Andres Jaramillo Botero
Director Científico

Taller anual: Del Gen al Cultivo

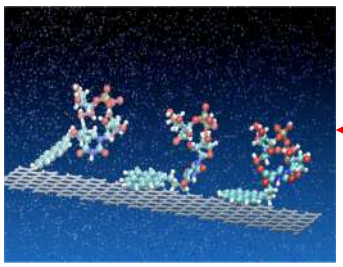
P2: Bio-Nanosensores: Prof. Andres Jaramillo Botero y Dr. Juan Manuel Marmolejo (práctica)
P3: Modelado Bio-Molecular: Prof. Carlos Arango y prof. Andres Jaramillo Botero

Parte I

Principios de Simulación Molecular

Parte II

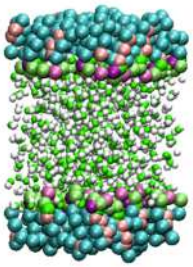
Simulación Molecular Aplicada a:



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)

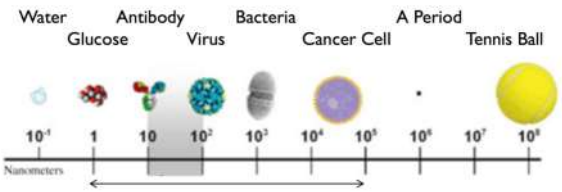
Taller 2: Diseño de nanosensores para biomarcadores

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

Objective

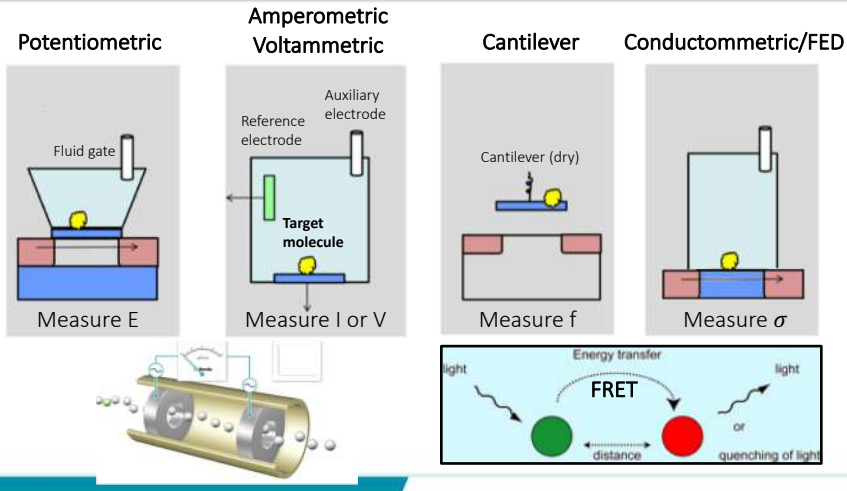
In-silico design, characterization and screening of nano-sensor device architectures for detection of biomarkers at nM-pM/L concentrations (mM/L)



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

Nano-bio-sensing mechanisms

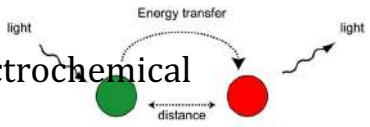
Surface functionalization, key to improve target selectivity/affinity

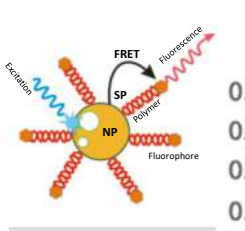


Nanosensores Jaramillo-Botero y Marmolejo, 2019

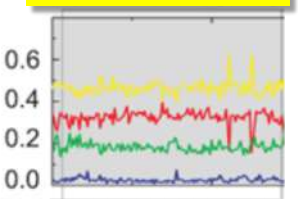
Indirect Sucrose Sensors

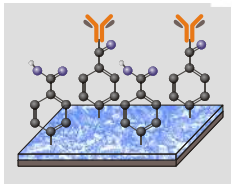
1. NP FRET
2. Electrochemical
3. FEDs

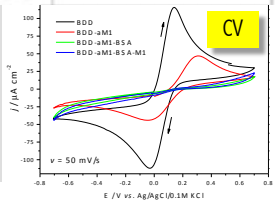




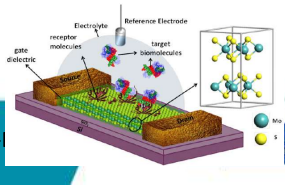
Fluorescence intensity/decay

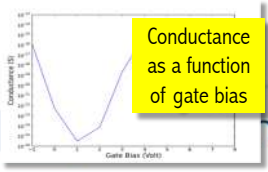






Focus on cytoplasmic sensing





Conductance as a function of gate bias

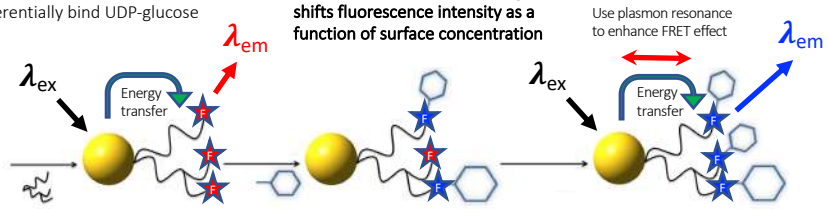
Nanosensores Jaramillo-

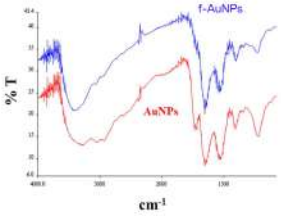
In-Vivo Gold-nanoparticle-based Sucrose/Starch FRET sensors

1- Au-NPs: surface modified to preferentially bind UDP-glucose

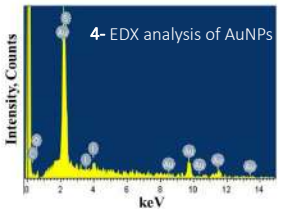
2- Au-NP surface-bound UDP-glucose, **shifts fluorescence intensity as a function of surface concentration**

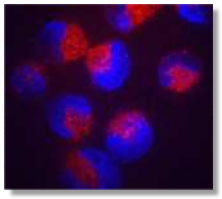
Use plasmon resonance to enhance FRET effect





3- FTIR spectra of Au-NP and f-Au-NP

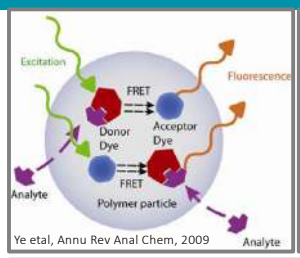




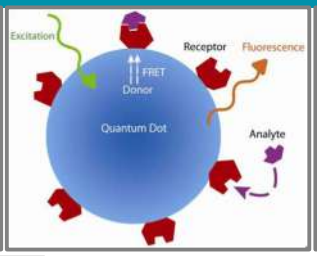
5- Fluorescent spectra or TEM image of f-AuNPs

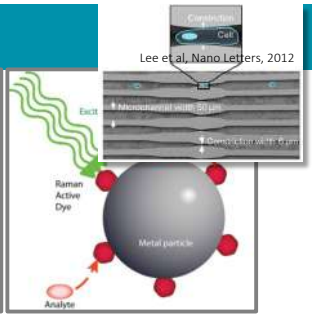
Jaramillo-Botero y Marmolejo, 2019

Nanoparticle based FRET options

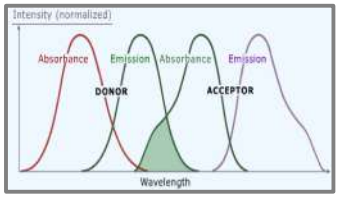


Ye etal, Annu Rev Anal Chem, 2009

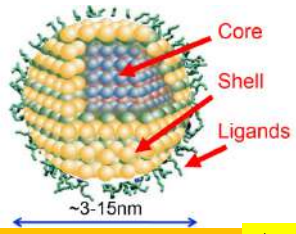




Lee et al, Nano Letters, 2012



Lewin's CELLS. George Plopper, David Sharp, Eric Sikorski. ©2015

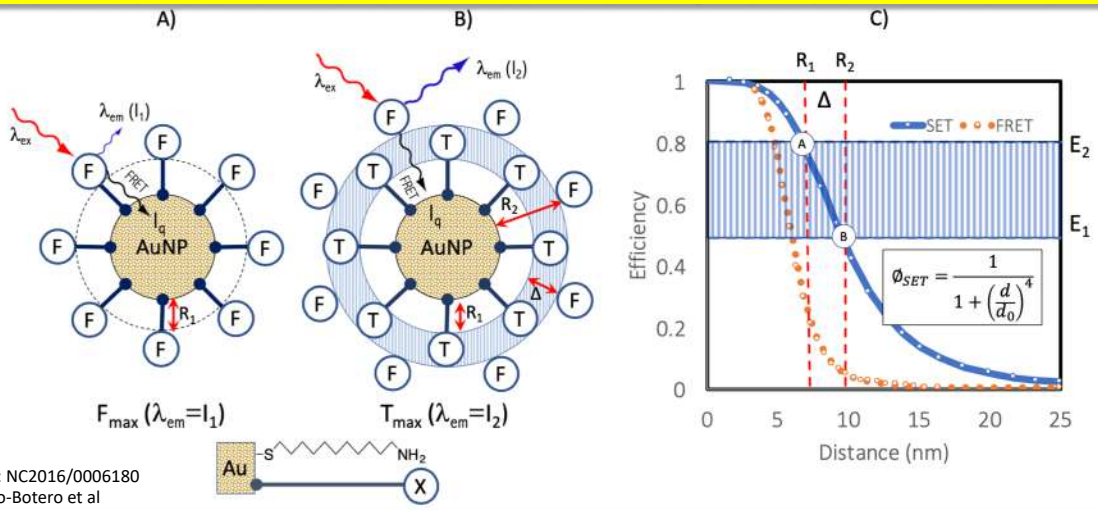


Challenges: cytosolic delivery of QDs and NPs to target, environment (autofluorescence of intracellular compar

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

SET quenching

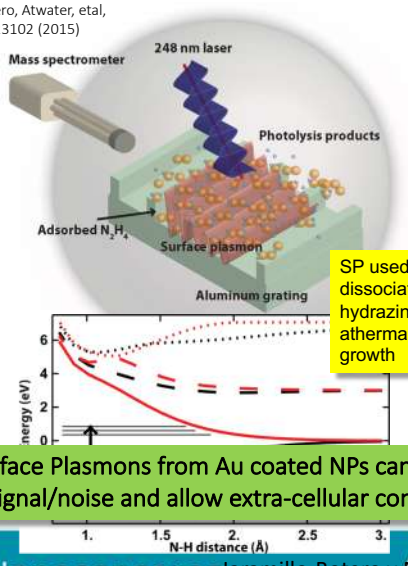
Changes in fluorescence spectra of the nanobiosensor in the presence of different concentrations of glucose under optimal experimental conditions.



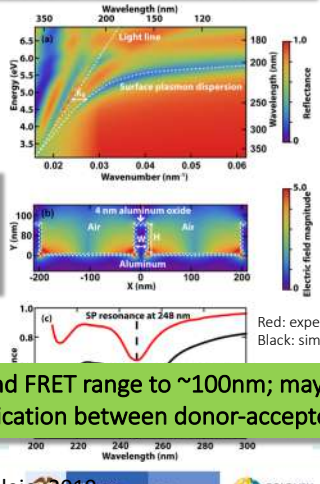
Patente: NC2016/0006180
Jaramillo-Botero et al

Plasmon enhanced SET/FRET

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



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



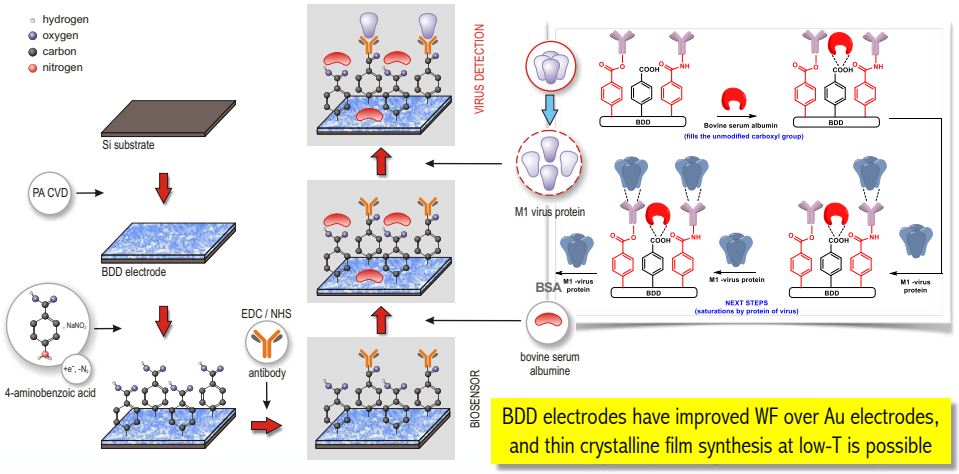
SP used to dissociate hydrazine in athermal GaN growth

Red: experiment
Black: simulation

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

Electrochemical: influenza case

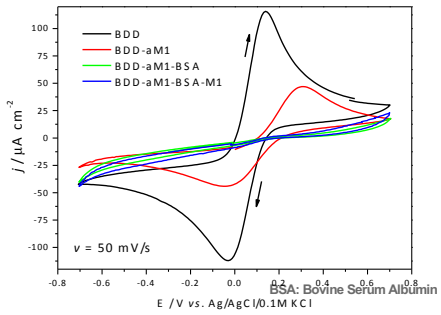
D. Nidzworski, K. Siuzdak, P. Niedziałkowski, R. Bogdanowicz, M. Sobaszek, J. Ryl, P. Weiher, M. Sawczak, E. Wnuk, W.A. Goddard, A. Jaramillo-Botero and T. Ossowski in prep for submission to Science, 2016

