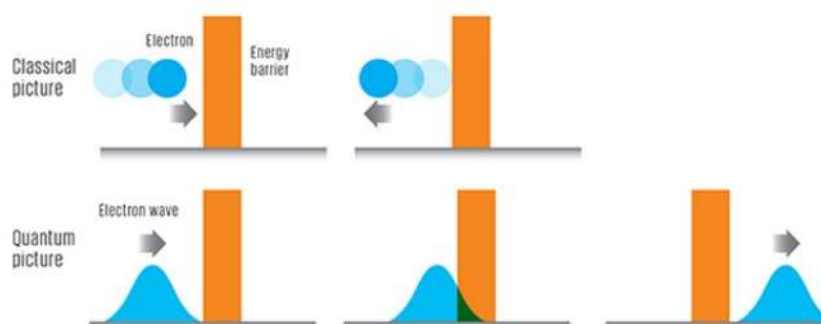


El futuro es de todos

Gobierno de Colombia



## Quantized energy states at atomic level



Nanosensores



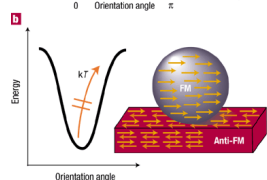
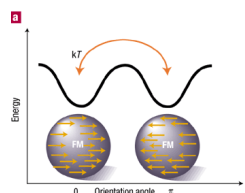
El futuro es de todos

Gobierno de Colombia



## Thermal fluctuations

- Thermal fluctuations can be commensurate with size of nano-system



"For very small ferromagnetic (FM) particles the magnetic anisotropy energy (responsible for keeping the magnetization oriented in certain directions) is comparable to the thermal energy ( $kT$ ). When this happens, the particles become *superparamagnetic*; as thermal fluctuations randomly flip the magnetization direction between parallel and antiparallel orientations. b. When the ferromagnetic nanoparticle is placed close to an antiferromagnetic (Anti-FM) surface the exchange bias interaction at the FM/Anti-FM interface provides additional anisotropy energy, which stabilizes the magnetization in one direction and prevents superparamagnetism."

Eisenmenger and Schuller, Nature Materials, 2003

### Melting Temperature

Nanocrystal size decreases  
↓  
surface energy increases  
↓  
melting point decreases

e.g., 3 nm CdSe nanocrystal melts at 700 K compared to bulk CdSe at 1678 K

## Nanosensores



El futuro es de todos

Gobierno de Colombia

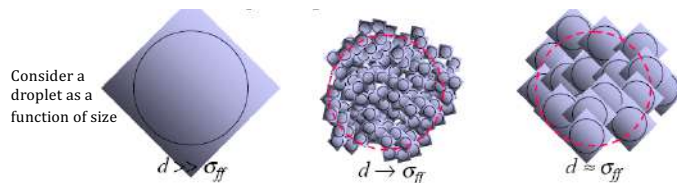
COLOMBIA CIENTÍFICA



## Surface Discreteness

Once the size of an entity approaches that of its building blocks:

- Surfaces can no longer be assumed 'smooth' – they are ill-defined
  - long alkanes used as lubricants in macrosystems, but act as dirt in nm scale
  - vdW forces in conventional gears taken to the nano hinder normal operation



- Thermal fluctuations affect shape and structure
- Obscures bulk concepts as surface tension, dielectric constant, pH

## Nanosensores

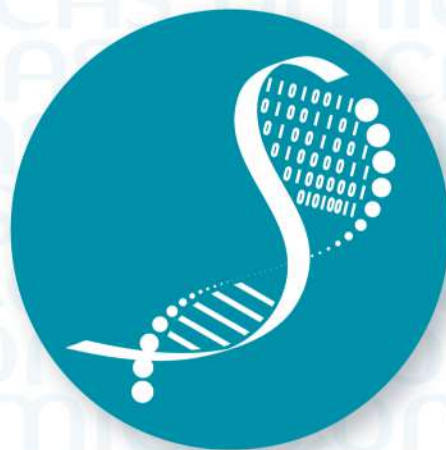


El futuro es de todos

Gobierno de Colombia

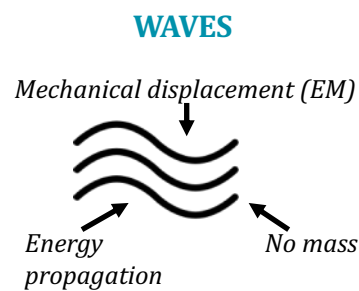
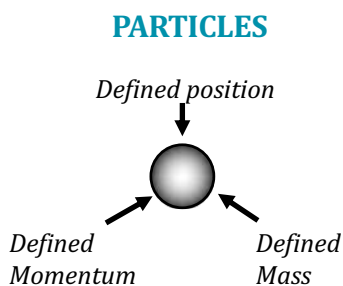
COLOMBIA CIENTÍFICA





## First-principles Quantum Mechanics

Diverging physical ideas: <1900



Nanosensores



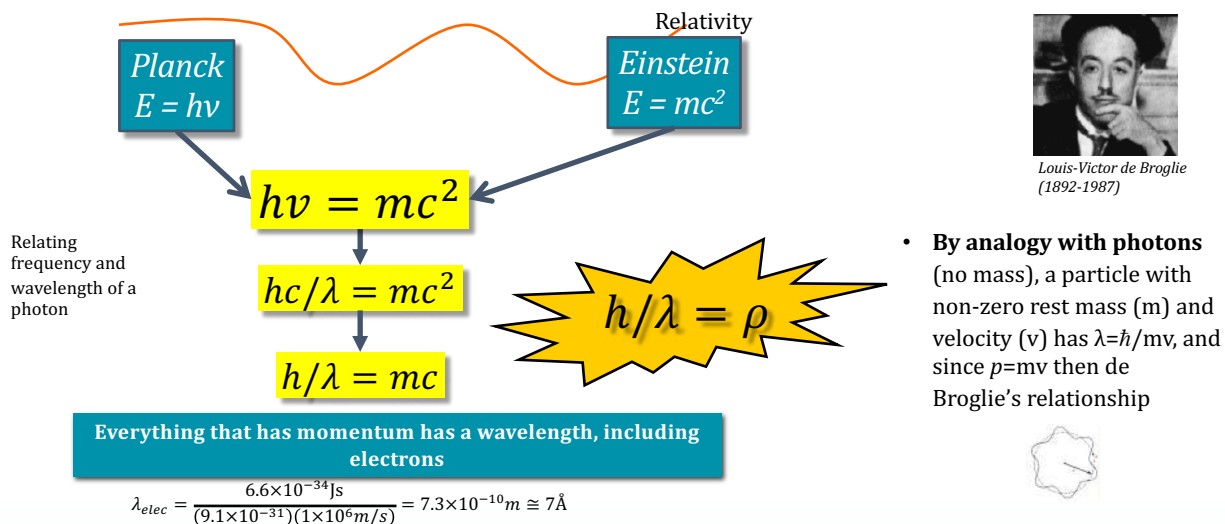
El futuro  
es de todos

Gobierno  
de Colombia





## Particle-wave duality and de Broglie



Nanosensores



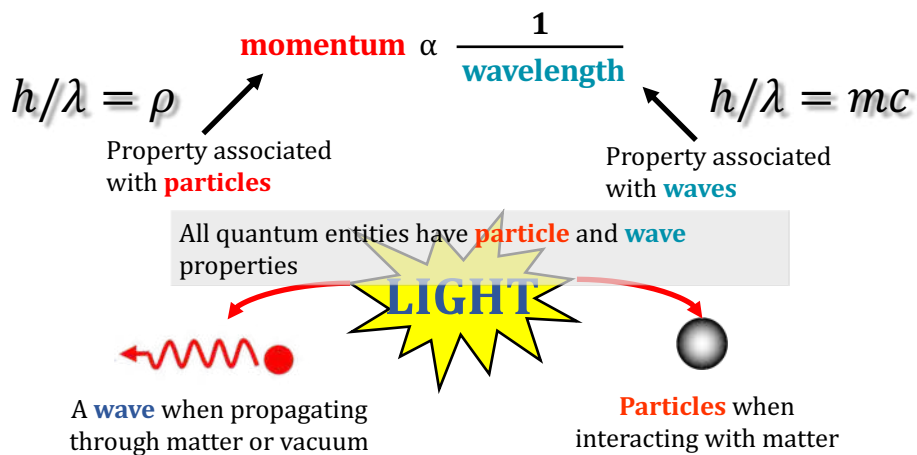
El futuro es de todos

Gobierno de Colombia

COLOMBIA CIENTÍFICA



## Wave-Particle duality



At that time, an equation that contemplated this duality was missing!!

Nanosensores



El futuro es de todos

Gobierno de Colombia

COLOMBIA CIENTÍFICA





## Schrödinger's Electronic Wave Eq.

- Bohr's atomic model 1D i.e. one quantum number describes distribution of e- ( $n$ )
- Schrödinger's model allowed the electron to occupy 3D space ( $n, l, m$ ).

Newton: "Where is/are the particle(s)?"

Schrodinger: "What is the probability distribution governing the positions?"

$$1 = \int P(R, t) dR = \int dR \psi^*(R, t) \psi(R, t) = \int dR |\psi(R, t)|^2$$



Erwin Schrödinger  
(1887-1961)

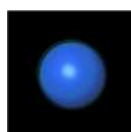


Schrödinger first wrote down his "wave equation" during a skiing Christmas holiday in 1925-26

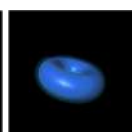
**n: principal** (integer): orbit size  
**l: azimuthal** (angular momentum): orbit form  
**m<sub>l</sub>: magnetic**: orbit orientation  
**m<sub>s</sub>: spin**

$$\hat{H}\psi(R, t) = i\hbar\partial\psi(R, t)/\partial t$$

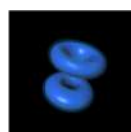
$$H(R)\psi(R) = E\psi(R)$$



$n=1, l=0, m=0$



$n=3, l=2, m=1$



$m=2$



$m=2$

Nanosensores



El futuro es de todos

Gobierno de Colombia

COLOMBIA CIENTÍFICA



## Historical precedents: summary

(1900's) Planck: energy occurs in quanta

$$E = h\nu = hc/\lambda$$

(1913) Bohr: atomic model

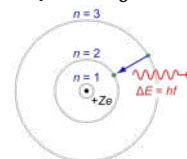
$$m_e v^2 / r = e^2 / 4\pi\epsilon_0 r^2$$

(1920's) Einstein: mass and energy are exchangeable

$$E = mc^2$$

(1921) de Broglie: wave-particle duality

$$h/\lambda = p$$



(1925) Schrödinger: electronic wave equation

$$H(R)\psi(R) = E\psi(R)$$

(1927) Heisenberg: adds uncertainty principle

"What is the probability distribution governing the positions?"

(1959) Feynman: (Caltech) Nanotechnology is born

Nanosensores

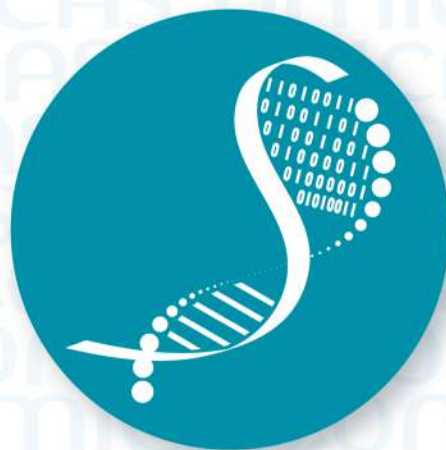


El futuro es de todos

Gobierno de Colombia

COLOMBIA CIENTÍFICA





## Molecular Mechanics and Dynamics

### Why avoid the ideal calculation?

Two reasons:

1. Too hard or impossible. Exact solutions only exist for a reduced number of cases (H, harmonic oscillator, particle in a box, ...). For systems with a large number of electrons, no analytical solutions have been found (electron-electron repulsion).
2. Approximate solutions to the Schrödinger equation can sometimes work well and usually give more “insight” than the exact solutions (e.g. Hückel calculations).

These approximations form the base for what is known today as Molecular Mechanics/Dynamics Simulations.

Let's review them.

## Approximations to Schrödinger's Equation

### 1. Born-Oppenheimer Approximation (1923)

- aka **Adiabatic Approximation**

- **Concept:**

- Nuclei are much heavier than electrons (H),
- Nuclei move in a much slower time scale than electrons.

$$\frac{M_{nuc}}{m_{el}} \approx 1,840$$

$$\frac{\omega_{el}}{\omega_{nuc}} \gg 1$$

- **Classical interpretation:**

- Nuclei interacting with electrons with spring-like forces leads to higher frequency oscillations of the light e's

- **Quantum interpretation:**

- For the time-dependent Schrödinger's equation we fix the nuclear geometry (at a particular time) and solve the e part of the total wavefunction

Nanosensores



El futuro es de todos

Gobierno de Colombia

COLOMBIA CIENTÍFICA



## Further Approximations that Lead to MM/MD

### 2. Nuclei moving as classical particles

- Since there are no explicit electronic contributions in the nuclear Schrödinger equation, it can be replaced by a Newtonian EOM
- Introduces the idea of a **Potential Energy Surface (PES)**

$$[K_n(R) + V_{nn}(R) + E_{el}^{el}(R)]\psi^n(R) = E\psi^n(R) \rightarrow M \frac{\partial^2 R}{\partial t^2} = F \leftarrow F = -\frac{\partial}{\partial R} [V_{nn}(R) + E_{el}^{el}(R)]$$

Nanosensores



El futuro es de todos

Gobierno de Colombia

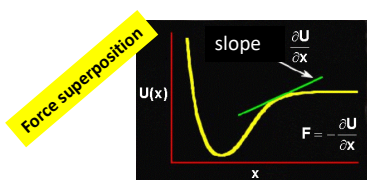
COLOMBIA CIENTÍFICA



## Further Approximations that Lead to MM/MD

### 3. Approximate PES with analytical potentials

- Avoid solving a Schrödinger equation altogether, and
- ATOMS as classical particles (w/implicit electrons) moving on analytical PES



GROUND STATE

E as a function of nuclear positions only.