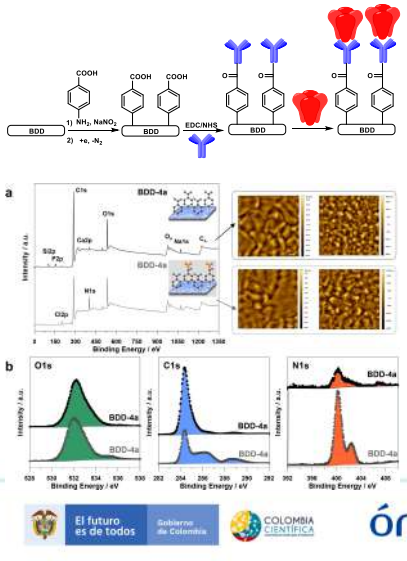


BDD electrodes have improved WF over Au electrodes, and thin crystalline film synthesis at low-T is possible

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

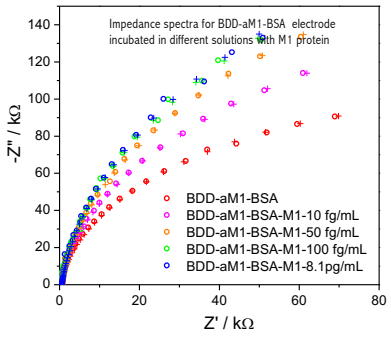


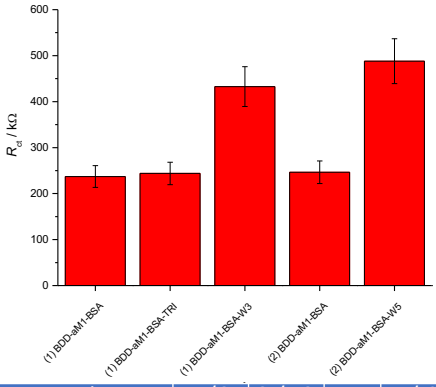


For pristine BDD electrode the difference between oxidation and reduction potential peak equals 0.17 V, whereas when M1 antibody was bound, current decreases and potential difference grows to 0.36 V. After incubation of BDD-aM1 electrode in BSA or M1 protein solution, no oxidation or reduction peak was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

Impedance spectra and EEQC

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

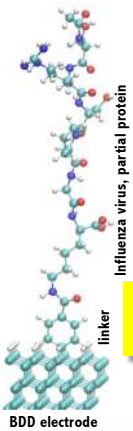


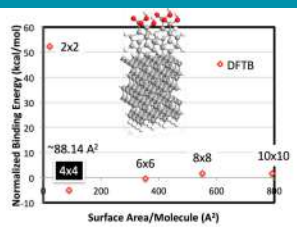


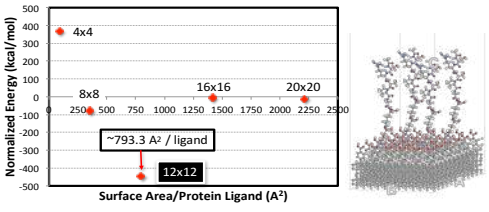
Impedance spectra of BDD-aM1-BSA electrode after incubation with different M1 concentrations recorded in 1 mM $K_3Fe(CN)_6$ + 0.1 PBS at E_f = + 0.13 V vs. Ag/AgCl/0.1M KCl

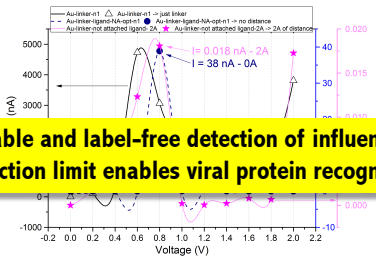
sample	R_e / Ω	Q_{dl} / μF Ω^{-1} s^n	n	R_{ct} / 10^5 Ω
BDD-aM1-BSA	391.7	1.18	0.944	2.13
BDD-aM1-BSA-10 fg/mL	325.9	1.15	0.948	3.20
BDD-aM1-BSA-50 fg/mL	389.5	1.13	0.955	4.28
BDD-aM1-BSA-100 fg/mL	327.0	1.11	0.952	5.12
BDD-aM1-BSA-8 pg/mL	358.6	1.09	0.953	5.24

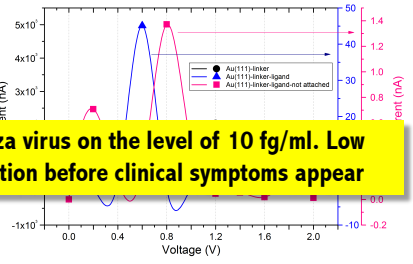
Surface coverage and IV analysis







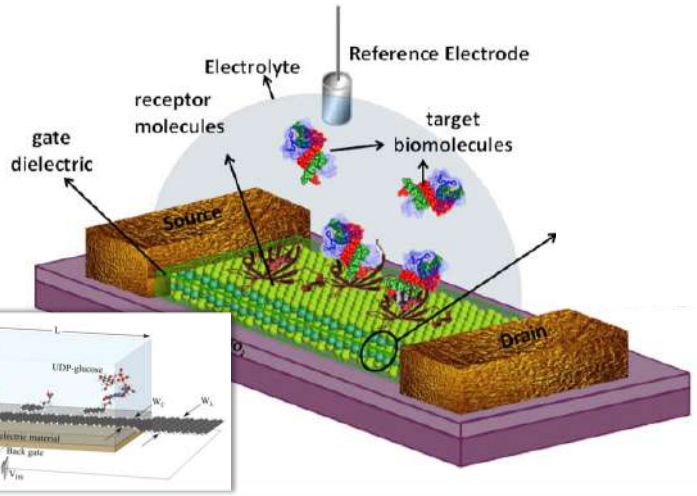




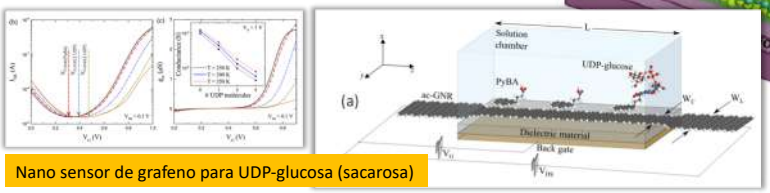
Reliable and label-free detection of influenza virus on the level of 10 fg/ml. Low detection limit enables viral protein recognition before clinical symptoms appear

Jaramillo-Botero y Marmolejo, 2019

Field Effect Devices (FEDs)

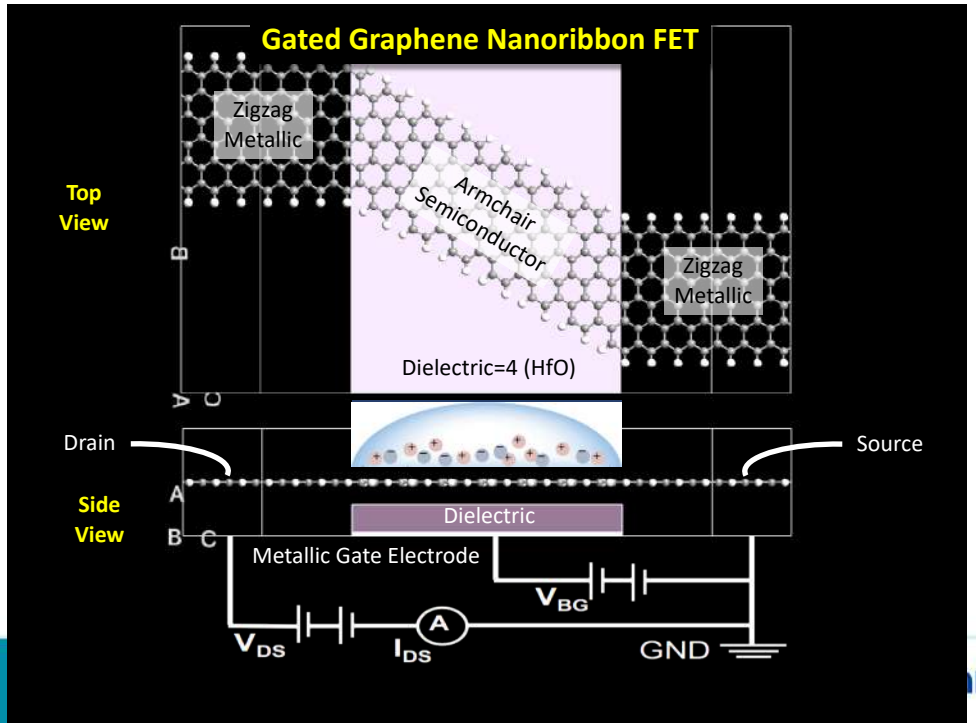


A. Jaramillo-Botero and Marmolejo-Tejada , IEEE Sensors, 2/2019



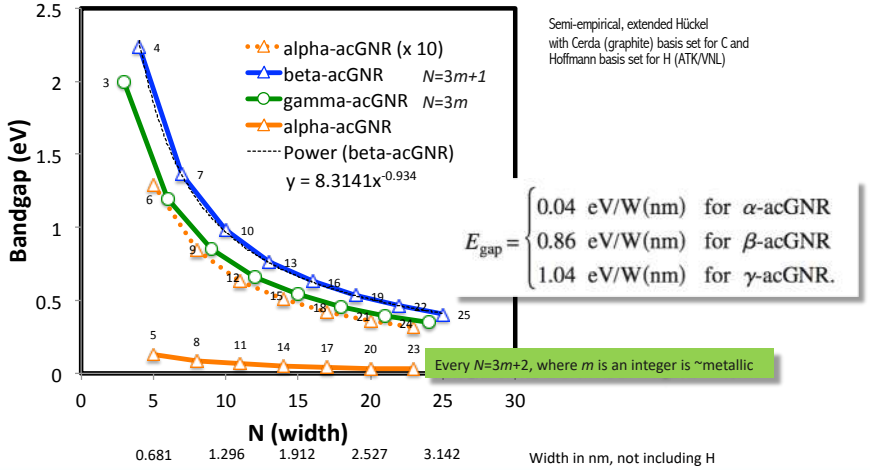
Nano sensor de grafeno para UDP-glucosa (sacarosa)

Nanosensores



ac-GNR Bandgap

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



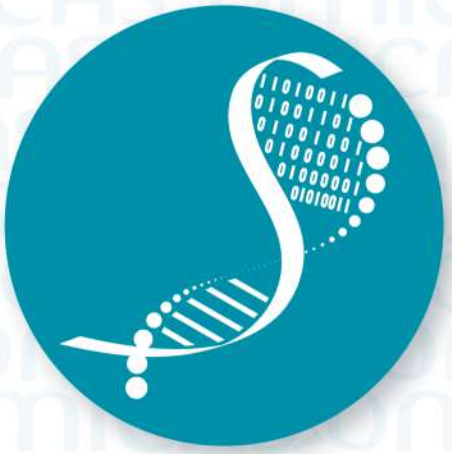
Semi-empirical, extended Hückel with Cerda (graphite) basis set for C and Hoffmann basis set for H (ATK/VNL)

$$E_{gap} = \begin{cases} 0.04 \text{ eV/W(nm)} & \text{for } \alpha\text{-acGNR} \\ 0.86 \text{ eV/W(nm)} & \text{for } \beta\text{-acGNR} \\ 1.04 \text{ eV/W(nm)} & \text{for } \gamma\text{-acGNR.} \end{cases}$$

Every $N=3m+2$, where m is an integer is ~metallic

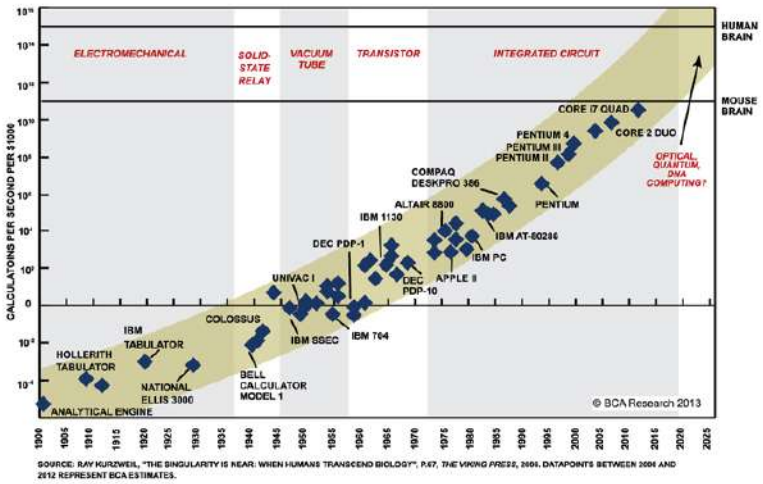
Band gaps and effective masses are inversely proportional to width, yet with a different proportionality constant

Nanosensores Jaramillo-Botero y Marmolejo, 2019



Computational Science

Computers: Moore's law

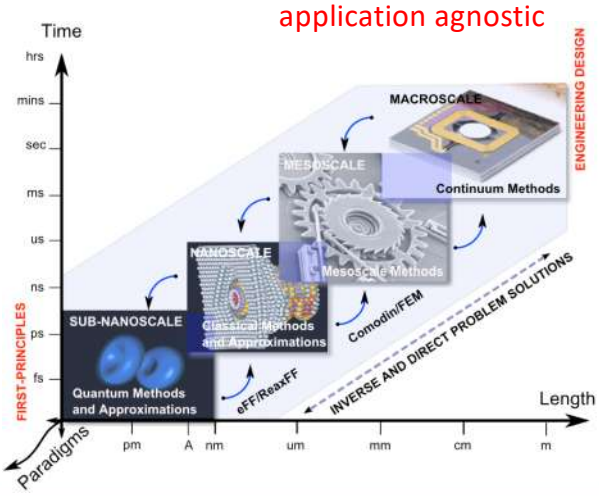


Computational Science: any, and all fields

- 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

Theory, methods and tools in computational nanoscience

application agnostic



QM methods:
- Fundamental
- But, too expensive
- <1K atoms, <1ps

FF methods:
- Trained analytical PE
- Cheaper than QM
- Millions of atoms
- Limited time-scaling

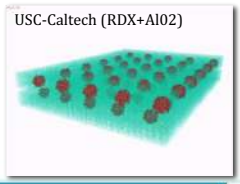
Coarse-Grain methods:
- Trained analytical forms
- Cheaper than atomistic
- 10's Millions atoms
- Increased time scale
- But, difficult chemistry
- Transferability

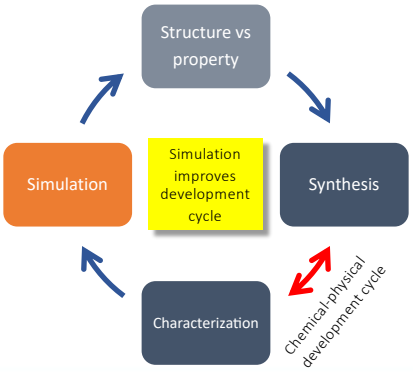
Continuum methods:
- Challenging 1:1 mapping
- Resolution loss
- But, rates and other parameters extractable from atomistic

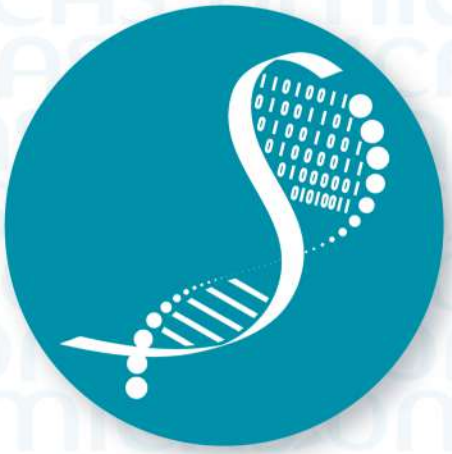
Applications: Biology, energy, construction, space, materials, defense, etc

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 oppossed 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







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"

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

Smaller than we've ever manufactured

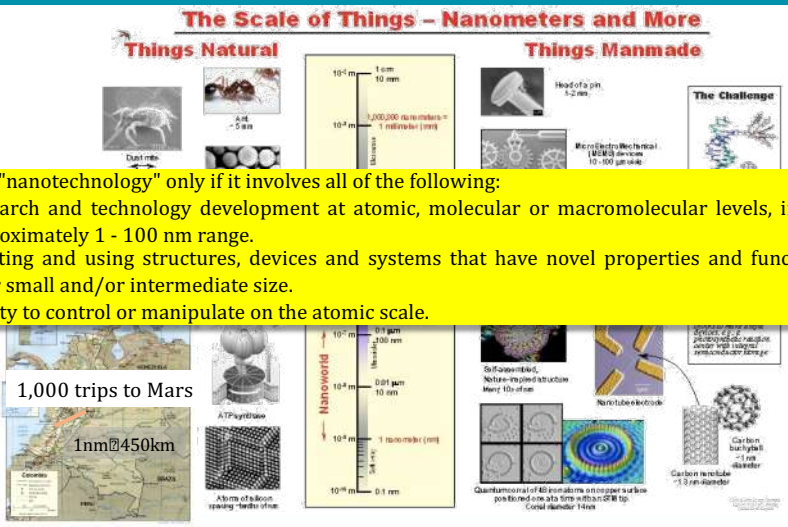
Not just "small;" "small and different"

Matthew Nordan, Lux Research, 2005.

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

Nanosensores

www.nano.gov



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.

What makes the nanoscale special?

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

These:

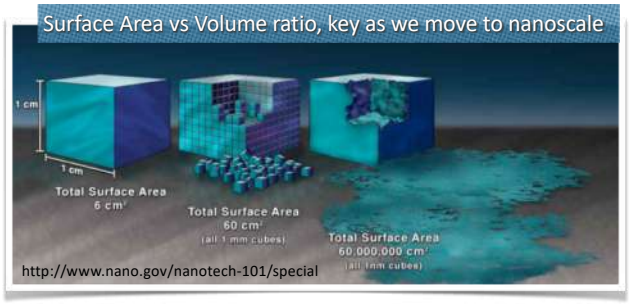
Many material properties, including melting point, fluorescence, surface tension, electrical conductivity, magnetic permeability, and chemical reactivity change as a function of particle size!

- 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.

Surface area (SA) to volume (V)

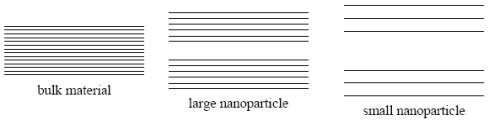
- A larger SA/V ratio as a function of entity size
  - Assume cube with side *l*, $V=l^3$ and $A=6l^2$ then $A/V=6/l$ increases for small *l*
  - In cells: surface must allow sufficient exchange to support contents, hence ratio limits size (e.g. Eukaryotic cell ~5–100μm)
  - Higher ratio leads to more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



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

Quantum Effects

- Consider the energy levels of a metal as its size decreases

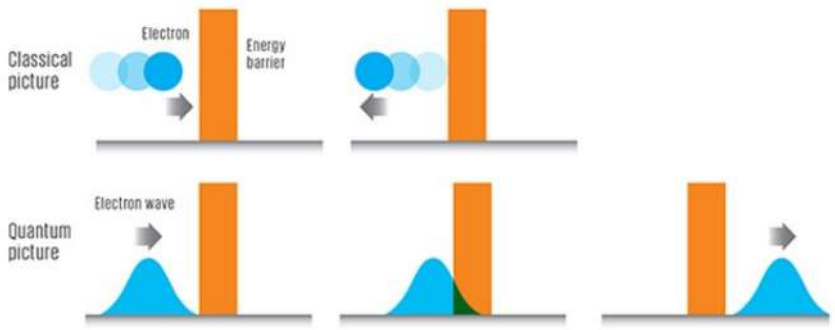


- Heisenberg's Uncertainty Principle: e.g. the more an electron is confined, the greater its momentum range, and vice versa
- Quantum effects can yield a range of exploitable phenomena, e.g.:
  - Nanoscale gold particles selectively accumulate in tumors and the motion of their electrons is confined, 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

Quantized energy states at atomic level

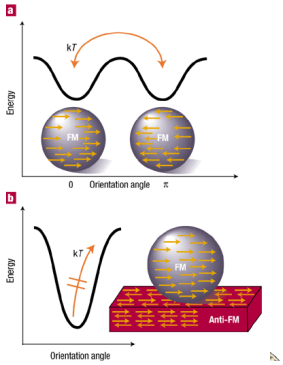
- Discrete quantum levels of a nanocluster may be tuned to modulate the electron transport, normally modulated by the pH, ions, and redox centers.
- Important Quantum effects include “electron tunneling” for STM, quantum Hall effect for resistance calibration instruments, spin polarization in MRI.
- 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.

Quantized energy states at atomic level



Thermal fluctuations

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



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

"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."

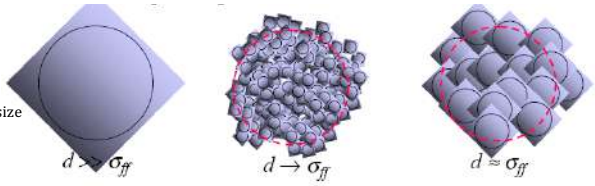
Eisenmenger and Schuller, Nature Materials, 2003

Surface Discreteness

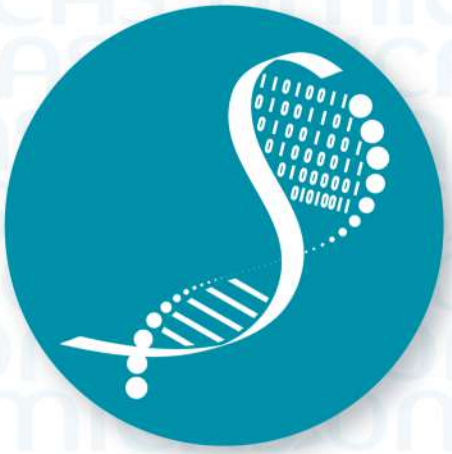
Once the size of an entity approaches that of its building blocks:

- 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

Consider a droplet as a function of size



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

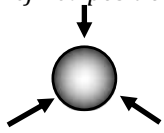


First-principles Quantum Mechanics

Diverging physical ideas: <1900

PARTICLES

Defined position

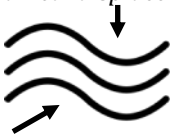


Defined Momentum

Defined Mass

WAVES

Mechanical displacement (EM)



Energy propagation

No mass

Particle-wave duality and de Broglie

Relativity

Planck $E = h\nu$

Einstein $E = mc^2$

$h\nu = mc^2$

Relating frequency and wavelength of a photon

$hc/\lambda = mc^2$

$h/\lambda = mc$

$h/\lambda = \rho$

Louis-Victor de Broglie (1892-1987)

- **By analogy with photons** (no mass), a particle with non-zero rest mass (m) and velocity (v) has $\lambda=\hbar/mv$, and since p=mv then de Broglie's relationship

Everything that has momentum has a wavelength, including electrons

$$\lambda_{elec} = \frac{6.6\times10^{-34}\text{Js}}{(9.1\times10^{-31})(1\times10^{6}m/s)} = 7.3\times10^{-10}m \cong 7\text{Å}$$

Wave-Particle duality

momentum α $\frac{\mathbf{1}}{\textbf{wavelength}}$

$h/\lambda = \rho$

Property associated with **particles**

$h/\lambda = mc$

Property associated with **waves**

All quantum entities have **particle** and **wave** properties

LIGHT

A **wave** when propagating through matter or vacuum

Particles when interacting with matter

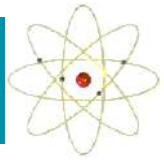
At that time, an equation that contemplated this duality was missing!!

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?"

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



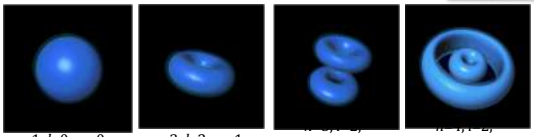
Erwin Shrödinger (1887-1961)

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

n: principal (integer): orbit size
l: azimutal (angular momentum): orbit form
m_l: magnetic: orbit orientation
m_s: spin

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

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



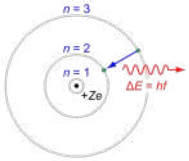
n=1, *l*=0, *m*=0 | *n*=3, *l*=2, *m*=1 | *m*=2 | *m*=2

Historical precedents: summary

(1900's) Planck: energy occurs in quanta → $E = h\nu = hc/\lambda$

(1913) Bohr: atomic model → $m_e v^2/r = e^2/4\pi\varepsilon_0 r^2$

(1920's) Einstein: mass and energy are exchangeable → $E = mc^2$



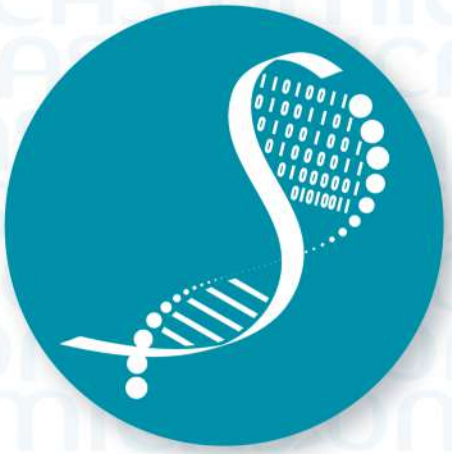
(1921) de Broglie: wave-particle duality → $h/\lambda = \rho$

(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



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.

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

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

   - 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

Further Approximations that Lead to MM/MD

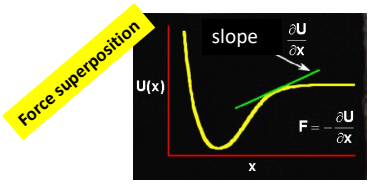
2. Nuclei moving as classical particles

- 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)

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

Further Approximations that Lead to MM/MD

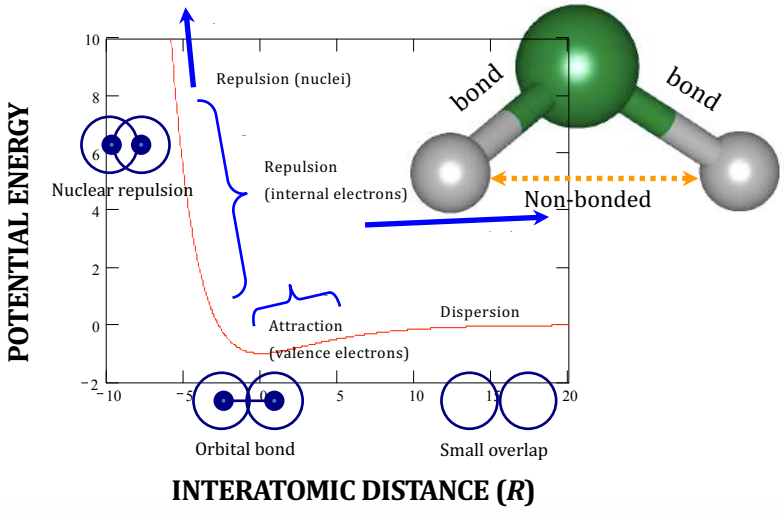
3. Approximate PES with analytical potentials
   - Avoid solving a Schrödinger equation altogether, and
   - ATOMS as classical particles (w/implicit electrons) moving on analytical PES



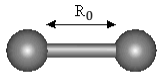
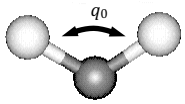
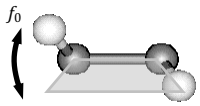
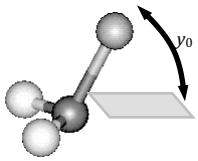
GROUND STATE

E as a function of nuclear positions only.