Nanosensores



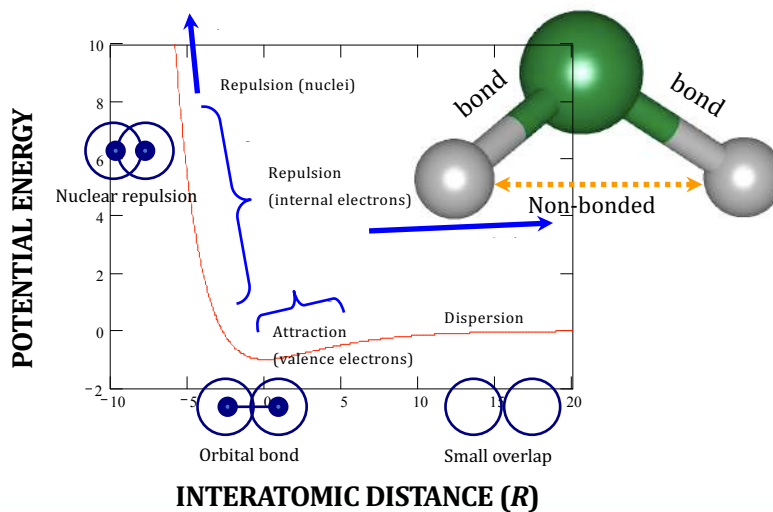
El futuro es de todos

Gobierno de Colombia

COLOMBIA CIENTÍFICA



## MM/MD (Classical): PES vs. Distance



Nanosensores



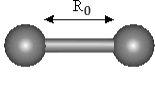
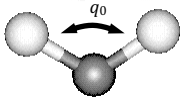
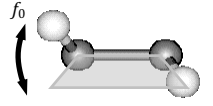
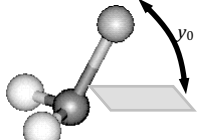
El futuro es de todos

Gobierno de Colombia

COLOMBIA CIENTÍFICA



# Bonded (valence) Interactions: spring-like interactions

	Description	Illustration	Typical Expressions	
			Energy (Potential)	Forces
"hard" DOF	Bond stretch		$U_r = \frac{1}{2} k_r (R - R_0)^2$	$-\frac{\partial U_r}{\partial R} = -k_r (R - R_0)$
	Bond Angle		$U_\theta = \frac{1}{2} k_\theta (\cos \theta - \cos \theta_0)^2$	$-\frac{\partial U_\theta}{\partial \theta} = k_\theta (\cos \theta - \cos \theta_0) \sin \theta$
Account (along with non-bond) for variations in structure and relative E	Torsion		$U_\phi = k_\phi [\cos(n\phi - d) + 1]$	$-\frac{\partial U_\phi}{\partial \phi} = k_\phi dn \sin(n\phi)$
	Inversion or Improper Torsion		$U_\psi = \frac{1}{2} k_\psi (\cos \psi - \cos \psi_0)^2$	$-\frac{\partial U_\psi}{\partial \psi} = k_\psi (\cos \psi - \cos \psi_0) \sin \psi$

Subindex 0 indicates rest value / Kr: Force constant (kcal/mol Å<sup>2</sup>) / K<sub>uc</sub>: Rotational barrier (kcal/mol) / n: periodicity / d: phase factor

Nanosensores  
Others: Cross-terms



El futuro es de todos

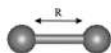
Gobierno de Colombia

COLOMBIA CIENTÍFICA



## Bond-stretch

Simple Harmonic

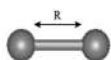


$$E(R) = \frac{K_b}{2} (R - R_o)^2$$

$$R_o = 0.9 - 2.2 \text{ Å}$$

$$K_b = 700 \text{ (Kcal/mol)/Å}^2$$

Units: multiply by 143.88 to convert mdynes/Å to (Kcal/mol)/Å<sup>2</sup>



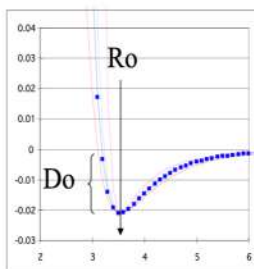
Morse

$$E(R) = D_o [e^{-\alpha(R-R_o)} - 1]^2$$

$D_o$  is the bond energy in Kcal/mol  
 $R_o$  is the equilibrium bond distance

$$\alpha = \sqrt{K_b / 2D_o}$$

Morse scaling parameter, which  
Most programs calculate from  $K_b$  and  $D_o$



Nanosensores



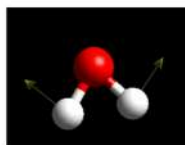
El futuro es de todos

Gobierno de Colombia

COLOMBIA CIENTÍFICA



## Angle bend

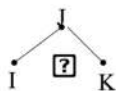


### Cosine Harmonic

$$E(\theta) = 1/2C[\cos(\theta) - \cos(\theta_0)]^2$$

Where the force constant is the second Derivative evaluated at the equilibrium angle

$$K_\theta = C \sin^2 \theta_0$$



Input parameters are always in terms of The force constant  $K_\theta$ . In general

$$K_q = \left. \frac{\partial^2 E(q)}{\partial q^2} \right|_{q=q_0}$$



### Cosine Periodic

$$E(\theta) = C[1 - B(-1)^N \cos(N\theta)]$$

This is particularly useful for organometallic systems where N=4 might be used for an Octahedral complex and N=3 might be used for a trigonal center. The parameter B is Either :

B = +1 (leading to a minimum for the linear geometry)  
B = -1 (leading to a maximum for the linear geometry)

The periodicity N can be N = 1, 2, 3, ..., 6

The constant C is related to the force constant as  $K_\theta = N^2 C$

The input is in terms of  $K_\theta$ , N and B

## Nanosensores



El futuro es de todos

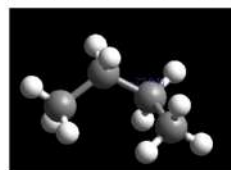
Gobierno de Colombia

COLOMBIA CIENTIFICA



## Torsions

Given any two bonds IJ and KL attached to a common bond JK



$$E(\phi) = \sum_{n=1}^p 1/2[k_n(1 - d\cos(n\phi))]$$

Where each  $k_n$  is in kcal/mol, n = 1, ..., 6 is the periodicity of the potential and d = +/- 1 is the phase factor.

d = +1 the cis conformation is the minimum

d = -1 the cis conformation is the maximum

Input data is K and d for each n. Two modes:

- All torsions (nine for ethane). K is re-scaled for Dreiding and CHARMM force field
- MM2 and Amber K is not re-scaled.
- If USE ALL is turned OFF the program uses only the FIRST non-zero torsion for JK without re-scaling

## Nanosensores



El futuro es de todos

Gobierno de Colombia

COLOMBIA CIENTIFICA



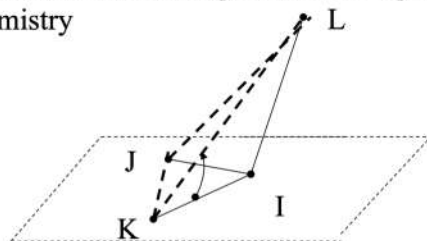
## Improper Torsions

In the CHARMM and Dreiding-I force fields, inversion is defined as if it were a torsion.

$$E(\phi) = 1/2 K_{\phi} [\phi - \phi_o]^2$$

For a tetrahedral carbon atom with equal bonds this angle is 35.264 Degrees. For non-zero equilibrium angle  $E(+\phi) \neq E(-\phi)$

This can be used to advantage for enforcing a particular stereochemistry



Improper Torsion  
 $\phi$  is the angle between  
 The IJK plane and the  
 LJK plane

Nanosensores



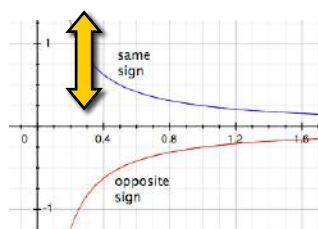
El futuro  
es de todos

Gobierno  
de Colombia

COLOMBIA  
CIENTÍFICA



## Non-bond distance-dependent Interactions



### Electrostatic Interactions

$$U_{Coulomb} = C_0 \sum_{i>j} \frac{Q_i Q_j}{\epsilon R_{ij}} S(R_{ij}, R_{on}, R_{off})$$

A function of charges, interatomic distance, and molecular dielectric (attenuates environment). Partial atomic charges from QM

Nanosensores



El futuro  
es de todos

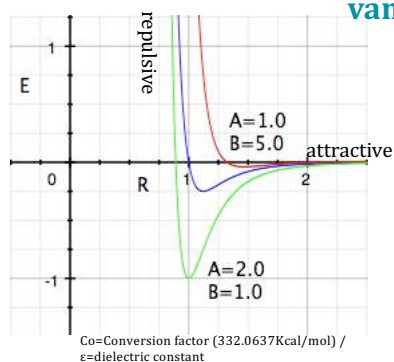
Gobierno  
de Colombia

COLOMBIA  
CIENTÍFICA





# Non-bond distance-dependent Interactions



## van der Waals Interactions

$$U_{vdW} = \sum_{R_{ij} > R_{cut}} \hat{U}_{vdW}(R) S(R_{ij}, R_{on}, R_{off})$$

$$[excl(1-2)-3]$$

### Typical vdW potential:

- Lennard-Jones 12-6

$$\hat{U}_{vdW} = \sum_i \sum_j \frac{-A_{ij}}{R_{ij}^6} + \frac{B_{ij}}{R_{ij}^{12}}$$

- "A" -> degree of "**stickiness**" of the van der Waals attraction (obtained from polarizability measurements or from QM) and
- "B" -> degree of "**hardness**" of the atoms (crystallographic data to observe contact distances)

Nanosensores



El futuro es de todos

Gobierno de Colombia

COLOMBIA CIENTÍFICA



Hydrogen Bonds Conventionally calculated via a pair wise interaction + 3 body angle term

$$E_{HB}(R, q_{AHD}) = E_b(R) E_a(\cos(q_{AHD}))$$

### Bond terms:

LJ12-10:  $E_b(R_{AD}) = AR_{AD}^{-12} - BR_{AD}^{-10} = D_e \left[ 5 \left[ \frac{R_e}{R_{AD}} \right]^{12} - 6 \left[ \frac{R_e}{R_{AD}} \right]^{10} \right]$

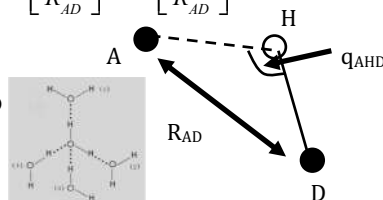
Morse:  $E_b(R_{AD}) = D_e [\chi^2 - 2\chi]$

$$\chi = e^{-\alpha(R_{AD} - R_e)} = e^{-\frac{\gamma}{2} \left( \frac{R_{AD}}{R_e} - 1 \right)}$$

$R_e$  is the equilibrium distance between **acceptor (A)** and **donor (D)**, A-D, and  $D_e$  is the energy well depth.

### Angle terms:

$$E_a(\cos(q_{AHD})) = \cos(q_{AHD})^4$$



### Hydrogen bonds:

- Account for unique water properties
- hold the 2 strands of DNA double helix together
- hold polypeptides together in secondary structures;
- help enzymes bind to their substrate;
- help antibodies bind to their antigen
- help transcription factors bind to each other;
- help transcription factors bind to DNA

Nanosensores



El futuro es de todos

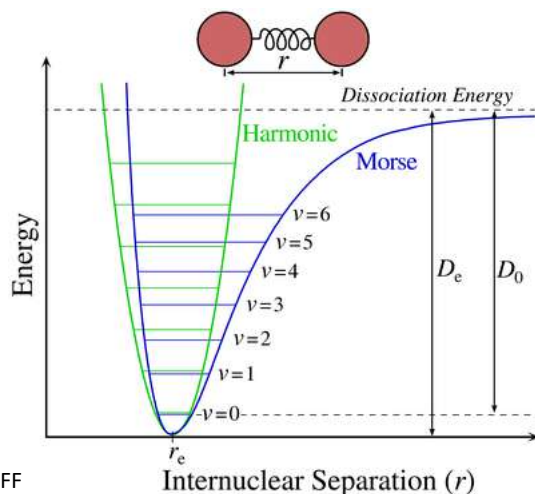
Gobierno de Colombia

COLOMBIA CIENTÍFICA





## Bond-Breaking?



Reactive force fields, e.g. ReaxFF  
Electron-explicit force fields, e.g. eFF

Nanosensores



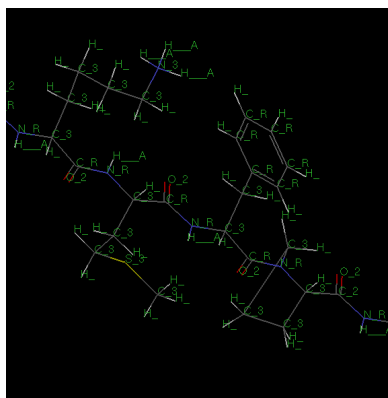
El futuro  
es de todos

Gobierno  
de Colombia

COLOMBIA  
CIENTÍFICA



## Atom types



- Atom Type rules make possible the correct assignment of force field parameters throughout the molecule  $K_{\theta}, K_n, \theta_o, R_o, D_o$
- The rules are easy for “chemists” to understand and easy to code
- Examples: C\_1, C\_2, C\_3 indicate  $sp, sp^2$ , and  $sp^3$  hybridized carbon atoms

Nanosensores



El futuro  
es de todos

Gobierno  
de Colombia

COLOMBIA  
CIENTÍFICA



## Conventional and unconventional Force Fields

### Conventional

- Dreiding (Caltech): *J. Phys. Chem.* 1990, 94, 26, 8897-8909
- UFF (Caltech): *J. Am. Chem. Soc.* 1992, 114, 25, 10024-10035
- AMBER (UCSF): *Proteins*. 2006 Nov 15; 65(3): 712-725
- CHARMM (Harvard): *J. Comput. Chem.* 4 (2): 187-217, 1983
- MM2: *Tetrahedron*, Vol 46, Issue 24, 1990, Pages 8005-8018

### Unconventional

- ReaxFF (Caltech): *J. Phys. Chem. A* 2001, 105, 41, 9396-9409
- eFF (Caltech): *J Comp Chem*, 32, 497-512 (2011)
- PQEq (Caltech): *J Chem Phys.* 2017 Mar 28;146(12):124117.