MM/MD (Classical): PES vs. Distance



Bonded (valence) Interactions: spring-like interactions

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

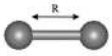
Subindex 0 indicates rest value / K_R: Force constant (kcal/mol A^2) / $K_{t,n}$: Rotational barrier (kcal/mol) / n: periodicity / d: phase factor

Nanosensores

Others: Cross-terms

Bond-stretch

Simple Harmonic

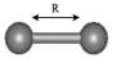


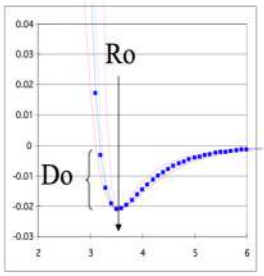
$$E(R) = \frac{K_b}{2}(R-R_o)^2$$

Ro = 0.9 – 2.2 Å

K_b = 700 (Kcal/mol)/Å ^{2}

Units: multiply by 143.88 to convert mdynes/ Å to (Kcal/mol)/Å ^{2}





Morse

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

Do is the bond energy in Kcal/mol
Ro is the equilibrium bond distance

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

Morse scaling parameter, which
Most programs calculate from Kb and Do

Nanosensores

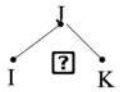
Angle bend

Cosine Harmonic

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

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

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



Input parameters are always in terms of The force constant K_θ . In general

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

Cosine Periodic

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

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)

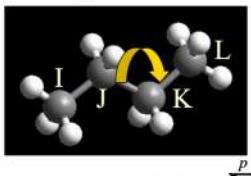
The periodicity N can be N = 1,2,3,…, 6

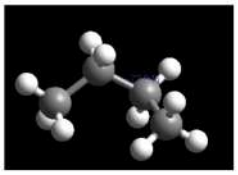
The constant C is related to the force constant as $K_\theta = N^2 C$

The input is in terms of K_θ , N and B

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:

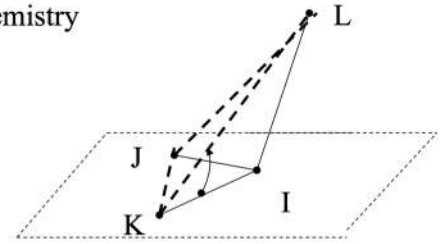
a) All torsions (nine for ethane). K is re-scaled for Dreiding and CHARMM force field
b) MM2 and Amber K is not re-scaled.
c) If USE ALL is turned OFF the program uses only the FIRST non-zero torsion for JK without re-scaling

Improper Torsions

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

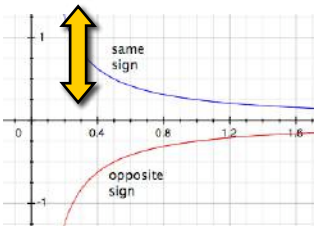
$$E(\phi) = 1/2K_{\phi}[\phi - \phi_o]^2$$

For a tetrahedral carbon atom with equal bonds this angles 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
ϕ is the angle between The IJK plane and the LJK plane

Non-bond distance-dependent Interactions



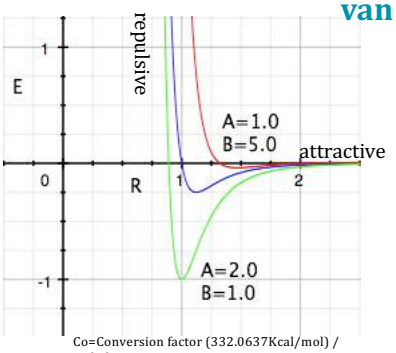
Electrostatic Interactions

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

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

Non-bond distance-dependent Interactions

van der Waals Interactions



Co=Conversion factor (332.0637Kcal/mol) / ε=dielectric constant

$$U_{vdW} = \sum_{\substack{R_{ij} > Rcut \\ [excl(1\text{–}2,1\text{–}3)]}} \hat{U}_{vdW}(R) S(R_{ij}, R_{on}, R_{off})$$

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)

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

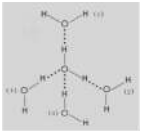
$$E_{HB}(R, q_{AHD}) = E_b(R) E_a\left(\cos\left(q_{AHD}\right)\right)$$

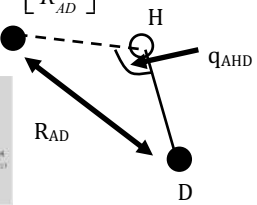
Bond terms:

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

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

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





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

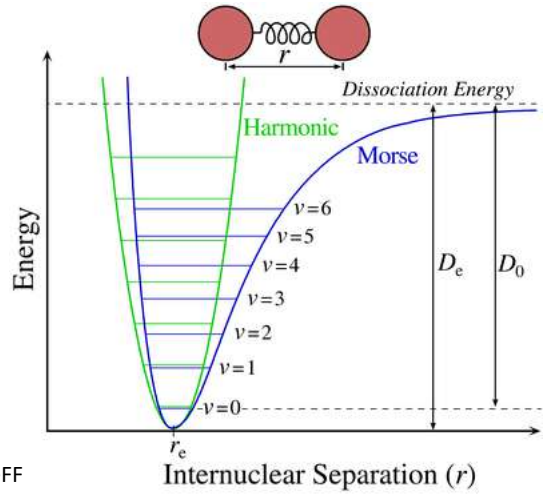
Angle terms:

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

Hydrogen bonds:

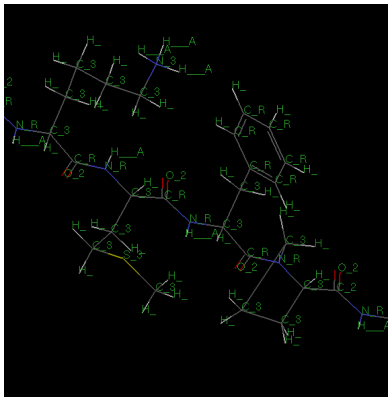
- Account for unique water properties
- hold the 2 strands of DNA double helix together
- hold polypeptides together in secondary structures;
- help enzymes bind to their substrate;
- help antibodies bind to their antigen
- help transcription factors bind to each other;
- help transcription factors bind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

Bond-Breaking?



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

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

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)
- Gromacs (www.gromacs.org)
- NAMD (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 IJKL
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

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:

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

QM

Equation of motion for nuclei (motion on the PES)

PES

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

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

MM

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

Nanosensores

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"

$$F_i = -\nabla_{\theta_i} U = -\left[\nabla_{\theta_i} U[\theta] + \nabla_{\theta_i} U[x]\right]$$

Force Field → Molecular Dynamics

Potential Energy → Energy Minimization
Synonymously used as geometry optimization

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

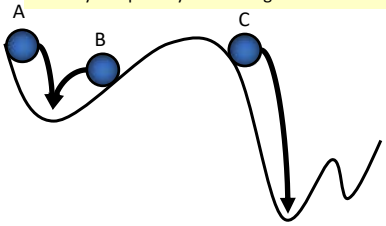
MM: Energy Minimization (EM)

- 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(x1,x2,…,xi) -> 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

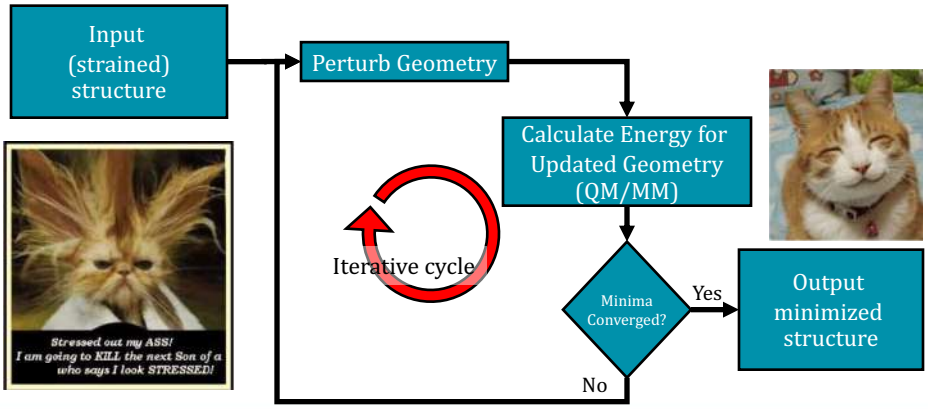
- Temperature (=velocity) is zero (except SA)
- Only sample 1 system configuration



  - 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

EM in MD



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

$$A\left(p^N(t), r^N(t)\right)$$

- 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?

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.

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

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

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

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

  - 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 !!

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

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 …

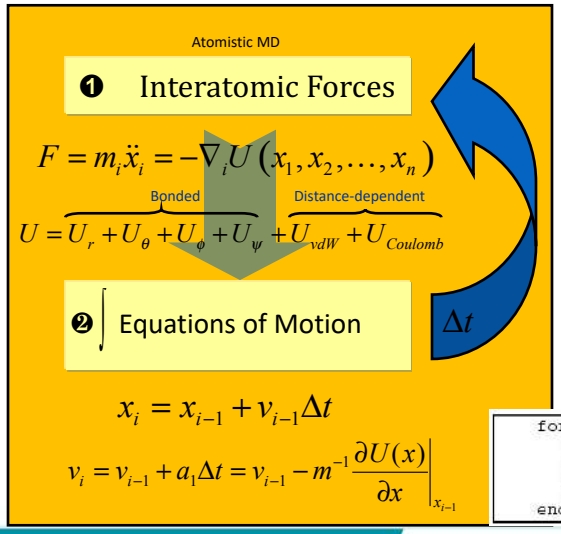
MD:

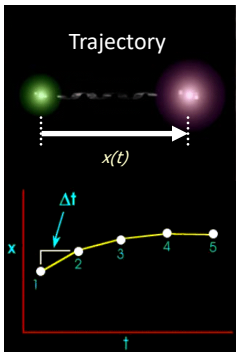
- To sample the conformational space of a system at T>0K.
- To model temperature and pressure effects.
- To obtain thermodynamics and time-dependent (kinetic) properties.
- To compute multi-component system properties …

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_2)
  - No excited states
  - Time (e.g. enough to reach equilibrium or detect infrequent events, i.e. longer than relaxation time of quantities of interest)

Molecular Dynamics: a 2-step process






```
for all time steps do
   compute intramolecular forces ;
   compute non-bonded forces ;
   integrate Newton's equation of motion ;
end do;
```

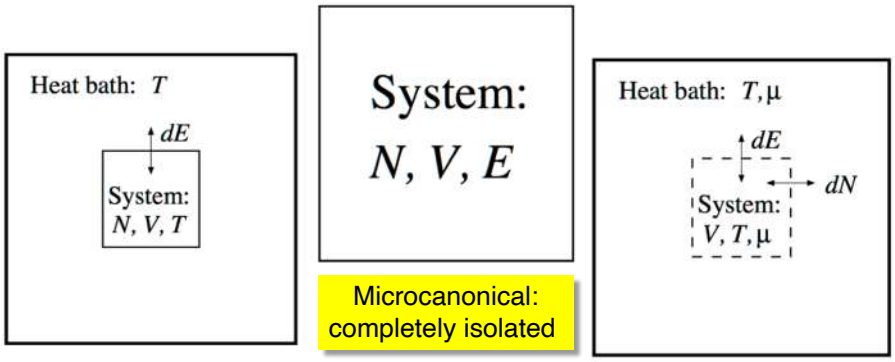

Simulation Ensembles

IF	GIVES
nVE=constant:	• **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).
(μ)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, μ=chemical potential

Ensembles



Microcanonical: completely isolated

Canonical: System in contact with a heat bath of temperature T, energy exchange but no particle exchange

Grand Canonical: In contact with a heat bath of temperature T and particle bath of chemical potential μ: energy and particle exchange

 Jaramillo-Botero y Marmolejo, 2019

Important Properties of Interest

- Energy (internal)

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

- Temperature

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

- Pressure

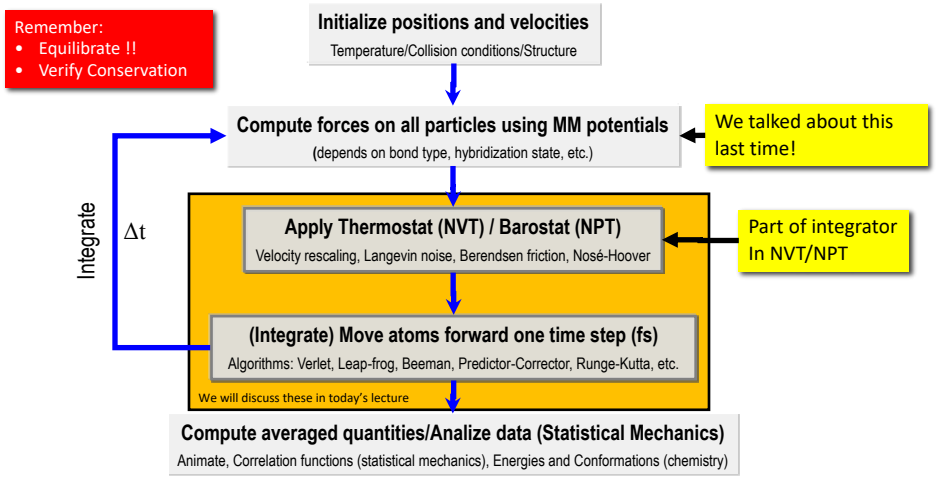
$$P = \frac{1}{V}\left[NK_BT - \frac{1}{3}\sum_{i=1}^{N}\sum_{j=i+1}^{N} r_{ij} f_{ij} \right]$$

- Heat Capacity

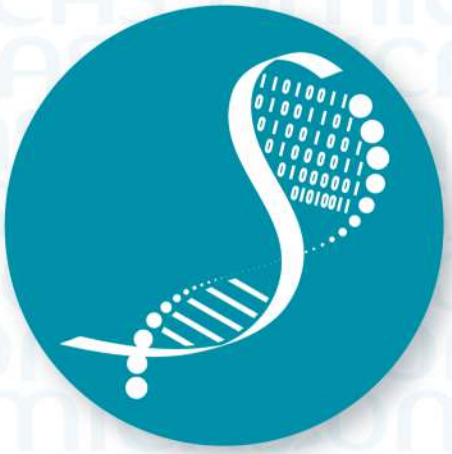
$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = \left\langle \left(E - \langle E \rangle \right)^2 \right\rangle \Big/ K_B T$$

Others: Correlations, transport, conformations …

MD Flowchart (ensembles)



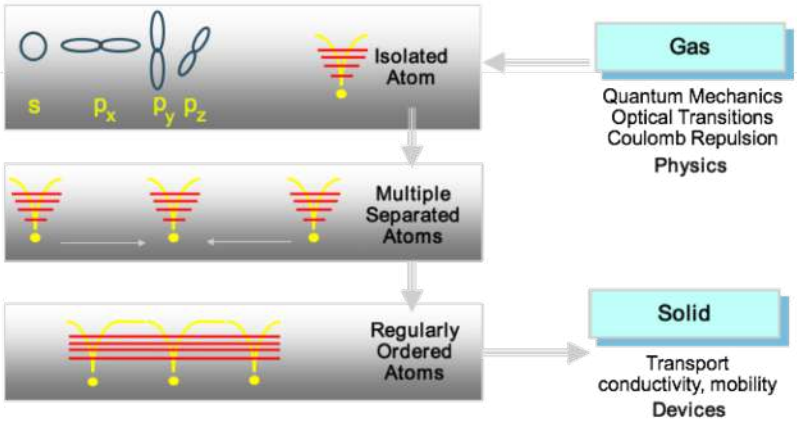
Nanosensores



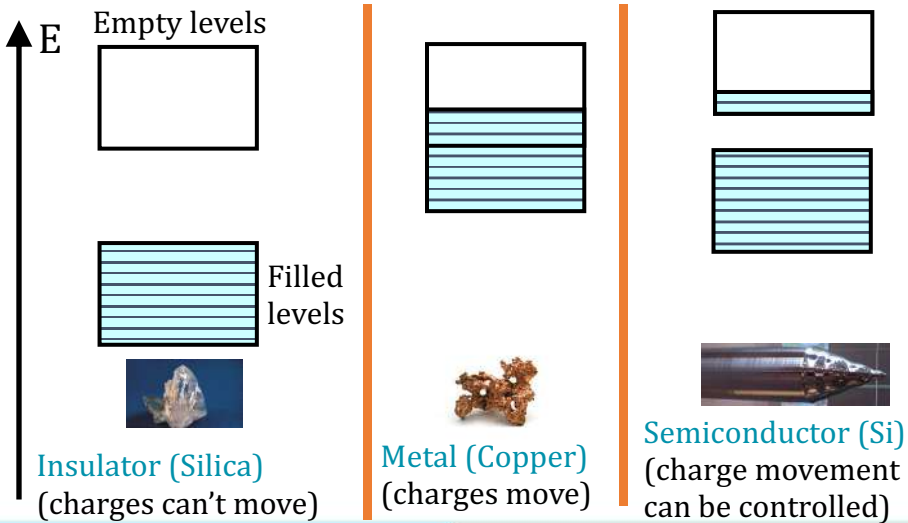
Electronic Transport Properties in the Nanoscale

Electron Conduction in Solids

- Bands are channels in which electrons move "freely".

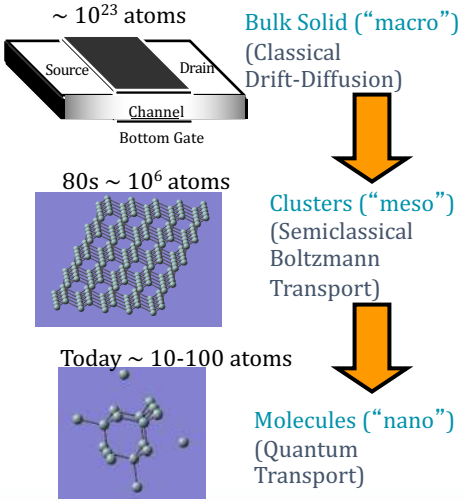


Filling up the Bands with Electrons



Pushing the simulation envelope

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

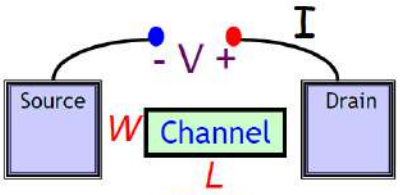


Determining the Most Appropriate Model

- Length Scales and Interactions Determine the Most Appropriate Model.

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

Change in paradigm



$$\frac{V}{I} \equiv R = \frac{\rho}{W} L$$

1985 - - -> 10 µm → 1 µ m

2010 - - -> 0.1 µm → 10 nm → 1 nm

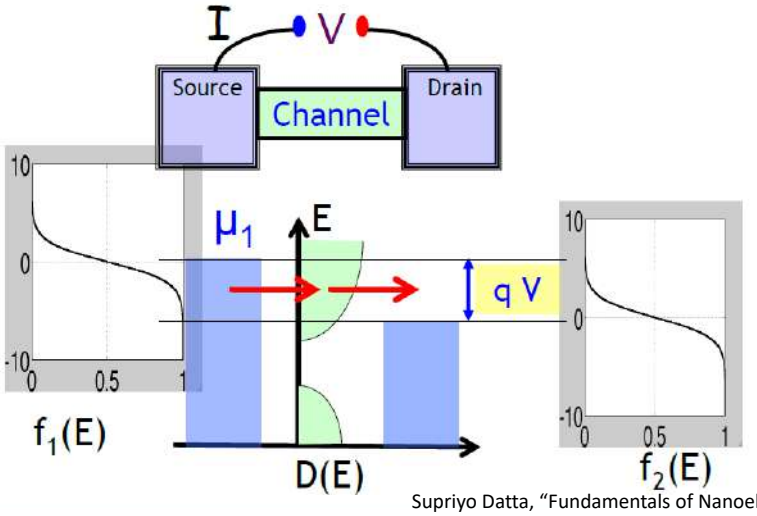
Diffusive

Ballistic

$$R = \frac{\rho}{W}(L + mfp)$$

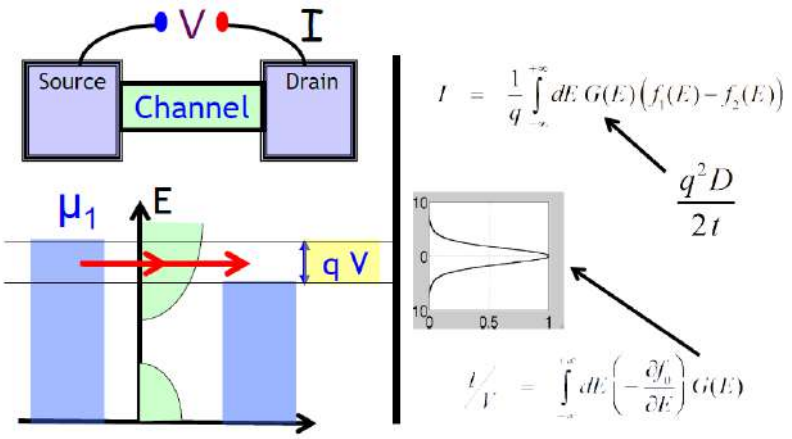
Supriyo Datta, "Fundamentals of Nanoelectronics", PurdueX (2015).

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



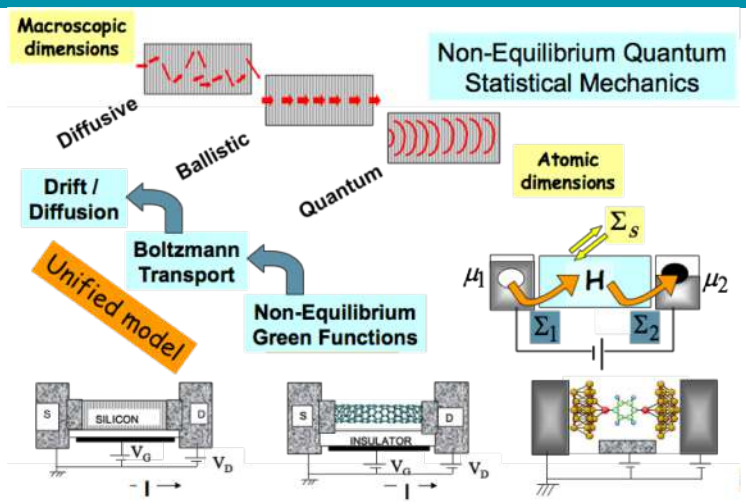
Supriyo Datta, "Fundamentals of Nanoelectronics", PurdueX (2015).

Why electrons flow



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

Quantum Transport far from Equilibrium

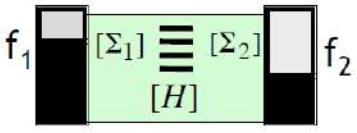


Supriyo Datta, "Fundamentals of Nanoelectronics", PurdueX (2015).

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.

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"

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

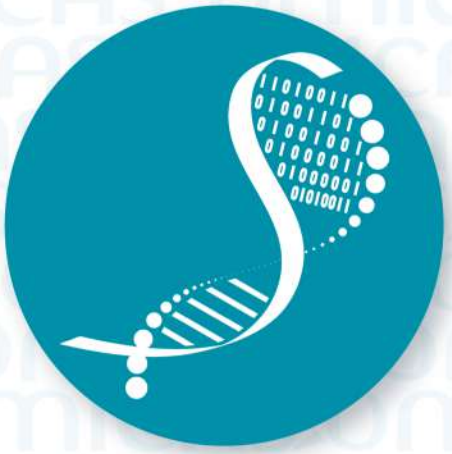
(3) "Density of states"

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

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

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

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



Biosensors

Generalities

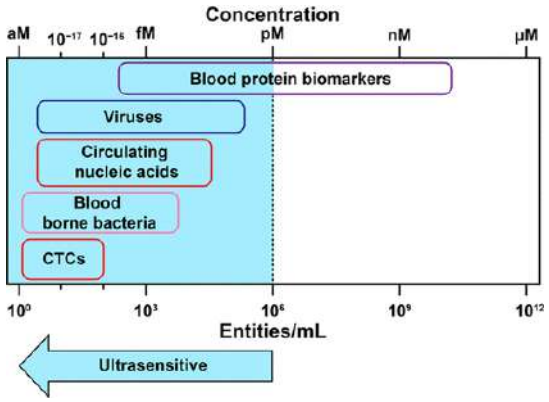
- A biosensor is an analytical device, used for the detection of a chemical substance, that combines a biological component with a physicochemical detector.
- The transducer or the detector element, which transforms one signal into another one, works in a physicochemical way, resulting from the interaction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

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.



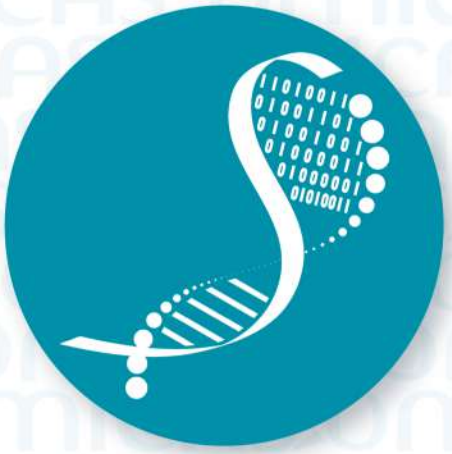
Yanfang Wu, Richard D. Tilley and J. Justin Gooding, *J. Am. Chem. Soc. 2019, 141, 3, 1162-1170*

Nanosensores

Challenges

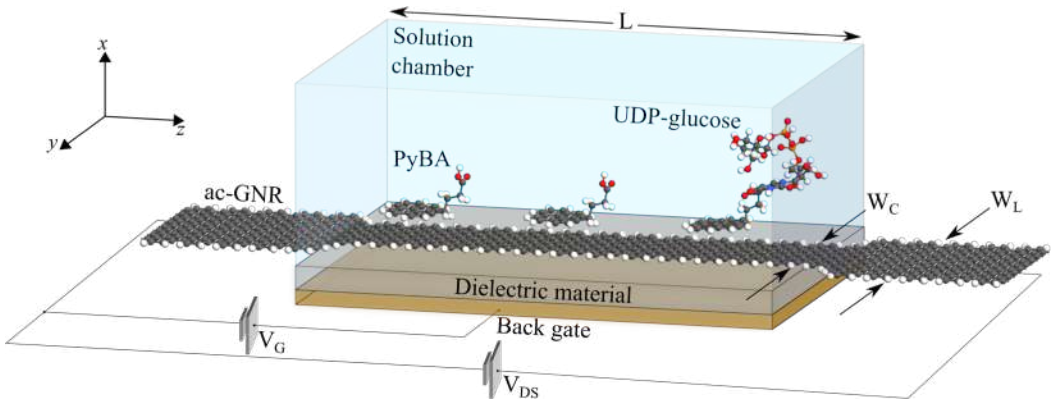
- Achieving sub-picomolar detection limits has three major challenges:
  1. Assay sensitivity
     - One strategy to gain greater sensitivity involves confining the sensing volume to the nanoscale, as used in nanopore- or nanoparticle- based sensors
  2. Response time
     - Methods to improve response 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*