### Most Used Molecular Dynamics Codes (open source)

- LAMMPS ([lammps.sandia.gov](http://lammps.sandia.gov))
- Gromacs ([www.gromacs.org](http://www.gromacs.org))
- NAMD ([www.ks.uiuc.edu](http://www.ks.uiuc.edu))

Term	Force Field	Potential
Bonds	Dreiding MM2 AMBER CHARMM	Harmonic Cubic Harmonic Harmonic
Angles	Dreiding MM2 AMBER CHARM	Simple Harmonic MM2 Simple Harmonic Simple Harmonic
Torsions	All	Cosine expansion
Inversions	Dreiding MM2 AMBER CHARMM	Umbrella Not used Improper Torsion JILK Improper Torsion LJKL
Van der Waals	Dreiding MM2 AMBER CHARMM	LJ 12-6 Exp-6 LJ 12-6 LJ 12-6
Off diagonal nonbond	Dreiding MM2 AMBER CHARMM	Combination rule Combination rule except for C-H (exp-6) Combination rule except for H-X of H bonds (LJ 12-10) Combination rule except for H-X of H bonds
Hydrogen bond	Dreiding MM2 AMBER CHARMM	LJ 12-10 Not used Not used LJ 12-10

Nanosensores



El futuro es de todos

Gobierno de Colombia

COLOMBIA CIENTÍFICA



## Summary: From QM to MM/MD

Schrodinger equation:

$$H_T \Psi(r, R) = E_T \Psi(r, R)$$

where  $H_T = K_n + K_e + V(r, R)$

Born-Oppenheimer approximation:

$$\Psi(r, R) = \psi(r, R) \Theta(R)$$

Equation of motion for electrons:

$$(K_e + V) \psi(r, R) = E_e(R) \psi(r, R)$$

Equation of motion for nuclei (motion on the PES)

Quantum:  $[K_n + E_e(R)] \Theta(R) = E_T \Theta(R)$

Classical MD (Newtonian Mechanics):  $m \frac{d^2 R}{dt^2} = -\nabla E_e(R)$

Force Field is needed to build up Potential Energy Surface (PES)

QM  
PES  
MM

Nanosensores



El futuro es de todos

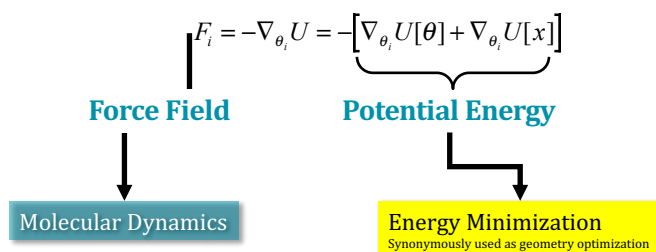
Gobierno de Colombia

COLOMBIA CIENTÍFICA



## QM->PES->FFs->MM/MD

- The Potential Energy depends on the atomic coordinates and the type of bond in accordance with the nature of the element (type of atom), its hybridization state, and other chemical properties.
- Different functional forms of this potential energy lead to the development of different “Force Fields”



Nanosensores



El futuro es de todos

Gobierno de Colombia

COLOMBIA CIENTÍFICA



## MM: Energy Minimization (EM)

- Purpose: find PE minima in a (hyper) surface
- Why?
  - Minimum points on the PES correspond to stable states (geometries or arrangement of atoms) of the system
- Applications:
  - Geometry optimization (static)
  - Conformation search (for highly populated structures)
  - Study the potential energy surfaces (dynamic)
    - Energy barriers between different conformers or
    - Steepness of a PES around a local minimum
- Keep in mind:
  - Non-trivial systems may have a very large number of minima on the PES (i.e. multidimensional function). Expensive.
  - (Usually) a global minima cannot be analytically guaranteed for non-trivial system (numerical solution) starting from an arbitrary conformation - not necessarily highly populated state

Nanosensores



El futuro es de todos

Gobierno de Colombia

COLOMBIA CIENTÍFICA



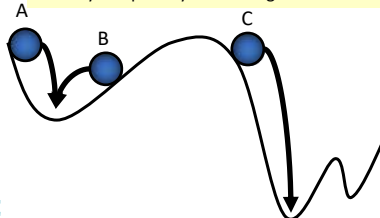
## MM: Energy Minimization (EM)

- The minimization problem in molecular simulations can be stated as:
  - Given the QM or MM energy with the Cartesian or internal coordinates of the atoms  $E(x_1, x_2, \dots, x_i)$  -> find the values of all  $x$ 's where  $E$  has a minimum value.
  - At a minimum point:

$$\frac{\partial E}{\partial \vec{x}} = 0; \quad \frac{\partial^2 E}{\partial \vec{x}^2} > 0$$

Eigenvalues of Hessian

- Temperature (=velocity) is zero (except SA)
- Only sample 1 system configuration



- We can obtain:
  - From gradient
    - Direction=where
    - Magnitude=steepness
    - Move atom in response to force to lower  $E$
  - From Hessian
    - Curvature=direction change (minimum or stationary)

Most minimization methods move downhill to the nearest minimum

Nanosensores



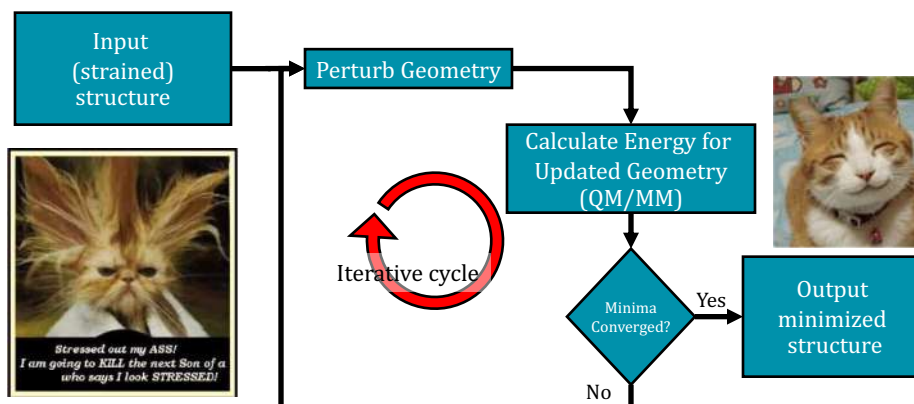
El futuro es de todos

Gobierno de Colombia

COLOMBIA CIENTÍFICA



## EM in MD



Nanosensores



El futuro es de todos

Gobierno de Colombia

COLOMBIA CIENTÍFICA



## Molecular Dynamics: Motivation

- **Very similar to physical experiments:**
  - Prepare a sample (N particle model)
  - Connect sample to measuring device (computer)
  - Let sample evolve under certain conditions (perform calculations)
  - Measure properties during time interval (equilibrate, then measure)
- **An Observable (A):** a function of particles position and momenta
 
$$A(p^N(t), r^N(t))$$
- Recall **EM** is used to determine time-independent, temperature-agnostic (velocity=0) minima in the PES, from which one can extract useful properties (limited small systems)
- But, how do we determine a **correct** initial “atomistic” configuration for a system that could compare reasonably to the “macroscopic” ones from experiments, let alone perform dynamics using what we know from MM?

Nanosensores



El futuro es de todos

Gobierno de Colombia

COLOMBIA CIENTÍFICA



## Molecular Dynamics: Motivation

- From statistical mechanics (Boltzmann and Gibbs):
  - Average values are defined as ensemble averages. Replace a single system evolving in time with a large number of replications of the system that are considered concurrently, i.e.

$$\langle A \rangle_{ensemble} = \int \int dp^N dr^N A(p^N(t), r^N(t)) \rho(p^N, r^N)$$

This is hard and expensive ! Involves 6N integrals (r,p)

Probability density  $\rho(p^N, r^N) = \frac{1}{Q} \exp \left[ \frac{-H(p^N, r^N)}{k_B T} \right]$

Partition function  $Q = \int \int dp^N dr^N \exp \left[ \frac{-H(p^N, r^N)}{k_B T} \right]$

- From The *Ergodic hypothesis*, replace an ensemble average (expectation value) by the time average, i.e.

$$\langle A \rangle_{time} = \langle A \rangle_{ensemble}$$

Much easier to compute the time average, so if we let the system evolve in time indefinitely it should eventually pass through all possible states !!

$$A_{time} = \lim_{\tau \rightarrow \infty} \frac{1}{\tau} \int_{t=0}^{\tau} A(p^N(t), r^N(t)) dt$$

Nanosensores



El futuro es de todos

Gobierno de Colombia

COLOMBIA CIENTÍFICA



## When to use EM and when to use MD?

### Recall, we can use MM-EM:

- To determine stable configuration states of a single system.
- To determine 0K properties of a single system configuration.
- To calculate normal modes and vibrational modes of a system.
- To calculate relative energies and transition states/structures.
- To calculate IR-spectra, IV or NMR-spectra.
- To compute single-component system properties ...

### MD:

- To sample the conformational space of a system at  $T > 0K$ .
- To model temperature and pressure effects.
- To obtain thermodynamics and time-dependent (kinetic) properties.
- To compute multi-component system properties ...

Nanosensores



El futuro  
es de todos

Gobierno  
de Colombia



## MD: Applications

- **Liquids:** phase transitions, viscosity, heat flow, multicomponents
- **Defects:** propagation, interstitials, grains, dislocations (point-linear-planar)
- **Fracture:** propagation, initiation, evolution, speed
- **Surfaces:** roughness, diffusion, melting, faceting
- **Friction:** tribology, adhesion
- **Clusters:** melting, role of surface and anisotropy, catalysis
- **Spectra:** scattering
- **Biomolecules:** protein, nucleic acids, membranes - conformation, free energy, surface free energy
- **Transport properties:** phase transitions, phonons, thermoelectrics
- **Non-equilibrium phenomena:** plasmas, combustion, turbulent flow,...
- **Limitations ...**
  - Transferability
  - As good as the force field
  - Light atoms (not He, Ne, H<sub>2</sub>)
  - No excited states
  - Time (e.g. enough to reach equilibrium or detect infrequent events, i.e. longer than relaxation time of quantities of interest)

Nanosensores

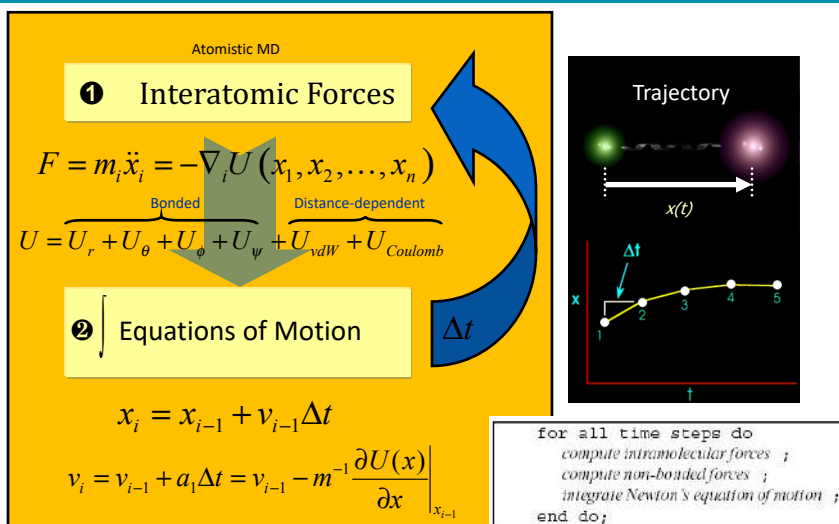


El futuro  
es de todos

Gobierno  
de Colombia



## Molecular Dynamics: a 2-step process



Nanosensores



El futuro  
es de todos

Gobierno  
de Colombia

COLOMBIA  
CIENTÍFICA



## Simulation Ensembles

IF

nVE=constant:

GIVES

- **Microcanonical ensemble.** Total energy and volume controlled. Free run, no velocity or pressure scaling. Requires PBC for solvated simulations.

nVT=constant:

- **Canonical ensemble.** T controlled through random perturbations on atoms per step to simulate interaction with a heat bath [Andersen, 1980], velocity rescaling to maintain kinetic temperature, or adding friction terms.

nPT=constant:

- **Isobaric ensemble.** P controlled via changes in system volume to match desired pressure (scale positions and boundaries by factor).

( $\mu$ )VT=constant:

- **Grand-canonical ensemble.** N is allowed to fluctuate. Closely represents experimental conditions, gives direct access to the equation of state.

Jaramillo-Botero y Marmolejo, 2019

n=number of particles; V=Volume; E=Energy; T=Temperature; P=Pressure;  $\mu$ =chemical potential



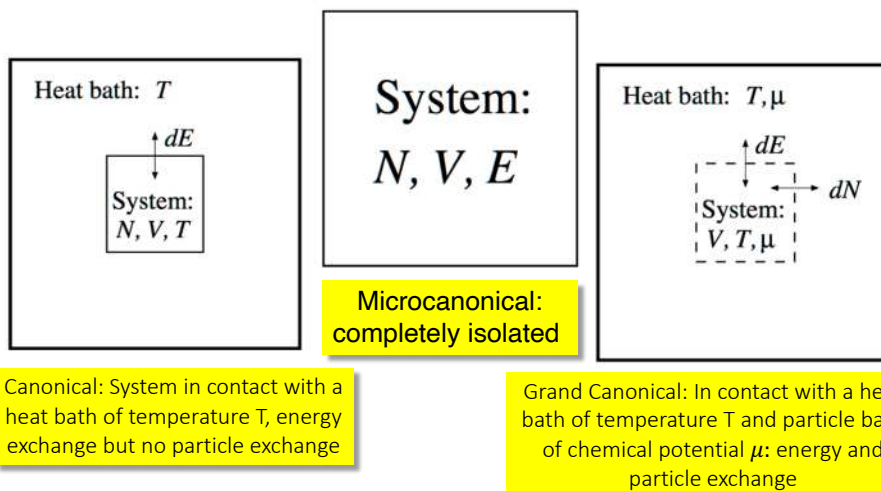
El futuro  
es de todos

Gobierno  
de Colombia

COLOMBIA  
CIENTÍFICA



## Ensembles



Nanosensores

Jaramillo-Botero y Marmolejo, 2019

El futuro es de todos

Gobierno de Colombia

COLOMBIA CIENTÍFICA



## Important Properties of Interest

- Energy (internal)
- Temperature
- Pressure
- Heat Capacity

$$U = \langle E \rangle = \frac{1}{M} \sum_{i=1}^M E_i$$

$$T(t) = \sum_{i=1}^N \frac{m_i v_i^2(t)}{K_B N_{dof}} = \sum_{i=1}^N \frac{|p_i(t)|^2}{m_i K_B N_{dof}}$$

$$P = \frac{1}{V} \left[ N K_B T - \frac{1}{3} \sum_{i=1}^N \sum_{j=i+1}^N r_{ij} f_{ij} \right]$$

$$C_V = \left( \frac{\partial U}{\partial T} \right)_V = \langle (E - \langle E \rangle)^2 \rangle / K_B T$$