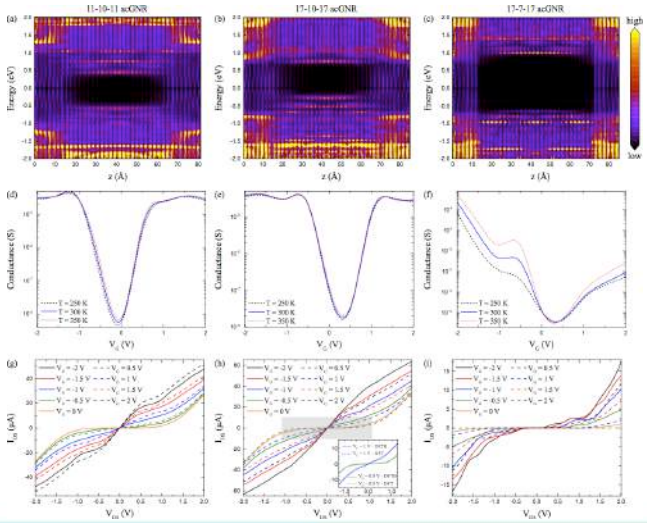
Applications

UDP-glucose sensor



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

UDP-glucose sensor



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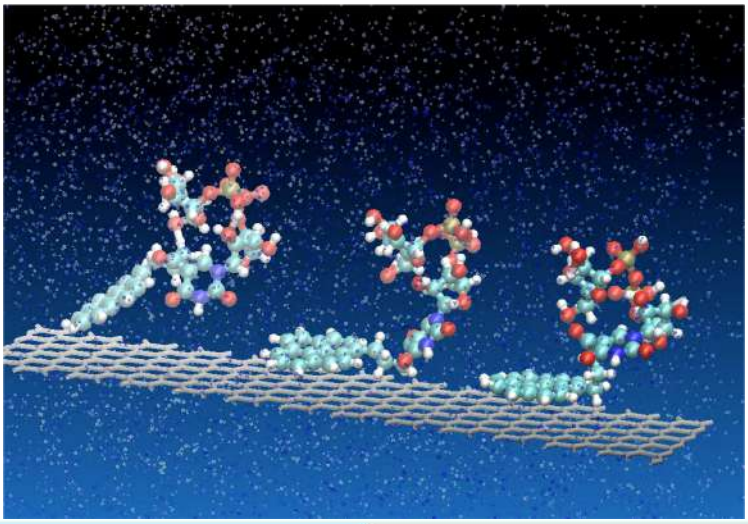
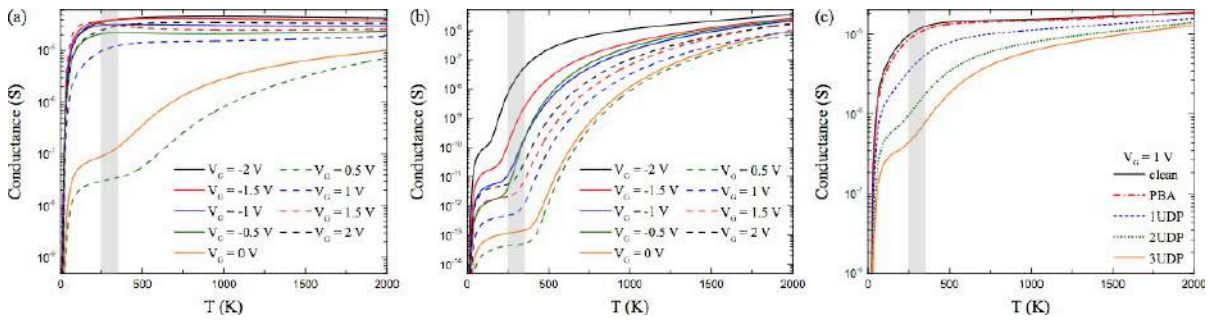
UDP-glucose sensor



UDP-glucose sensor



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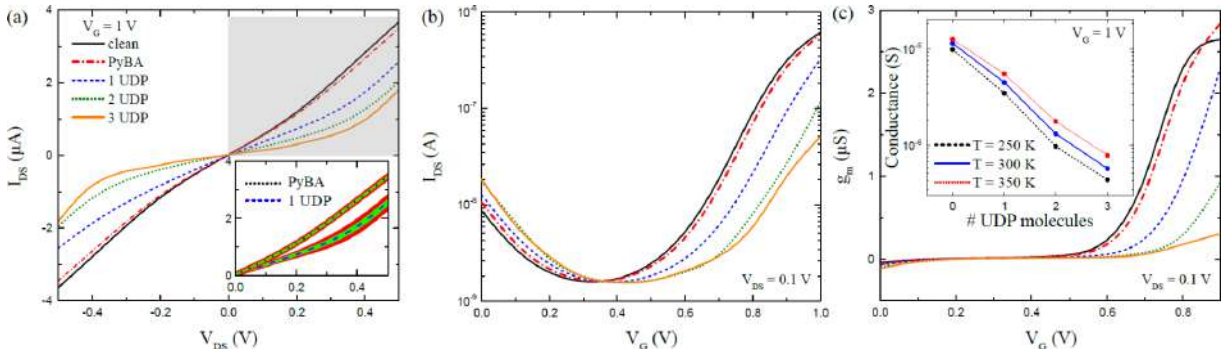

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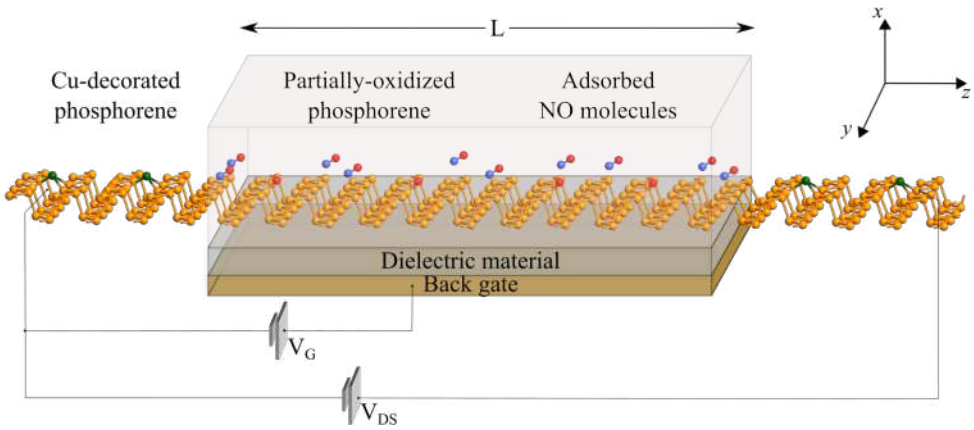
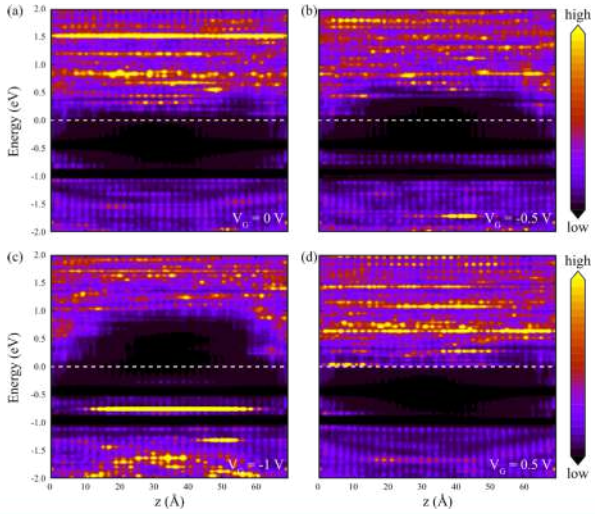
Volatile organic compounds (VOCs) sensor



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

Phosphorene FET



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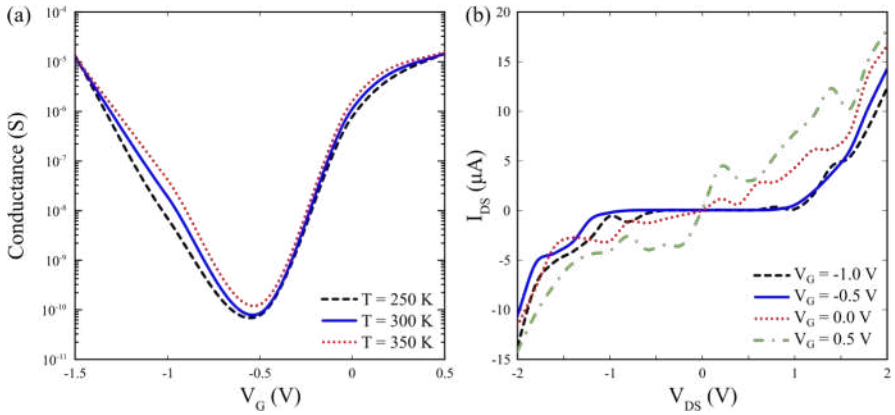

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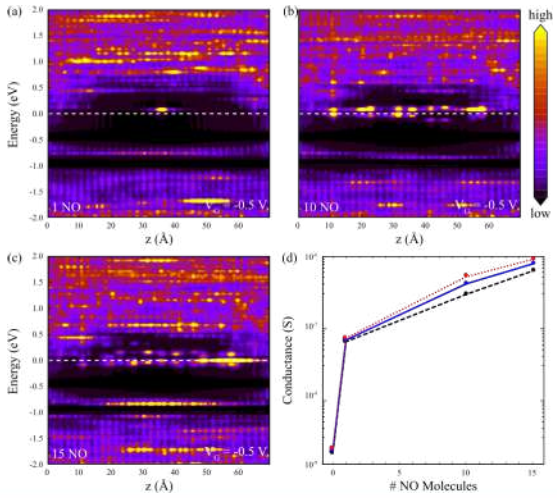
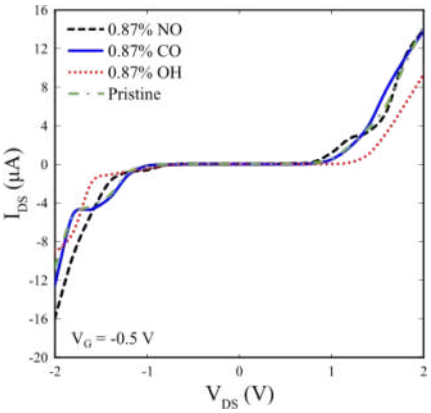
Nitric Oxide (NO) sensor





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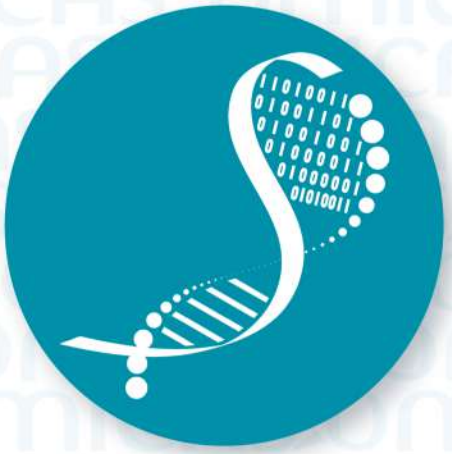
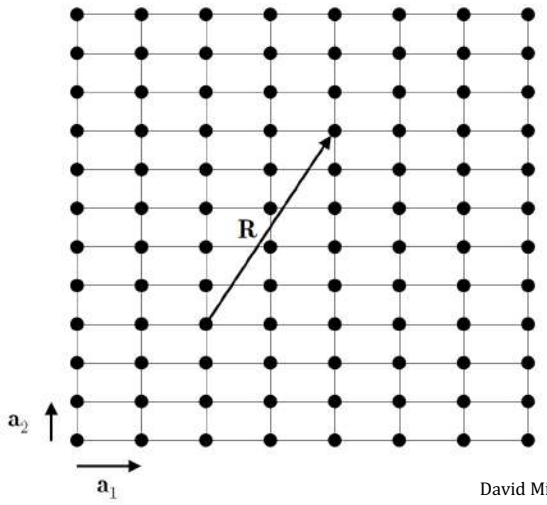
Nanosensores



Setting up calculations

Crystalline structures

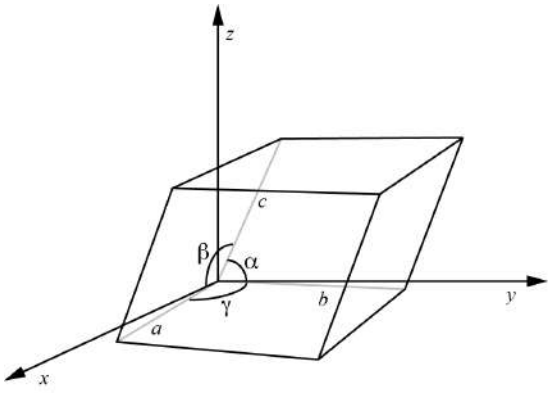


- Crystal:
  - Material whose measurable properties are periodic in space.
- Crystal structure:
  - It is one that can fill all space by the regular stacking of identical blocks or unit cells.

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

Crystalline Systems

- Unit cell:
  - Smallest repetitive volume which contains the complete lattice pattern of a crystal.
  - a, b and c are the edge lengths.
  - α, β and γ are interaxial angles.

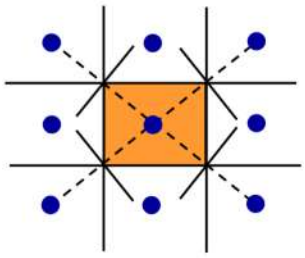


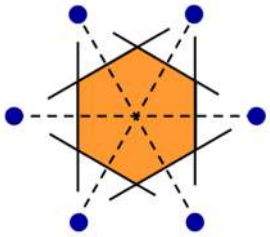
Reciprocal space

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

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:

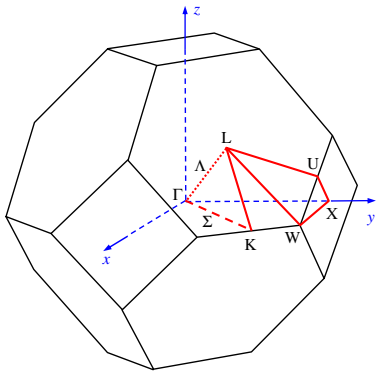




B. Grenier and R. Ballou, *Crystallography: Symmetry groups and group representations*, EPJ Web of Conferences 22, 00006 (2012)

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

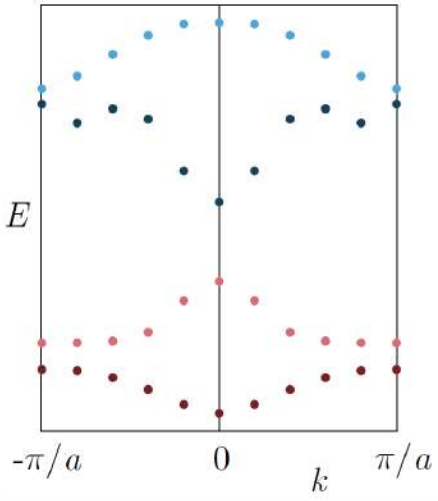
B. Grenier and R. Ballou, *Crystallography: Symmetry groups and group representations*, EPJ Web of Conferences 22, 00006 (2012)

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 ε_{nk} for each band n and momentum k.