**Others:** Correlations, transport, conformations ...

Nanosensores

El futuro es de todos

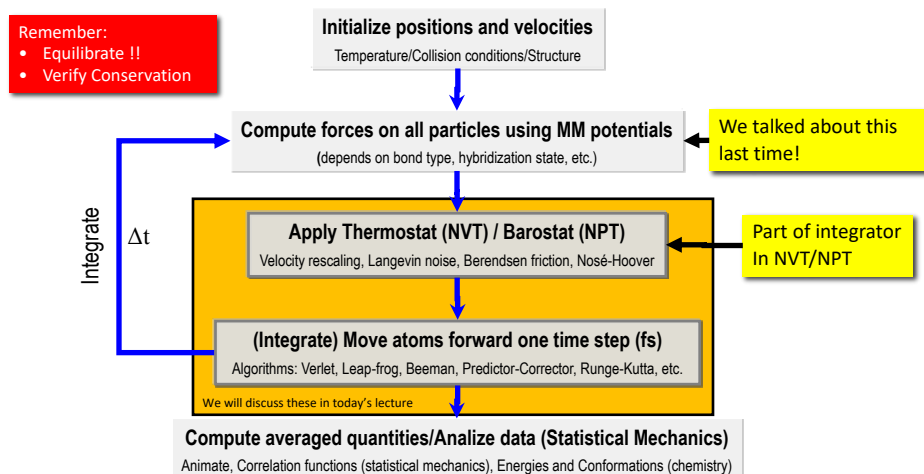
Gobierno de Colombia

COLOMBIA CIENTÍFICA





## MD Flowchart (ensembles)



Nanosensores



El futuro es de todos

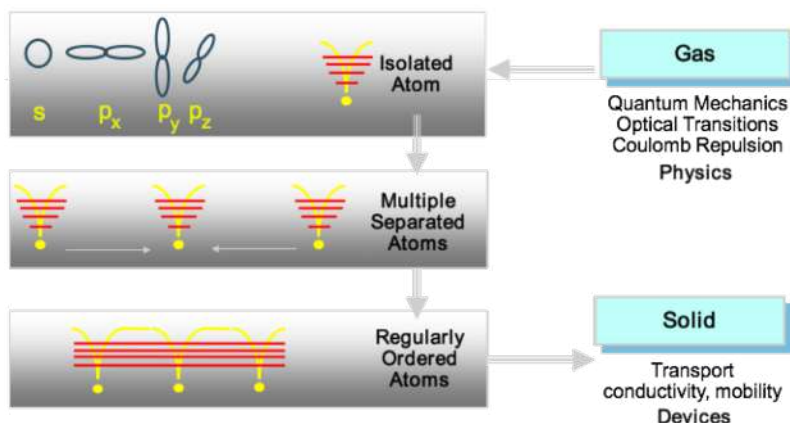
Gobierno de Colombia



## Electronic Transport Properties in the Nanoscale

## Electron Conduction in Solids

- Bands are channels in which electrons move “freely”.



Nanosensores



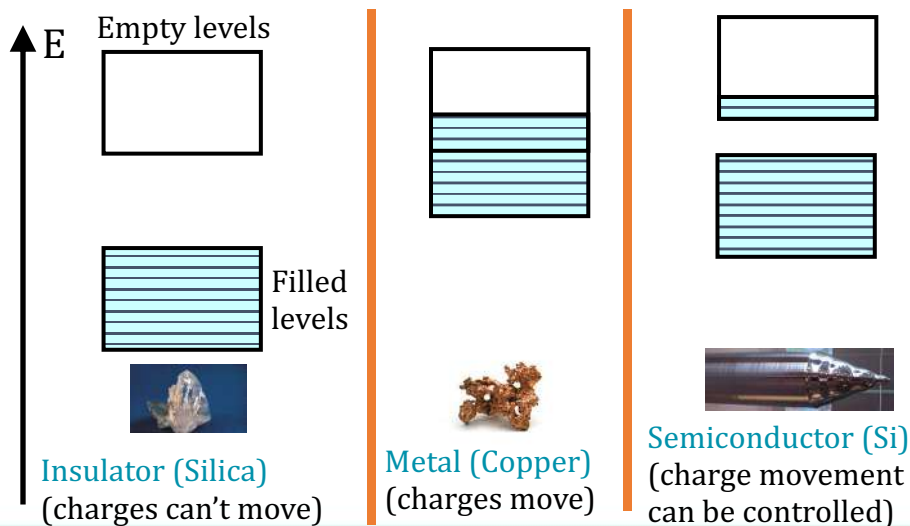
El futuro es de todos

Gobierno de Colombia

COLOMBIA CIENTÍFICA



## Filling up the Bands with Electrons



Nanosensores



El futuro es de todos

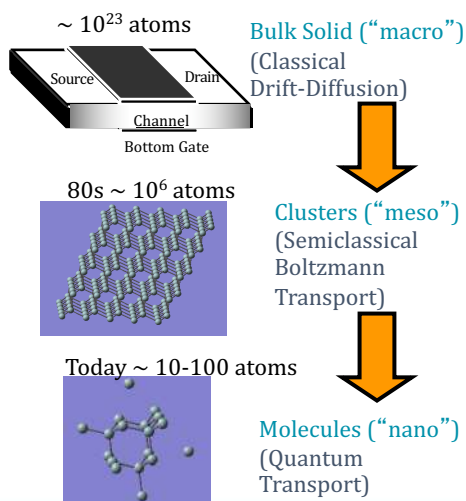
Gobierno de Colombia

COLOMBIA CIENTÍFICA



## Pushing the simulation envelope

- Quantum corrections to classical concepts are usually experimentally motivated.
- Problem: Cannot derive Quantum concepts from Classical equations.



Nanosensores



El futuro es de todos

Gobierno de Colombia

COLOMBIA CIENTÍFICA



## Determining the Most Appropriate Model

- Length Scales and Interactions Determine the Most Appropriate Model.

	$L \ll l_{e-ph}$			$L \sim l_{e-ph}$	$L \gg l_{e-ph}$
	$L < \lambda$	$L < l_{e-e}$	$L \gg l_{e-e}$		
<b>Transport Regime</b>	Quantum	Ballistic	Fluid	Fluid	Diffusive
<b>Scattering</b>	Rare	Rare	e-e (Many), e-ph (Few)		Many
<b>Model:</b>					
Drift-Diffusion					
Hydrodynamic	Quantum Hydrodynamic				
Monte Carlo					
Schrodinger/Green's Functions	Wave				
<b>Applications</b>	Nanowires, Superlattices	Ballistic Transistor	Current IC's	Current IC's	Older IC's

Nanosensores



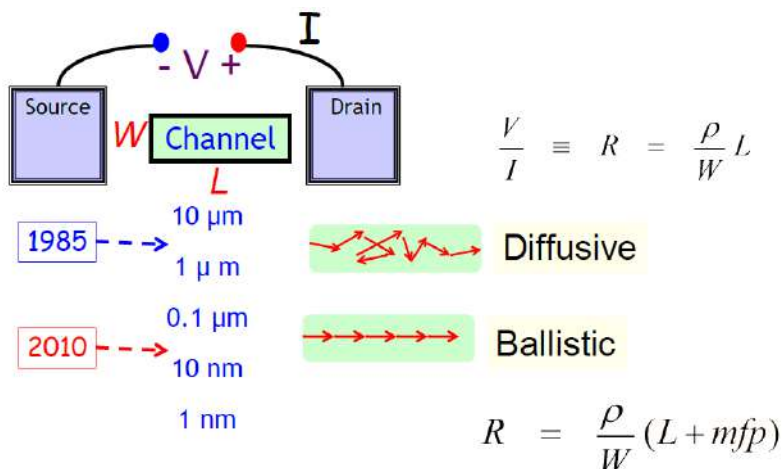
El futuro es de todos

Gobierno de Colombia

COLOMBIA CIENTÍFICA



## Change in paradigm

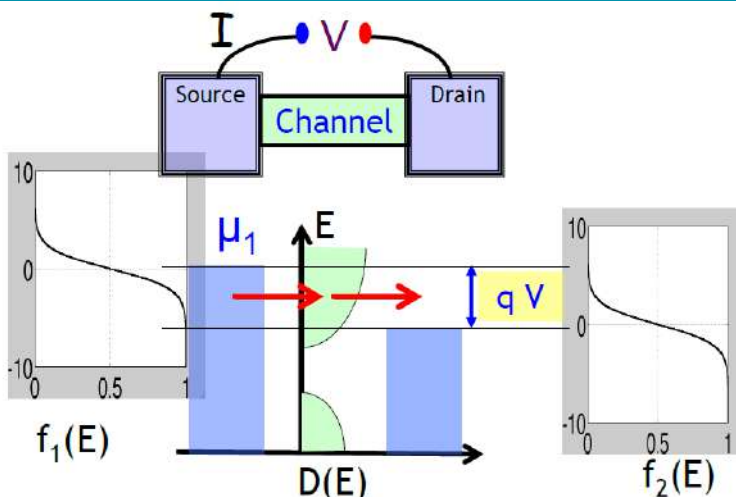


Supriyo Datta, "Fundamentals of Nanoelectronics", PurdueX (2015).

## Nanosensores



## Two key concepts: $D(E)$ , $f(E)$

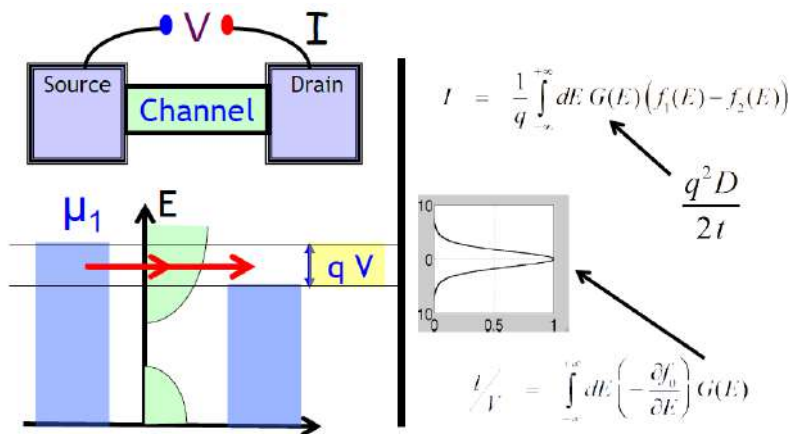


Supriyo Datta, "Fundamentals of Nanoelectronics", PurdueX (2015).

## Nanosensores



## Why electrons flow



Supriyo Datta, "Fundamentals of Nanoelectronics", PurdueX (2015).

Nanosensores



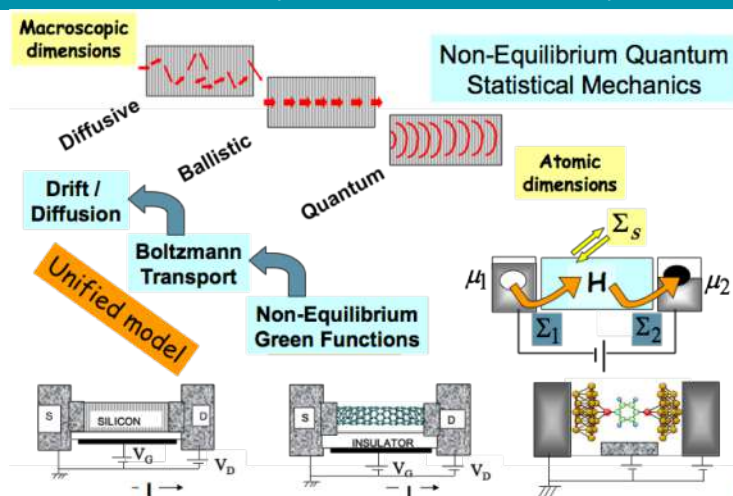
El futuro es de todos

Gobierno de Colombia

COLOMBIA CIENTÍFICA



## Quantum Transport far from Equilibrium



Supriyo Datta, "Fundamentals of Nanoelectronics", PurdueX (2015).

Nanosensores



El futuro es de todos

Gobierno de Colombia

COLOMBIA CIENTÍFICA



## Non-Equilibrium Green's Functions (NEGF)

- Most fundamental and accurate method.
- Considered by many to be the most difficult quantum approach.
- Formulation of scattering rather straightforward and theoretically sound including incoherence and irreversibility.
- Implementation of scattering rather difficult.
- Computationally intensive.

Nanosensores



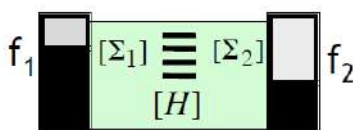
El futuro es de todos

Gobierno de Colombia

COLOMBIA CIENTÍFICA



## Non-Equilibrium Green's Functions (NEGF)



$$\Sigma = \Sigma_1 + \Sigma_2$$

$$\Gamma = \Gamma_1 + \Gamma_2$$

$$\Sigma^{in} = f_1 \Gamma_1 + f_2 \Gamma_2$$

$$\Gamma_{1,2} = i[\Sigma_{1,2} - \Sigma_{1,2}^+]$$

(1) Green's function

$$G^R = [EI - H - \Sigma]^{-1}$$

(2) "Electron density"

$$G^n = G^R \Sigma^{in} G^A$$

(3) "Density of states"

$$A = G^R \Gamma G^A = G^A \Gamma G^R$$

$$= i[G^R - G^A]$$

(4) Current per unit energy at terminal 'p'

$$\tilde{I}_p = \frac{q}{h} \text{Trace}[\Sigma_p^{in} A - \Gamma_p G^n]$$

Supriyo Datta, "Fundamentals of Nanoelectronics", PurdueX (2015).

Nanosensores

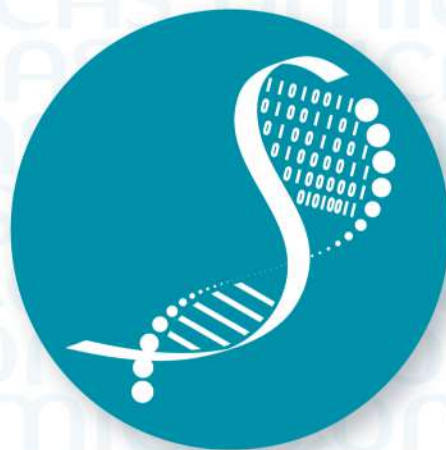


El futuro es de todos

Gobierno de Colombia

COLOMBIA CIENTÍFICA





## Biosensors

### Generalities

- A biosensor is an analytical device, used for the detection of a chemical substance, that combines a biological component with a physicochemical detector.
- The transducer or the detector element, which transforms one signal into another one, works in a physicochemical way, resulting from the interaction of the analyte with the biological element, to easily measure and quantify.



## Biotransducer

- Biosensors can be classified by their biotransducer type.
- The most common types of biotransducers used in biosensors are:
  - Electrochemical biosensors
  - Optical biosensors
  - Electronic biosensors
  - Piezoelectric biosensors
  - Gravimetric biosensors
  - Pyroelectric biosensors

## Nanosensores



El futuro es de todos

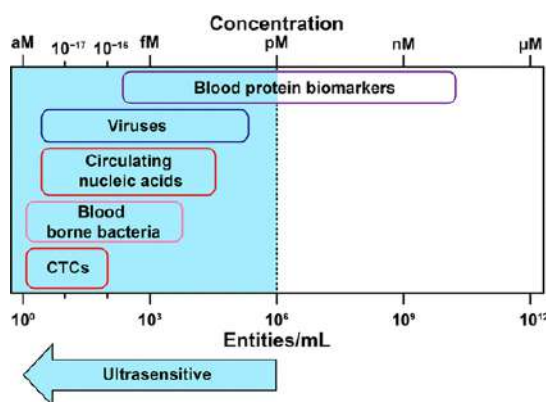
Gobierno de Colombia

COLOMBIA CIENTÍFICA



## Opportunities

- There are many opportunities in the sensing field for detecting and measuring very low analyte concentrations.
- Sub-picomolar detection limits represent useful concentration ranges for the detection of many disease biomarkers.



Yanfang Wu, Richard D. Tilley and J. Justin Gooding, *J. Am. Chem. Soc.* 2019, 141, 3, 1162-1170

## Nanosensores



El futuro es de todos

Gobierno de Colombia

COLOMBIA CIENTÍFICA





## Challenges

- Achieving sub-picomolar detection limits has three major challenges:
  1. **Assay sensitivity**
    - One strategy to gain greater sensitivity involves confining the sensing volume to the nanoscale, as used in nanopore- or nanoparticle- based sensors
  2. **Response time**
    - Methods to improve response time typically focus on obtaining an intimate mixture between the sensor and the sample either by extending the length scale of nanoscale sensors using nanostructuring or by dispersing magnetic nanoparticles through the sample to capture the analyte
  3. **Selectivity (including limiting background signals).**
    - One solution to help address the challenge of selectivity is loading nanoparticles with many biorecognition species is

Yanfang Wu, Richard D. Tilley and J. Justin Gooding, *J. Am. Chem. Soc.* 2019, 141, 3, 1162-1170

Nanosensores



El futuro  
es de todos

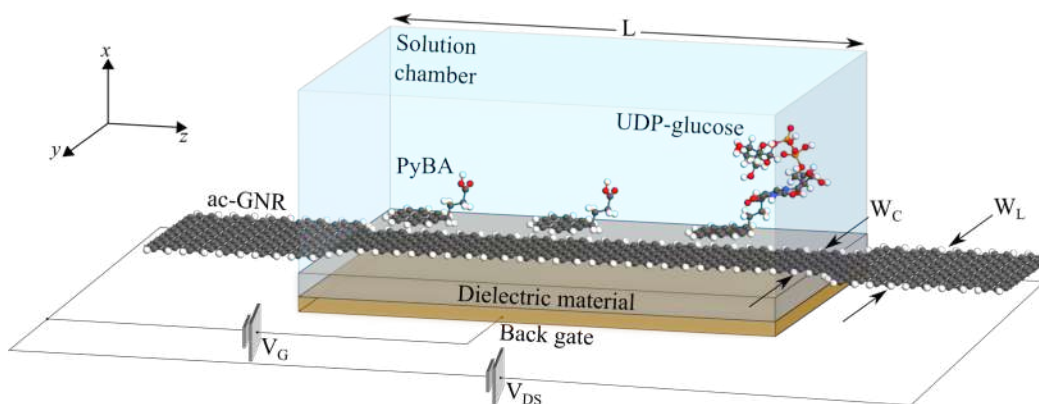
Gobierno  
de Colombia

COLOMBIA  
CIENTÍFICA



Applications

## UDP-glucose sensor



Jaramillo-Botero A; Marmolejo-Tejada JM. All-Armchair Graphene Nanoribbon Field Uriding Phosphate Glucose Sensor: First-Principles In-Silico Design and Characterization, IEEE Sensors Journal, Volume 19, Issue 11 (2019)

Nanosensores



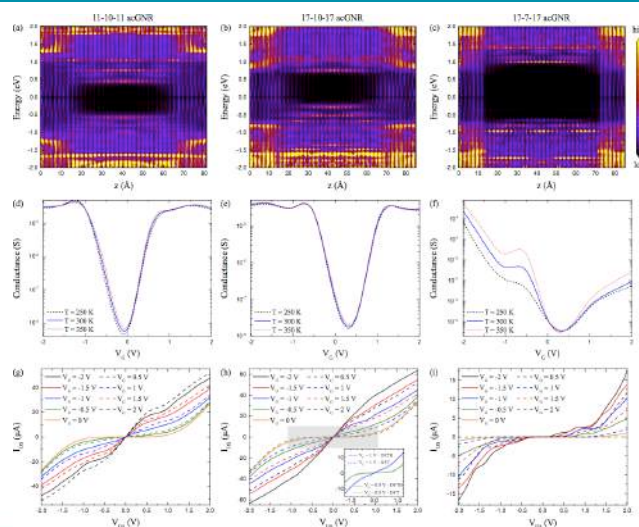
El futuro es de todos

Gobierno de Colombia

COLOMBIA CIENTIFICA



## UDP-glucose sensor



Jaramillo-Botero A; Marmolejo-Tejada JM. All-Armchair Graphene Nanoribbon Field Uriding Phosphate Glucose Sensor: First-Principles In-Silico Design and Characterization, IEEE Sensors Journal, Volume 19, Issue 11 (2019)

Nanosensores



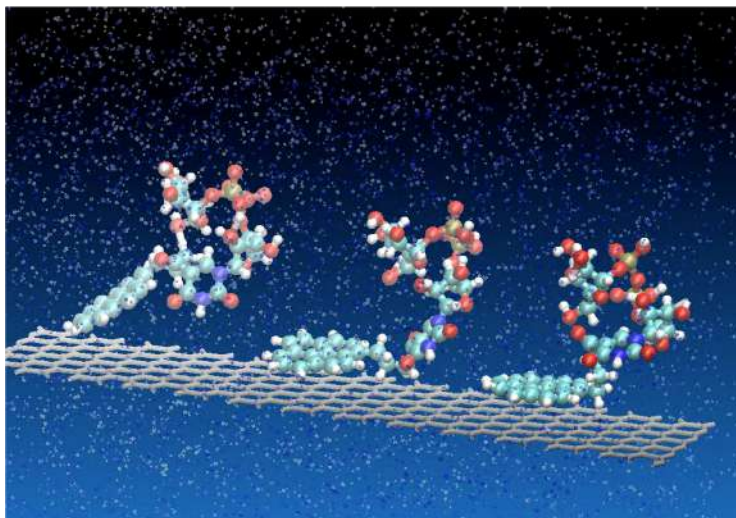
El futuro es de todos

Gobierno de Colombia

COLOMBIA CIENTIFICA



## UDP-glucose sensor



Nanosensores



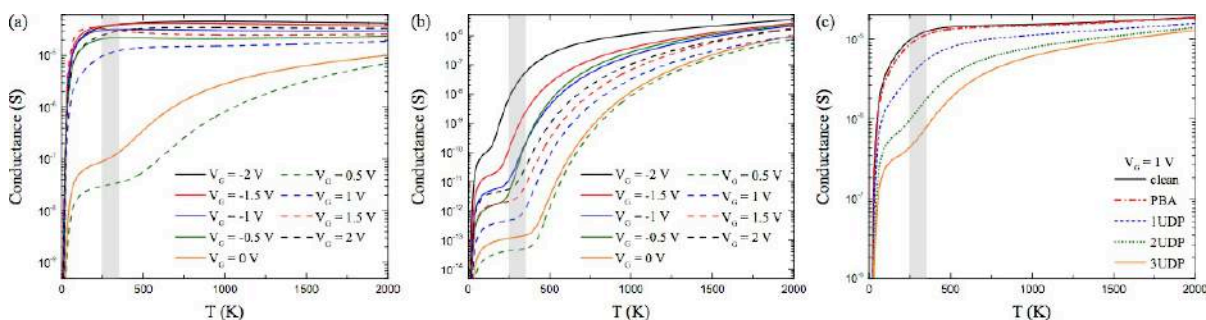
El futuro  
es de todos

Gobierno  
de Colombia

COLOMBIA  
CIENTÍFICA



## UDP-glucose sensor



Jaramillo-Botero A; Marmolejo-Tejada JM. All-Armchair Graphene Nanoribbon Field Urinding Phosphate Glucose Sensor: First-Principles In-Silico Design and Characterization, IEEE Sensors Journal, Volume 19, Issue 11 (2019)

Nanosensores



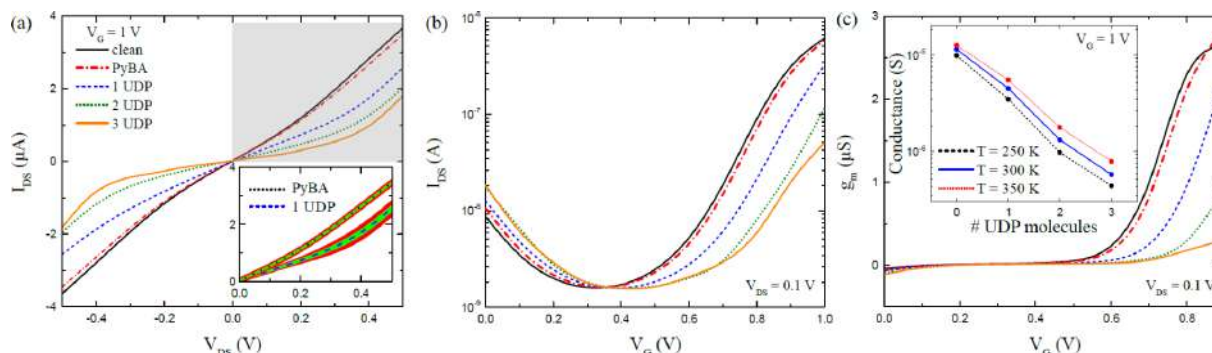
El futuro  
es de todos

Gobierno  
de Colombia

COLOMBIA  
CIENTÍFICA



## UDP-glucose sensor

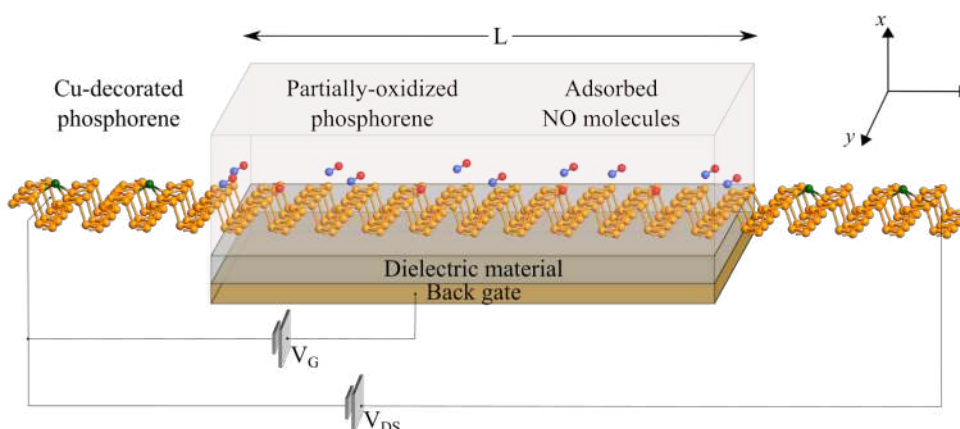


Jaramillo-Botero A; Marmolejo-Tejada JM. All-Armchair Graphene Nanoribbon Field Effect Transistor Phosphate Glucose Sensor: First-Principles In-Silico Design and Characterization, IEEE Sensors Journal, Volume 19, Issue 11 (2019)

## Nanosensores



## Volatile organic compounds (VOCs) sensor

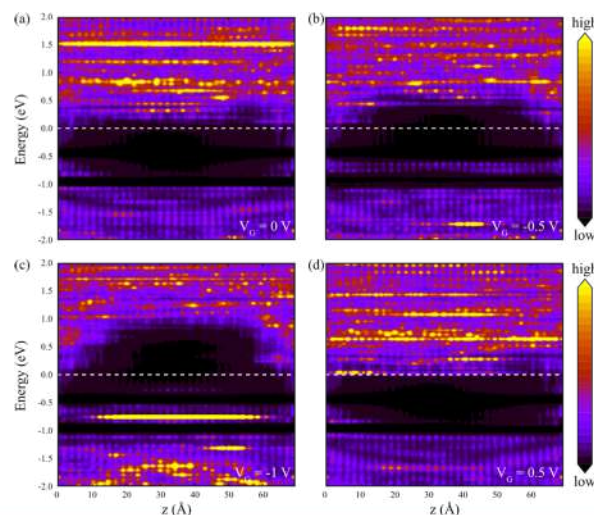


J. M. Marmolejo-Tejada and A. Jaramillo-Botero. Partially-oxidized phosphorene sensor for the detection of sub-nano Molar concentrations of nitric oxide: A first-principles study, Phys. Chem. Chem. Phys., 2019,21, 19083-19091

## Nanosensores



## Phosphorene FET



J. M. Marmolejo-Tejada and A. Jaramillo-Botero. Partially-oxidized phosphorene sensor for the detection of sub-nano Molar concentrations of nitric oxide: A first-principles study, Phys. Chem. Chem. Phys., 2019,21, 19083-19091