Band structure diagrams

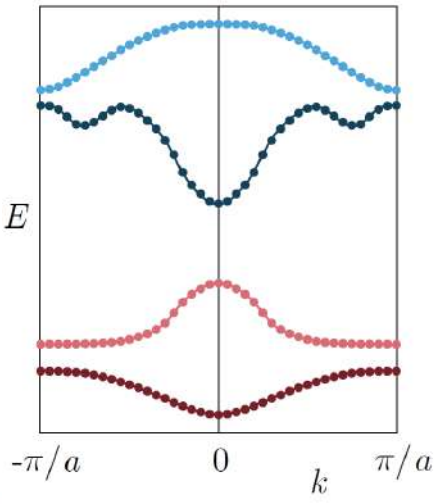
- Solving the one-electron Schrödinger equation gives energy eigensolutions.
- We continue with the other allowed values of k.



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

Band structure diagrams

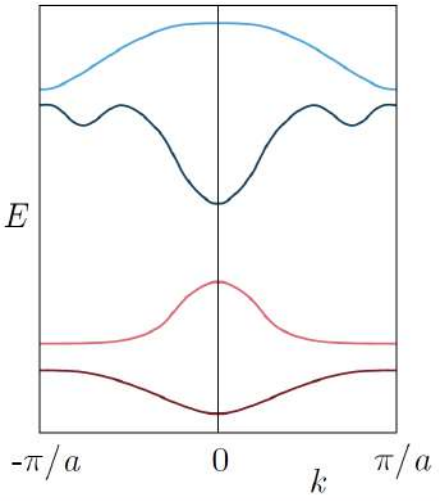
- A larger crystal gives more allowed values of k.
- This sets of "dots" effectively become like lines.
  - We refer to the group of dots on a line as a "band".



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

Band structure diagrams

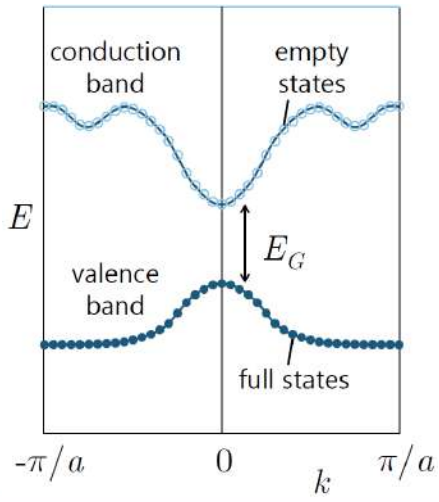
- There are multiple bands in a band structure, in fact, an infinite number, but usually only a few are important for the properties of a material.
- In each band, we only have to plot k-values from $-\pi/a$ to π/a.
- This range is known as the (first) Brillouin zone.



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

Semiconductors and insulators

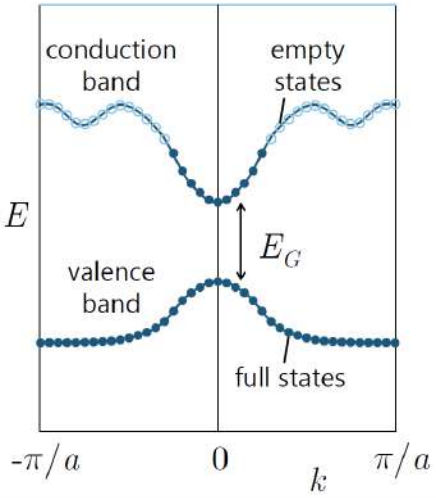
- Semiconductors and insulators have an (almost) completely full band (the valence band) separated by a "bandgap" of energy E_G from an (almost) completely empty band (the conduction band).



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

Metals

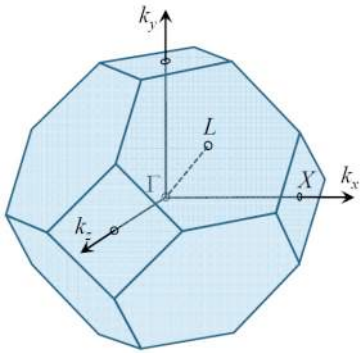
- Because of the number of electrons in the metal atoms, the lowest conduction band is partially full of electrons.
  - e.g., half-full even at zero temperature.
    - Hence metals conduct electricity well.



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

Brillouin zone in 3D

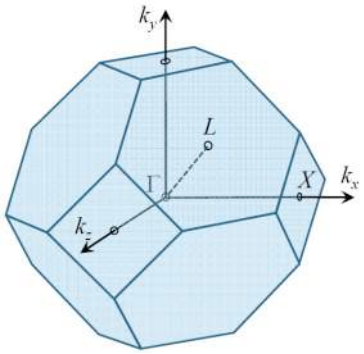
- The Brillouin zone for the diamond or zinc-blende lattice is a 3D object.
  - Two important directions are:
    - *X*: Along one of the coordinate directions.
    - *L*: Along one of the cube space diagonals.
  - The center is the Γ (gamma) point.



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

Brillouin zone in 3D

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



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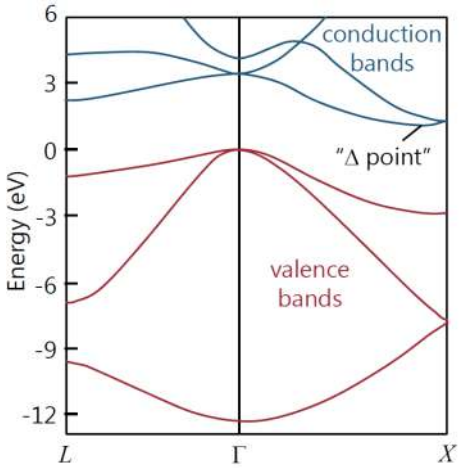
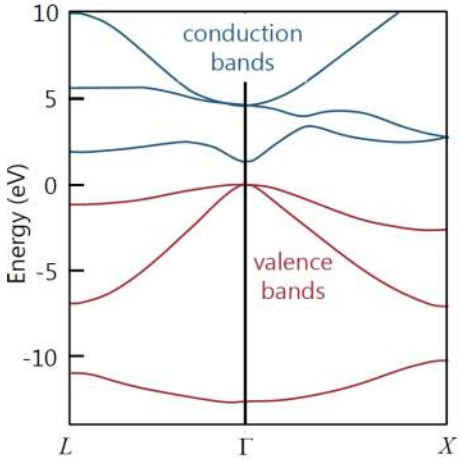
Si and GaAs band structure





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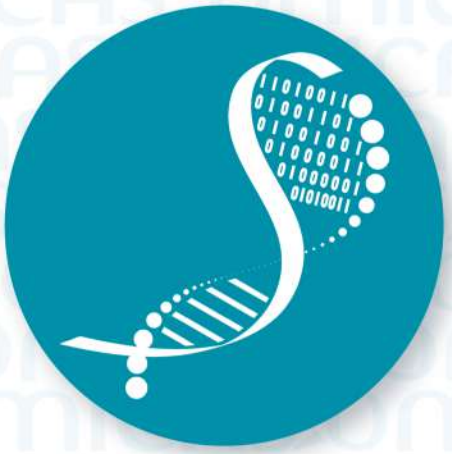
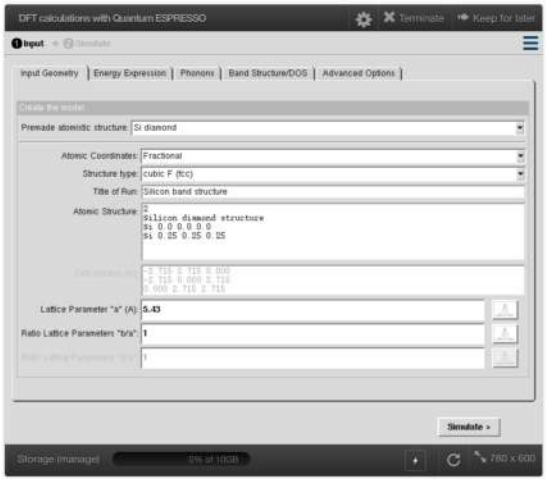


Hands-on tutorials

DFT calculations with Quantum ESPRESSO

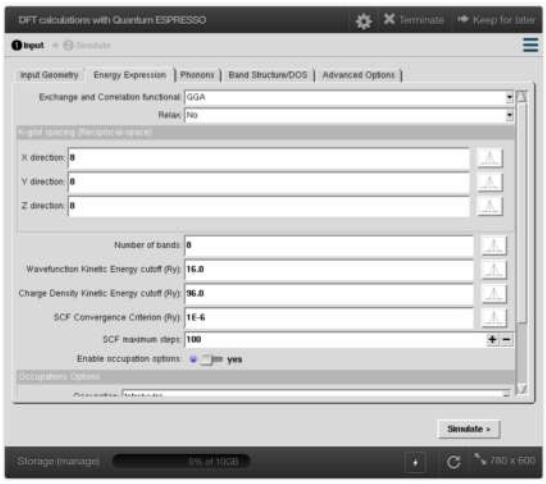
- We will begin our test calculations using the online tool: https://nanohub.org/tools/dftqe
- This tool allows us to run quantum ESPRESSO (a powerful electronic structure code based on density-functional theory, plane waves, and pseudopotentials) for performing several calculations:
  - Total energy.
  - 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



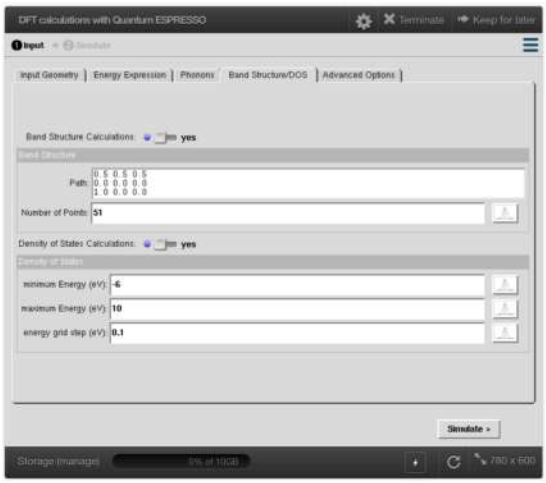
- The tool already has some premade atomistic structures with their corresponding cell parameters and atom coordinates.
  - Choose Si diamond.

Silicon Band Structure



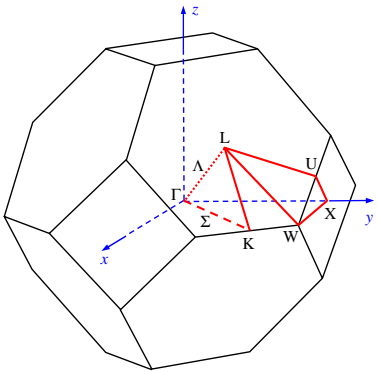
- We can choose LDA or GGA functionals and enable/disable relaxation.
  - Choose GGA and no relaxation, but you should also explore the other options.
- Specify k-points in the reciprocal space, as well as other calculation parameters.
  - We will use default values for the moment.

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 $X(1.0, 0.0, 0.0)$.

Remember the 1st Brillouin zone for a 3D cubic reciprocal lattice

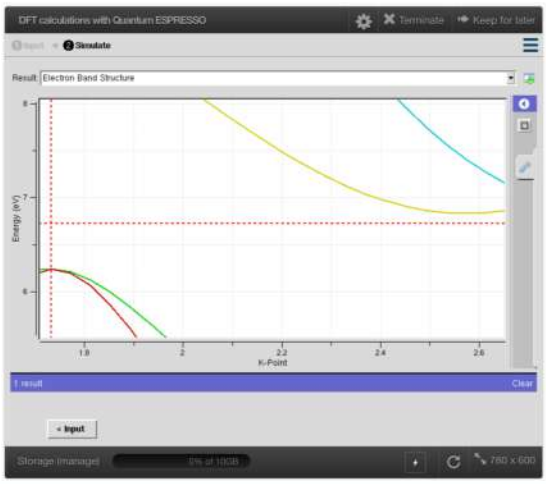


Γ:	Brillouin zone's center
K:	middle of an edge between two hexagonal faces
L:	center of an hexagonal face
U:	middle of an edge between a square face and an hexagonal one
X:	center of a square face
W:	corner

Silicon Band Structure

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

Silicon Band Structure



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

Input scripts

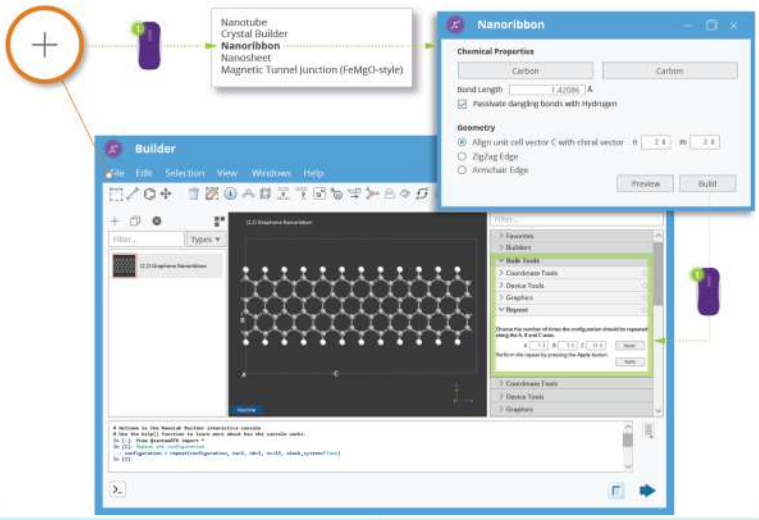
- So far, we have not discussed the particularities of our input script, but you should study all the input scripts necessary for this calculation and get familiar with their structure and format.
  - Fore more details on each command, check the input file description help at: https://www.quantum-espresso.org/Doc/INPUT_PW.html

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.