Nanosensores



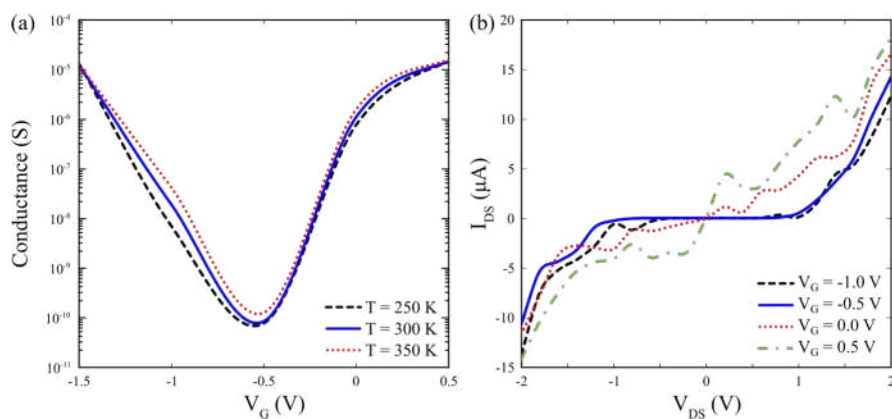
El futuro es de todos

Gobierno de Colombia

COLOMBIA CIENTÍFICA



## Phosphorene FET



J. M. Marmolejo-Tejada and A. Jaramillo-Botero. Partially-oxidized phosphorene sensor for the detection of sub-nano Molar concentrations of nitric oxide: A first-principles study, Phys. Chem. Chem. Phys., 2019,21, 19083-19091

Nanosensores



El futuro es de todos

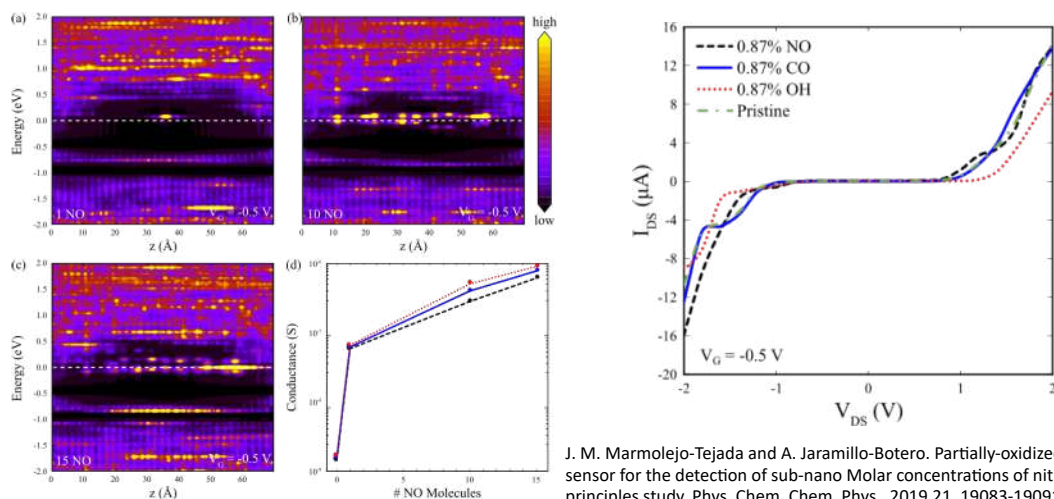
Gobierno de Colombia

COLOMBIA CIENTÍFICA





## Nitric Oxide (NO) sensor



J. M. Marmolejo-Tejada and A. Jaramillo-Botero. Partially-oxidized phosphorene sensor for the detection of sub-nano Molar concentrations of nitric oxide: A first-principles study, Phys. Chem. Chem. Phys., 2019,21, 19083-19091

## Nanosensores



El futuro  
es de todos

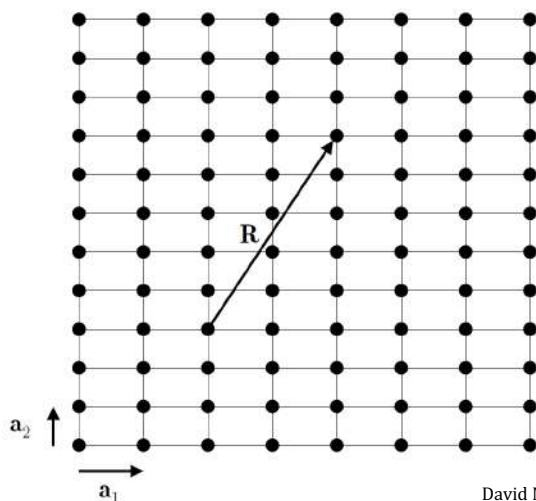
Gobierno  
de Colombia

COLOMBIA  
CIENTÍFICA



## Setting up calculations

## Crystalline structures



- Crystal:
  - Material whose measurable properties are periodic in space.
- Crystal structure:
  - It is one that can fill all space by the regular stacking of identical blocks or unit cells.

David Miller, "Quantum Mechanics for Scientists and Engineers", Stanford Online (2016).

Nanosensores



El futuro es de todos

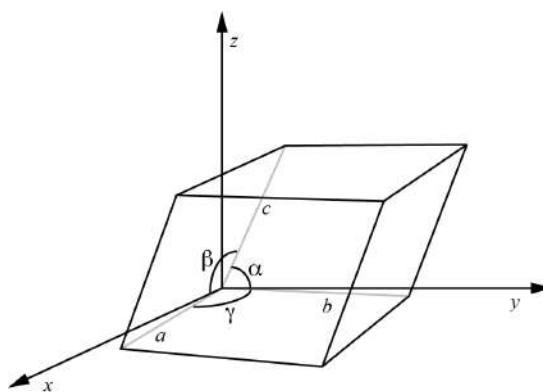
Gobierno de Colombia

COLOMBIA CIENTÍFICA



## Crystalline Systems

- Unit cell:
  - Smallest repetitive volume which contains the complete lattice pattern of a crystal.
  - $a$ ,  $b$  and  $c$  are the edge lengths.
  - $\alpha$ ,  $\beta$  and  $\gamma$  are interaxial angles.



Nanosensores



El futuro es de todos

Gobierno de Colombia

COLOMBIA CIENTÍFICA



## Reciprocal space

- The reciprocal lattice is defined as a network of points in the Fourier space:
  - $\vec{r} = h\vec{a}^* + k\vec{b}^* + l\vec{c}^*$
  - with  $h, k, l$  integers and  $\vec{a}^*, \vec{b}^*, \vec{c}^*$  the basis vectors of the reciprocal lattice:
  - $\vec{a}^* = C \frac{\vec{b} \times \vec{c}}{V}, \vec{b}^* = C \frac{\vec{c} \times \vec{a}}{V}, \vec{c}^* = C \frac{\vec{a} \times \vec{b}}{V},$
  - with  $C$  a constant and  $V$  the volume of the unit cell in direct space:
  - $C = \begin{cases} 2\pi & \text{in solid state physics} \\ 1 & \text{in crystallography} \end{cases}$
  - $V = (\vec{a} \times \vec{b}) \cdot \vec{c} = \vec{a} \cdot (\vec{b} \times \vec{c})$

Nanosensores



El futuro es de todos

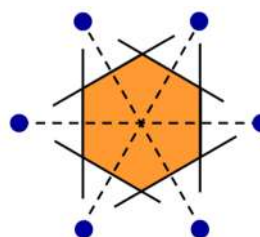
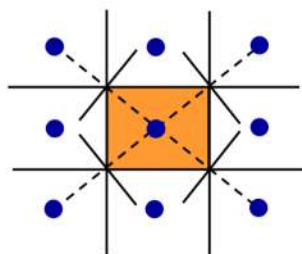
Gobierno de Colombia

COLOMBIA CIENTÍFICA



## The Brillouin zone

- Smallest polyhedron enclosed by the perpendicular bisectors of the nearest neighbors to a given point of the reciprocal space.
- First Brillouin zone for the two-dimensional rectangular and two-dimensional hexagonal reciprocal lattices:



B. Grenier and R. Ballou, *Crystallography: Symmetry groups and group representations*, EPJ Web of Conferences 22, 00006 (2012)

Nanosensores



El futuro es de todos

Gobierno de Colombia

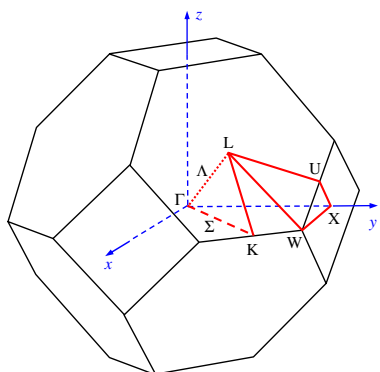
COLOMBIA CIENTÍFICA





## The Brillouin zone

- First Brillouin zone for a three dimensional cubic F reciprocal lattice.



Γ:	Brillouin zone's center
K:	middle of an edge between two hexagonal faces
L:	center of an hexagonal face
U:	middle of an edge between a square face and an hexagonal one
X:	center of a square face
W:	corner

B. Grenier and R. Ballou, *Crystallography: Symmetry groups and group representations*, EPJ Web of Conferences 22, 00006 (2012)

Nanosensores



El futuro  
es de todos

Gobierno  
de Colombia

COLOMBIA  
CIENTÍFICA



## Band structures

- The band structure of a material determines its electronic and optical properties.
- Band structure calculations require solving the Schrödinger equation using particle wave functions in a periodic potential:
  - $\psi_{nk}(r) = \exp(ikr)u_{nk}(r)$
  - where  $\psi(r)$  is an eigenfunction of the system and is defined as the product of a plane wave envelope and a periodic Bloch function  $u(r)$ ;  $n$  corresponds to the band index, while  $k$  corresponds to the wave vector associated with the direction of motion of the electron in the crystal and takes on values within the corresponding Brillouin zone.
- The band structure is determined by the orbital energies  $\varepsilon_{nk}$  for each band  $n$  and momentum  $k$ .

Nanosensores



El futuro  
es de todos

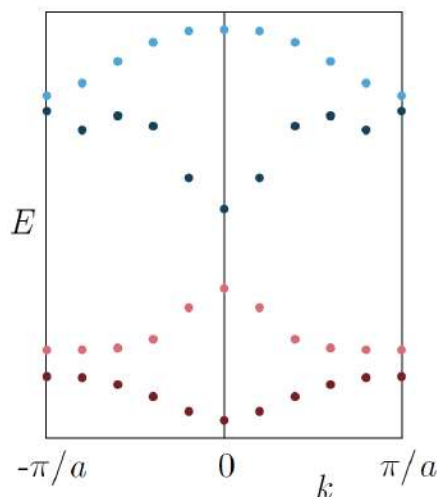
Gobierno  
de Colombia

COLOMBIA  
CIENTÍFICA



## Band structure diagrams

- Solving the one-electron Schrödinger equation gives energy eigensolutions.
- We continue with the other allowed values of  $k$ .



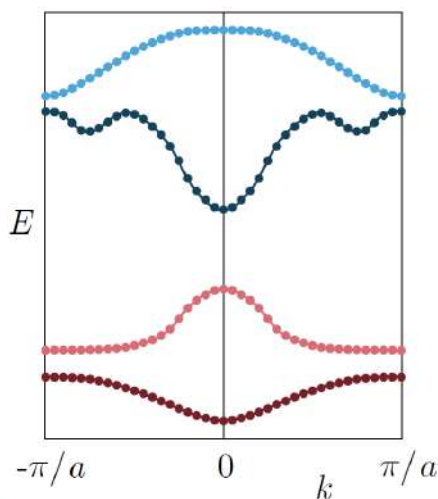
David Miller, "Quantum Mechanics for Scientists and Engineers", Stanford Online (2016).

Nanosensores



## Band structure diagrams

- A larger crystal gives more allowed values of  $k$ .
- This sets of "dots" effectively become like lines.
  - We refer to the group of dots on a line as a "band".



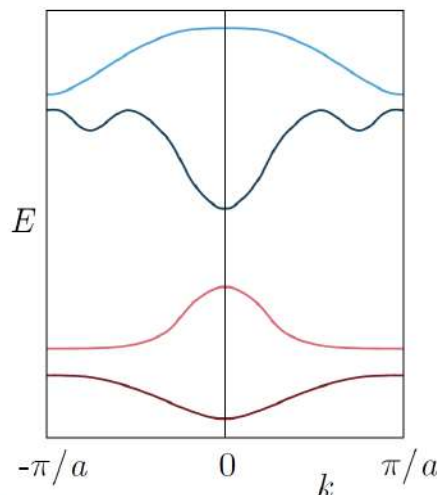
David Miller, "Quantum Mechanics for Scientists and Engineers", Stanford Online (2016).

Nanosensores



## Band structure diagrams

- There are multiple bands in a band structure, in fact, an infinite number, but usually only a few are important for the properties of a material.
- In each band, we only have to plot  $k$ -values from  $-\pi/a$  to  $\pi/a$ .
- This range is known as the (first) Brillouin zone.



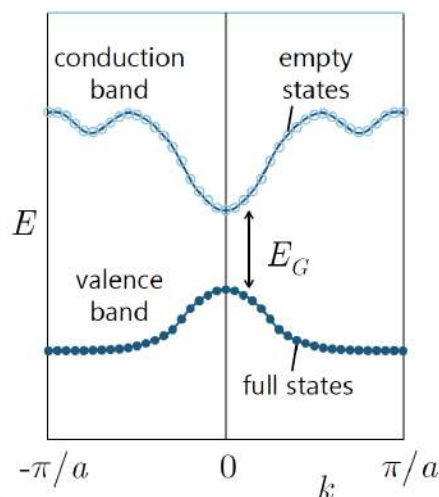
David Miller, "Quantum Mechanics for Scientists and Engineers", Stanford Online (2016).

Nanosensores



## Semiconductors and insulators

- Semiconductors and insulators have an (almost) completely full band (the valence band) separated by a "bandgap" of energy  $E_G$  from an (almost) completely empty band (the conduction band).



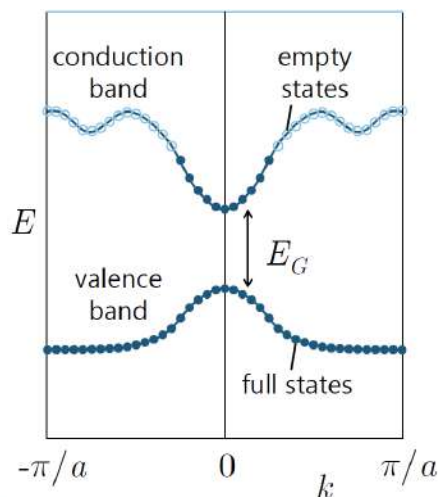
David Miller, "Quantum Mechanics for Scientists and Engineers", Stanford Online (2016).

Nanosensores



## Metals

- Because of the number of electrons in the metal atoms, the lowest conduction band is partially full of electrons.
  - e.g., half-full even at zero temperature.
    - Hence metals conduct electricity well.