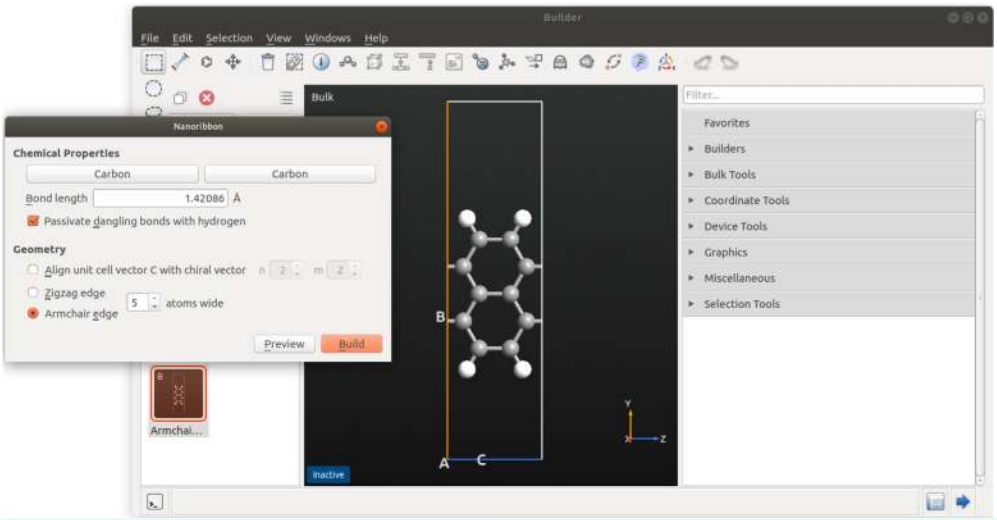
```
14
_a 20 _b 20 _c 4.26258 _alph 90 _beta 90 _gamm 90
C     5.00000     5.00000     2.84172
C     5.00000     6.23050     3.55215
C     5.00000     5.00000     1.42086
C     5.00000     7.46100     2.84172
C     5.00000     8.69150     3.55215
C     5.00000     6.23050     0.71043
C     5.00000     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
```

QuantumATK's Nanoribbon tool



Nanosensores

QuantumATK's Nanoribbon tool



Nanosensores

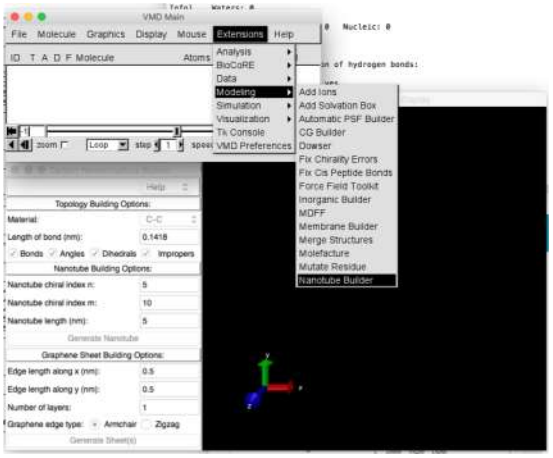
Characteristics of the xyz file

- The first line indicates the number of atoms, n.
- Second line is a comment.
  - In this case, we included the cell dimmensions 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 _gamm 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
```


VMD's Carbon Nanostructure Builder Tool

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



VMD's Carbon Nanostructure Builder Tool

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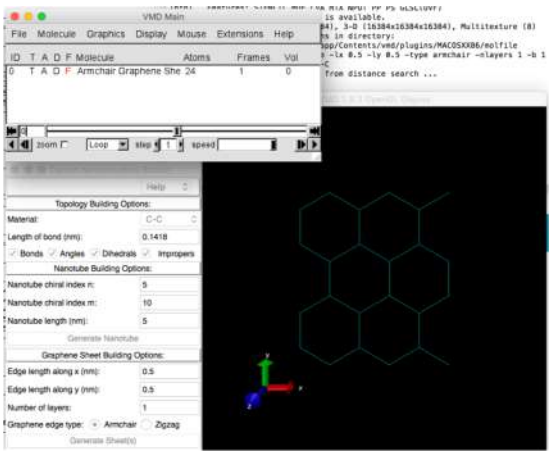
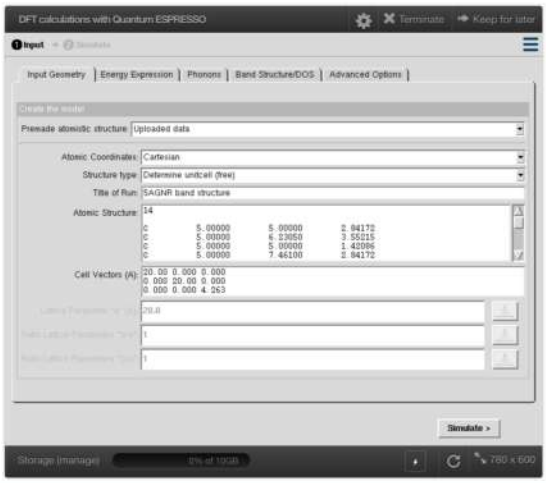
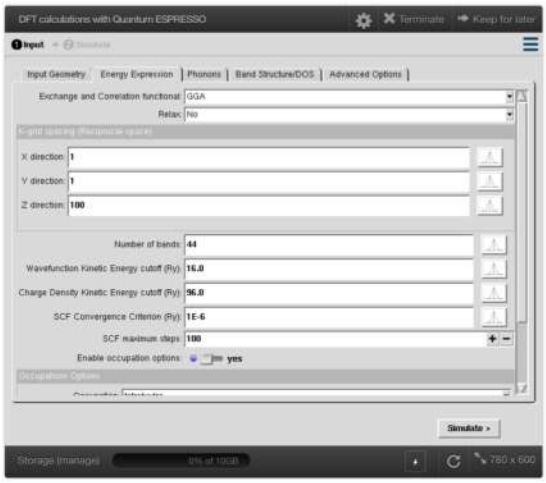


GNR Band Structure



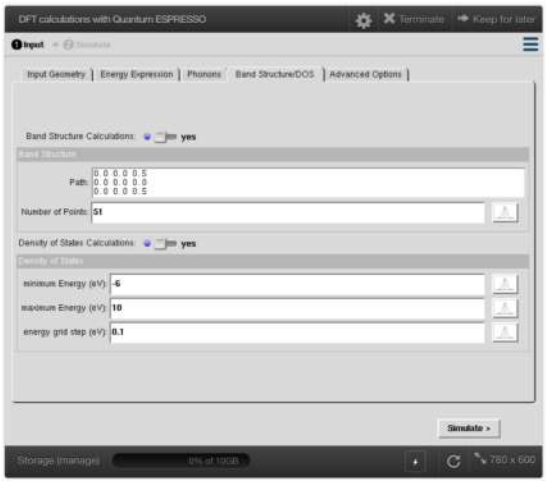
- Upload the coordinates of the system in xyz format.
  - The provided file has positions in Angstroms, then you should select Cartesian Atomic Coordinates.
- Select free type of unit cell and fill up the Cell Vectors in Angstroms.

GNR Band Structure



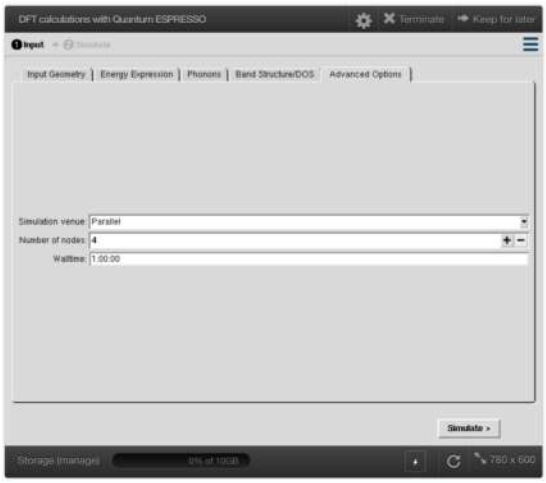
- Since the GNR is only periodic on the z-direction, we only increase the number of k-points on that direction.
  - The number of k-points in the other directions is set to 1.
- Type in the number of bands.
  - Remember carbon has 4 Valence electrons and hydrogen just 1.

GNR Band Structure



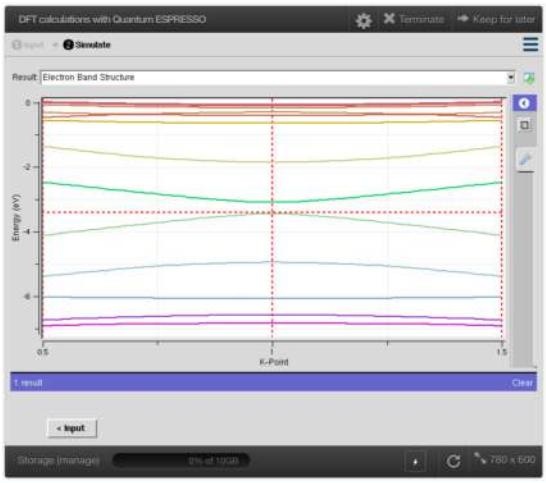
- We are interested in computing the band structure along the transport direction (z-direction).
  - Then, the path goes from $Z(0.0, 0.0, 0.5)$ to $\Gamma(0.0, 0.0, 0.0)$ to $Z(0.0, 0.0, 0.5)$.

GNR Band Structure



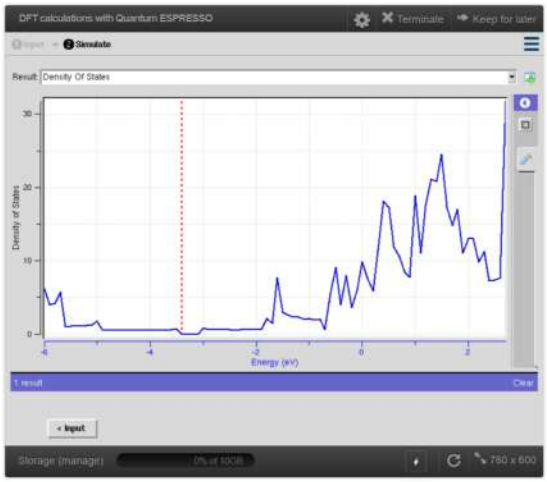
- Notice the calculation could take several minutes on a single core.
  - You may want to request a multi-core simulation and speedup the calculation.

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 ~0.35eV.

GNR Density of States



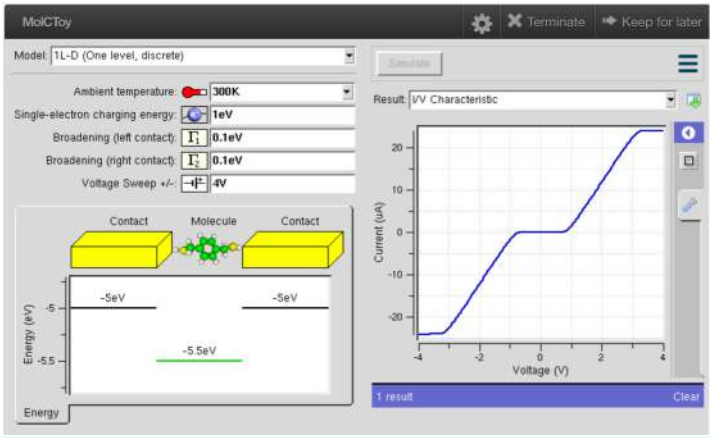
- We can also get the Density of States (DOS) of our AGNR.
  - How can we relate this to the band structure?

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.

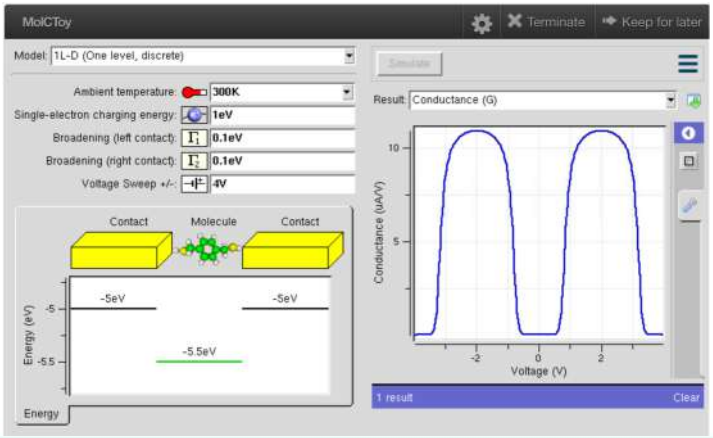
Electrical Conduction through a molecule

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



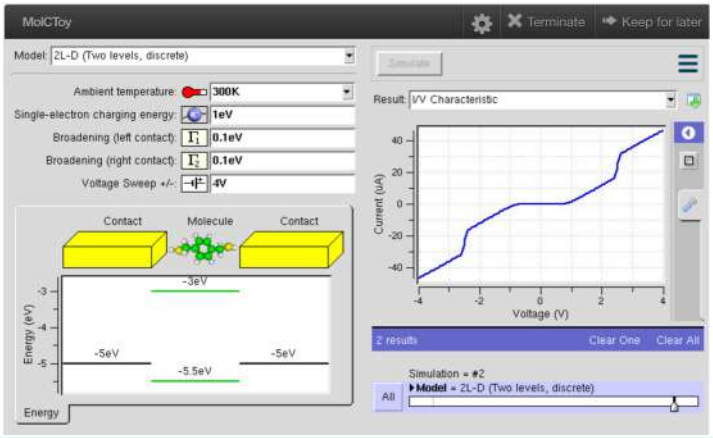
Electrical Conduction through a molecule

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



Electrical Conduction through a molecule

- What happens when 2 energy levels are considered?



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