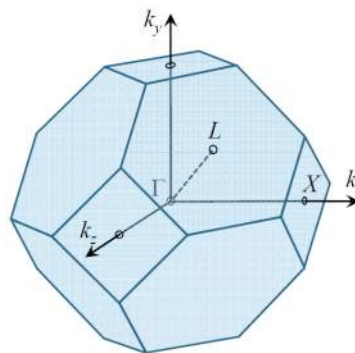
David Miller, "Quantum Mechanics for Scientists and Engineers", Stanford Online (2016).

Nanosensores



## Brillouin zone in 3D

- The Brillouin zone for the diamond or zinc-blende lattice is a 3D object.
  - Two important directions are:
    - X: Along one of the coordinate directions.
    - L: Along one of the cube space diagonals.
  - The center is the  $\Gamma$  (gamma) point.



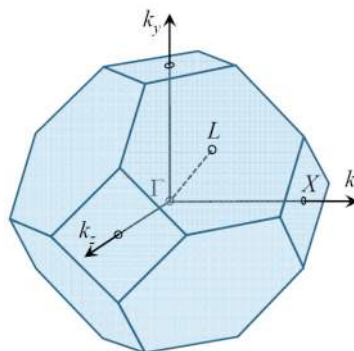
David Miller, "Quantum Mechanics for Scientists and Engineers", Stanford Online (2016).

Nanosensores



## Brillouin zone in 3D

- Typically, the band structure is calculated only along a few directions.
- Such as along the lines from the  $\Gamma$  point (at the center of the Brillouin zone) to the  $X$  point and the  $L$  point.



David Miller, "Quantum Mechanics for Scientists and Engineers", Stanford Online (2016).

## Nanosensores



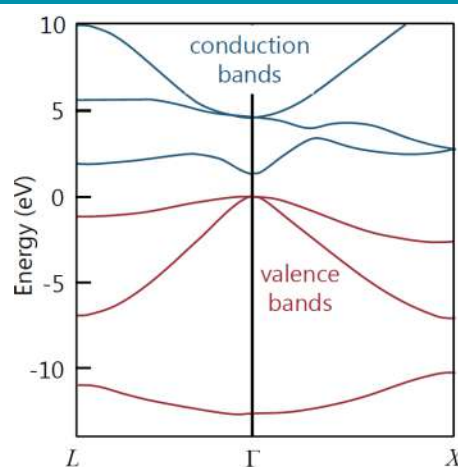
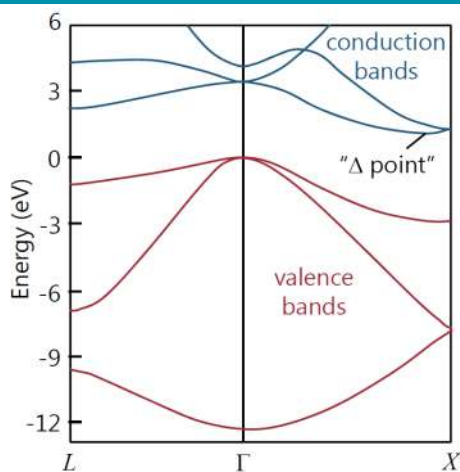
El futuro es de todos

Gobierno de Colombia

COLOMBIA CIENTÍFICA



## Si and GaAs band structure



David Miller, "Quantum Mechanics for Scientists and Engineers", Stanford Online (2016).

## Nanosensores

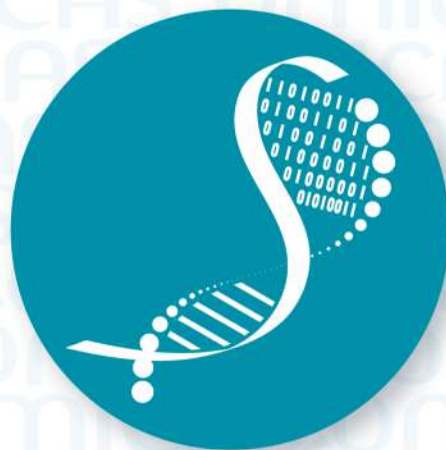


El futuro es de todos

Gobierno de Colombia

COLOMBIA CIENTÍFICA



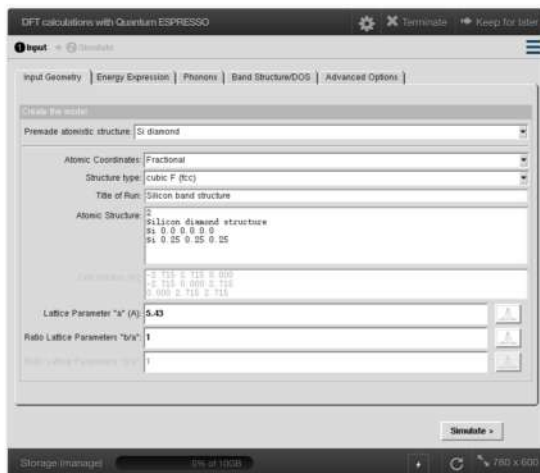


## Hands-on tutorials

### DFT calculations with Quantum ESPRESSO

- We will begin our test calculations using the online tool:  
<https://nanohub.org/tools/dftqe>
- This tool allows us to run quantum ESPRESSO (a powerful electronic structure code based on density-functional theory, plane waves, and pseudopotentials) for performing several calculations:
  - Total energy.
  - Energy minimization to predict structures.
  - Kohn-Sham band structure of periodic systems and phonons.
  - Cell and force relaxation.
  - Output of Stress and forces.

## Silicon Band Structure



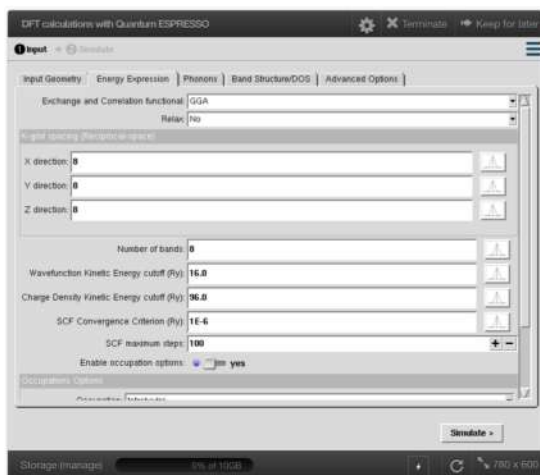
- The tool already has some premade atomistic structures with their corresponding cell parameters and atom coordinates.

- Choose Si diamond.

Nanosensores



## Silicon Band Structure



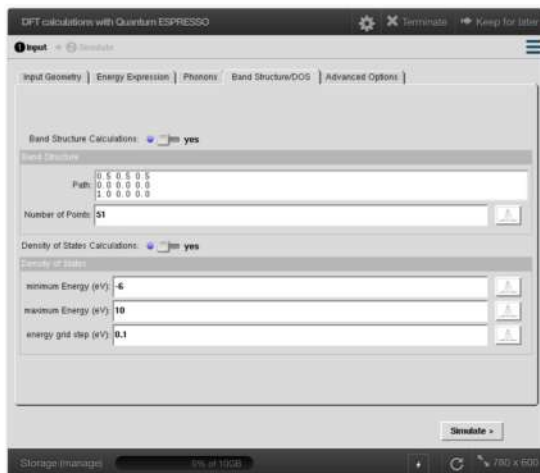
- We can choose LDA or GGA functionals and enable/disable relaxation.
- Choose GGA and no relaxation, but you should also explore the other options.
- Specify k-points in the reciprocal space, as well as other calculation parameters.
- We will use default values for the moment.

Nanosensores





## Silicon Band Structure



- Enable Band Structure Calculation, choose the path along the high-symmetry points you wish to explore and the number of k-points along the path.
- Notice your path goes from  $L(0.5, 0.5, 0.5)$  to  $\Gamma(0.0, 0.0, 0.0)$  to  $X(1.0, 0.0, 0.0)$ .

Nanosensores



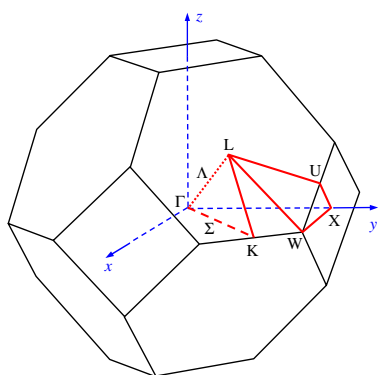
El futuro es de todos

Gobierno de Colombia

COLOMBIA CIENTÍFICA



Remember the 1<sup>st</sup> Brillouin zone for a 3D cubic reciprocal lattice



- $\Gamma$ : Brillouin zone's center
- K: middle of an edge between two hexagonal faces
- L: center of a hexagonal face
- U: middle of an edge between a square face and an hexagonal one
- X: center of a square face
- W: corner

Nanosensores



El futuro es de todos

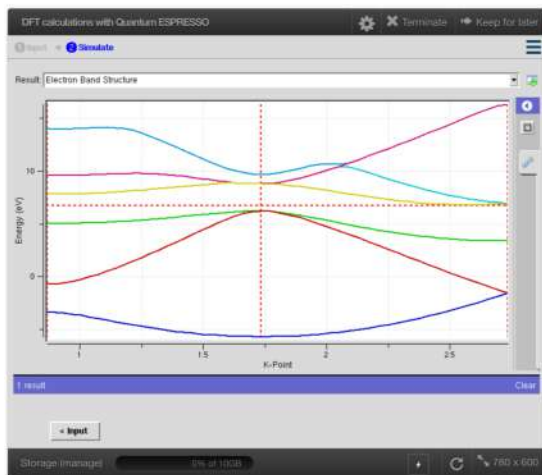
Gobierno de Colombia

COLOMBIA CIENTÍFICA





## Silicon Band Structure



- The red vertical lines mark the high-symmetry points (in this case,  $L$ ,  $\Gamma$  and  $X$ ).
- The red horizontal line shows the Fermi energy.

Nanosensores



El futuro es de todos

Gobierno de Colombia

COLOMBIA CIENTÍFICA



## Silicon Band Structure



- We can zoom in and measure the band gap.
  - For this case, we see an indirect gap of  $\sim 0.6\text{eV}$ .
- Exercise:
  - Repeat the calculation using LDA and compare the results.
  - How about relaxing the structure?

Nanosensores



El futuro es de todos

Gobierno de Colombia

COLOMBIA CIENTÍFICA



## Input scripts



- So far, we have not discussed the particularities of our input script, but you should study all the input scripts necessary for this calculation and get familiar with their structure and format.

- For more details on each command, check the input file description help at: [https://www.quantum-espresso.org/Doc/INPUT\\_PW.html](https://www.quantum-espresso.org/Doc/INPUT_PW.html)

Nanosensores



El futuro es de todos

Gobierno de Colombia

COLOMBIA CIENTÍFICA



## GNR Band Structure

- Let's continue using the nanohub's online tool for calculating the band structure of a GNR.
- This time, we will import the coordinates and type in the cell parameters.
  - Check the provided xyz file, which was created with Nanoribbon tool in QuantumATK.

```

14
_a 20 _b 20 _c 4.26258 _alph 90 _beta 90 _gamma 90
C 5.00000 5.00000 2.84172
C 5.00000 6.23050 3.55215
C 5.00000 5.00000 1.42086
C 5.00000 7.46100 2.84172
C 5.00000 8.69150 3.55215
C 5.00000 6.23050 0.71043
C 5.00000 7.46100 1.42086
C 5.00000 9.92200 2.84172
C 5.00000 8.69150 0.71043
C 5.00000 9.92200 1.42086
H 5.00000 4.05603 3.38672
H 5.00000 4.05603 0.87586
H 5.00000 10.86597 3.38672
H 5.00000 10.86597 0.87586

```

Nanosensores



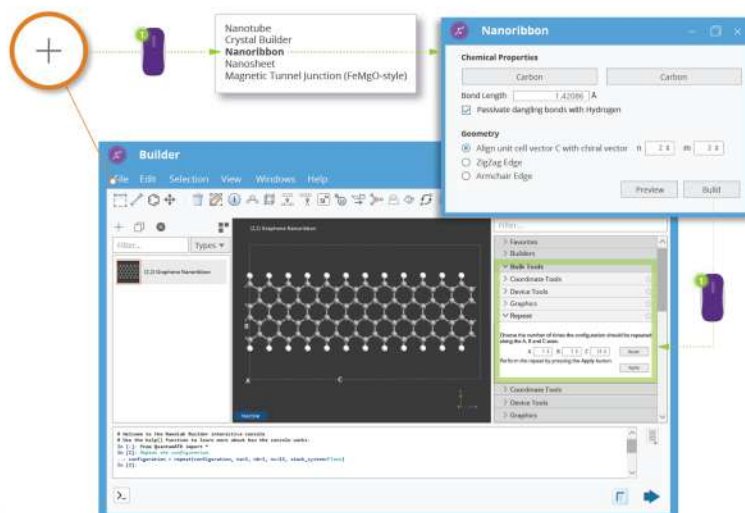
El futuro es de todos

Gobierno de Colombia

COLOMBIA CIENTÍFICA



## QuantumATK's Nanoribbon tool



Nanosensores

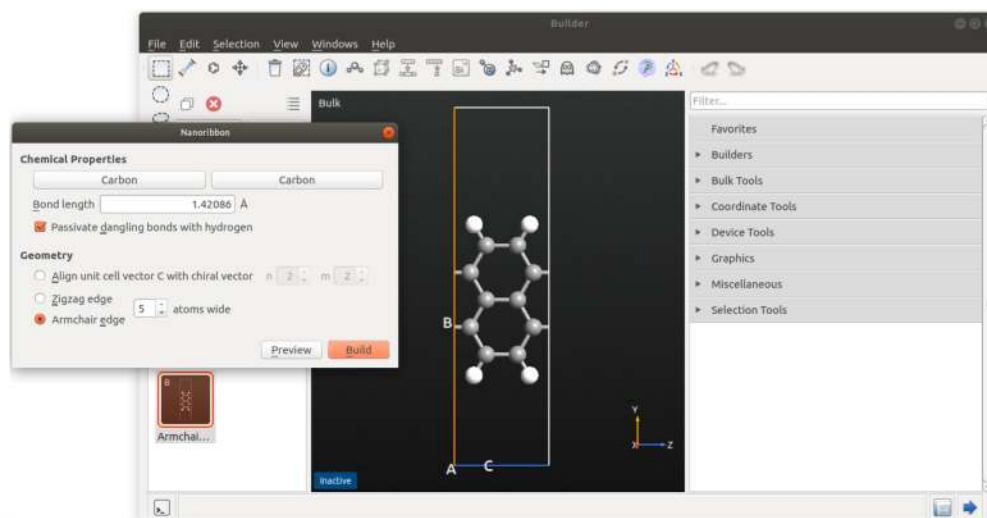


El futuro es de todos

Gobierno de Colombia



## QuantumATK's Nanoribbon tool



Nanosensores



El futuro es de todos

Gobierno de Colombia



## Characteristics of the xyz file

- The first line indicates the number of atoms,  $n$ .
- Second line is a comment.
  - In this case, we included the cell dimensions and angles.
  - Notice the structure is periodic on the z-direction.
- The following  $n$  lines contain the element symbol and corresponding position vector in Angstroms.

```

14
_a 20 _b 20 _c 4.26258 _alph 90 _beta 90 _gamma 90
C 5.00000 5.00000 2.84172
C 5.00000 6.23050 3.55215
C 5.00000 5.00000 1.42086
C 5.00000 7.46100 2.84172
C 5.00000 8.69150 3.55215
C 5.00000 6.23050 0.71043
C 5.00000 7.46100 1.42086
C 5.00000 9.92200 2.84172
C 5.00000 8.69150 0.71043
C 5.00000 9.92200 1.42086
H 5.00000 4.05603 3.38672
H 5.00000 4.05603 0.87586
H 5.00000 10.86597 3.38672
H 5.00000 10.86597 0.87586

```

Nanosensores



El futuro es de todos

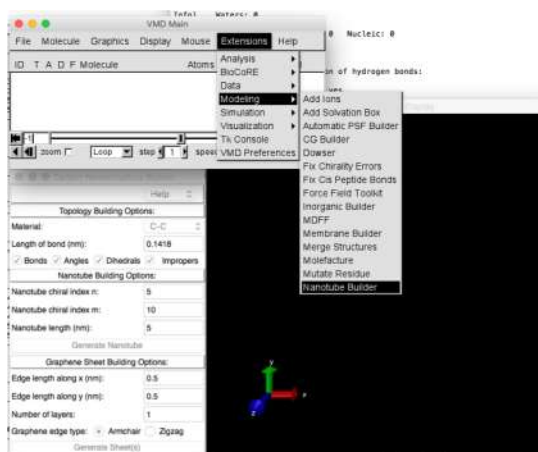
Gobierno de Colombia

COLOMBIA CIENTIFICA



## VMD's Carbon Nanostructure Builder Tool

- Note we can also use open source tools, such as VMD, for getting the system's coordinates.



Nanosensores



El futuro es de todos

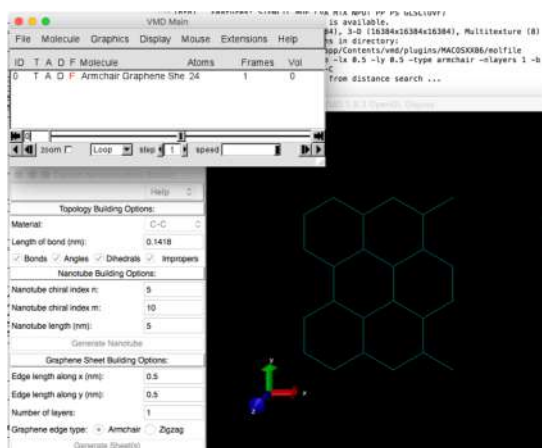
Gobierno de Colombia

COLOMBIA CIENTIFICA



## VMD's Carbon Nanostructure Builder Tool

- Note we can also use open source tools, such as VMD, for getting the system's coordinates.



Nanosensores



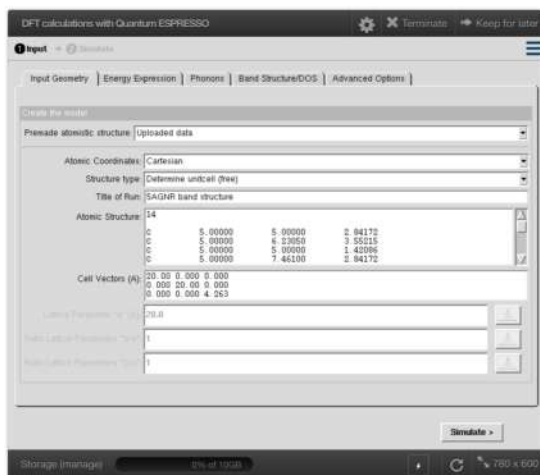
El futuro es de todos

Gobierno de Colombia

COLOMBIA CIENTÍFICA



## GNR Band Structure



- Upload the coordinates of the system in xyz format.
- The provided file has positions in Angstroms, then you should select Cartesian Atomic Coordinates.
- Select free type of unit cell and fill up the Cell Vectors in Angstroms.

Nanosensores



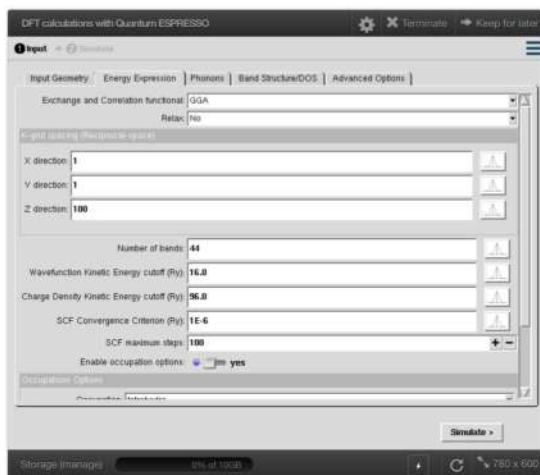
El futuro es de todos

Gobierno de Colombia

COLOMBIA CIENTÍFICA



## GNR Band Structure



- Since the GNR is only periodic on the z-direction, we only increase the number of k-points on that direction.
  - The number of k-points in the other directions is set to 1.
- Type in the number of bands.
  - Remember carbon has 4 Valence electrons and hydrogen just 1.

Nanosensores



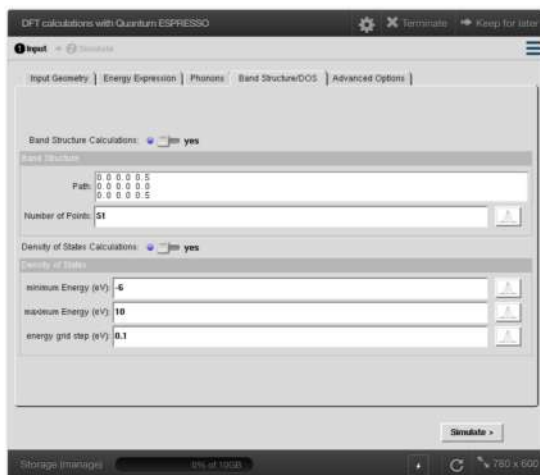
El futuro es de todos

Gobierno de Colombia

COLOMBIA CIENTÍFICA



## GNR Band Structure



- We are interested in computing the band structure along the transport direction (z-direction).
  - Then, the path goes from  $Z(0.0, 0.0, 0.5)$  to  $\Gamma(0.0, 0.0, 0.0)$  to  $Z(0.0, 0.0, 0.5)$ .

Nanosensores



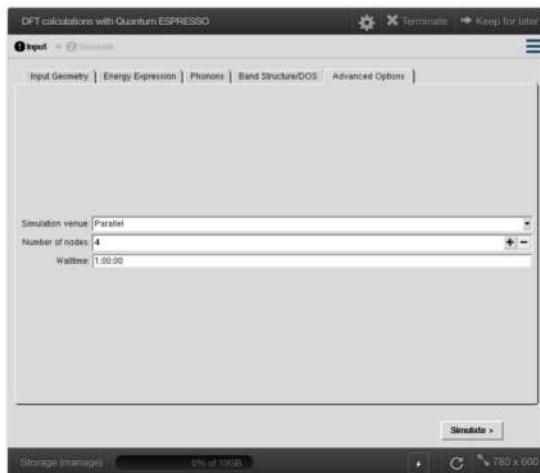
El futuro es de todos

Gobierno de Colombia

COLOMBIA CIENTÍFICA



## GNR Band Structure



- Notice the calculation could take several minutes on a single core.
- You may want to request a multi-core simulation and speedup the calculation.

Nanosensores



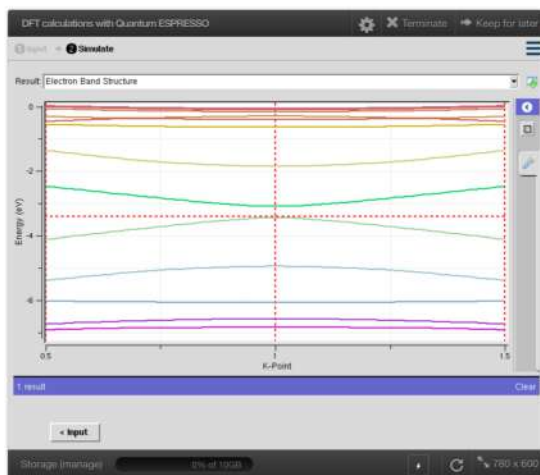
El futuro es de todos

Gobierno de Colombia

COLOMBIA CIENTÍFICA



## GNR Band Structure



- We can zoom in around the Fermi energy and measure the bandgap of our AGNR.
- In this case, we get a direct gap of  $\sim 0.35\text{eV}$ .

Nanosensores



El futuro es de todos

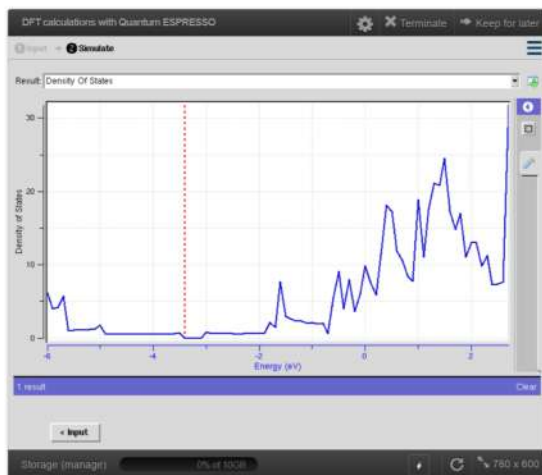
Gobierno de Colombia

COLOMBIA CIENTÍFICA





## GNR Density of States



- We can also get the Density of States (DOS) of our AGNR.
- How can we relate this to the band structure?

Nanosensores



El futuro es de todos

Gobierno de Colombia

COLOMBIA CIENTÍFICA



## Electrical Conduction through a molecule

- We can also use nanohub's tools for computing electrical conduction through a molecule:  
<https://nanohub.org/resources/molctoy>
- This tool computes current-voltage (I-V) characteristics and conductance spectrum (G-V) of a molecule sandwiched between two metallic contacts.

Nanosensores



El futuro es de todos

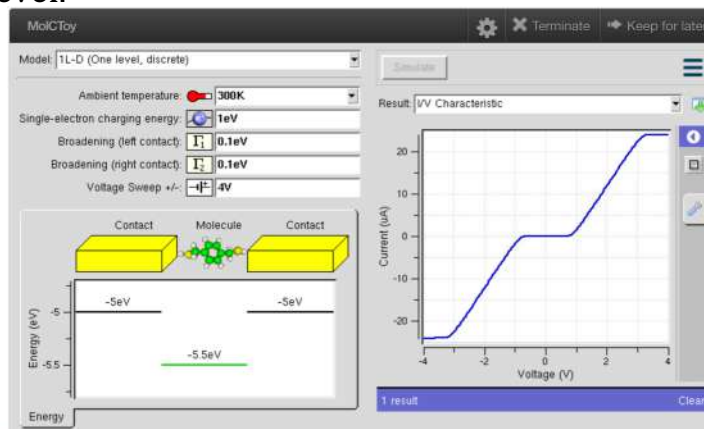
Gobierno de Colombia

COLOMBIA CIENTÍFICA



## Electrical Conduction through a molecule

- The 1 level discrete model represents a molecule with a single energy level.



Nanosensores



El futuro es de todos

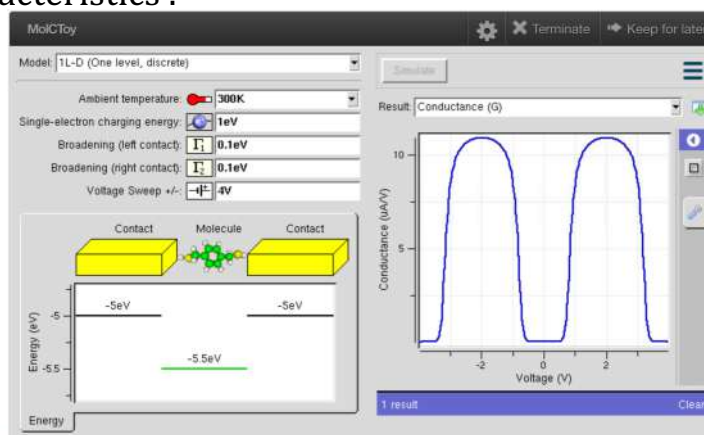
Gobierno de Colombia

COLOMBIA CIENTÍFICA



## Electrical Conduction through a molecule

- After running our calculation, we can observe Conductance and I/V characteristics.



Nanosensores



El futuro es de todos

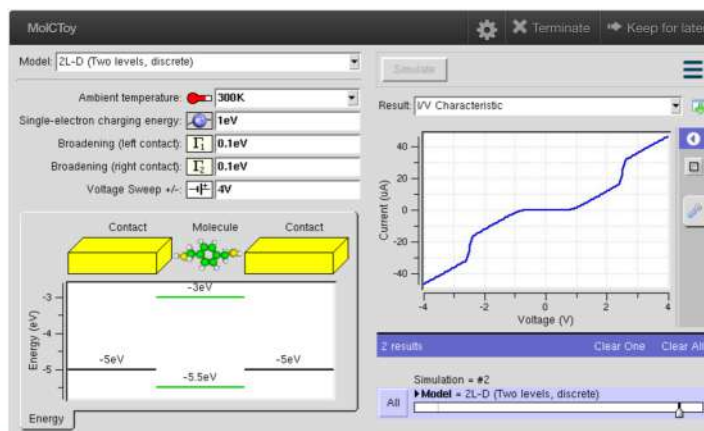
Gobierno de Colombia

COLOMBIA CIENTÍFICA



## Electrical Conduction through a molecule

- What happens when 2 energy levels are considered?



Nanosensores



El futuro es de todos

GOBIERNO DE COLOMBIA



Aliados



Apoyan



El futuro es de todos

GOBIERNO DE COLOMBIA

