Capita Selecta in Nanosciences and Nanotechnologies
Erasmus Mundus Master seminars
Chalmers, Dresden, Grenoble, Leuven

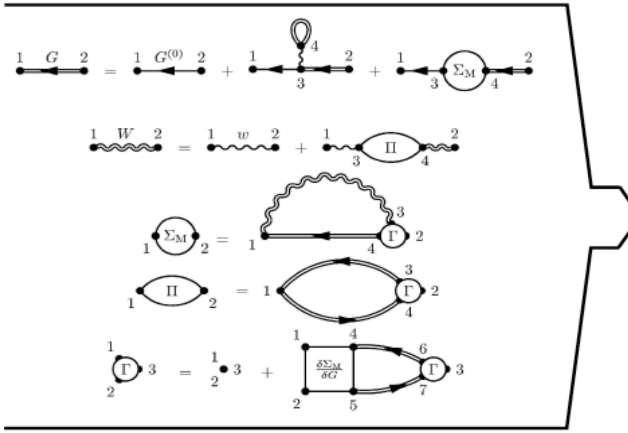
April the 28th, 2015

From prebiotic chemistry to photovoltaics: *ab initio* quantum simulations

X. Blase
Institut Néel, CNRS and U. Joseph Fourier, Grenoble, France.

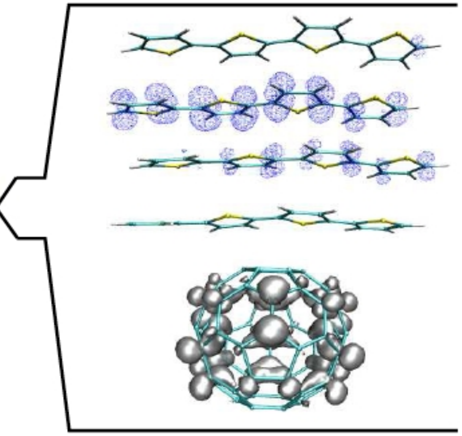
Introductory question: can we calculate the structural, optical, electronic, magnetic, superconducting, thermoelectric, *etc*. properties of condensed matter systems, including « nanoscale » systems, using computers and numerical simulations ?

Subsidiary question: if yes, with what accuracy and with which computers ?



A theoretical point of view on Nature: a dictionary of elementary electronic interactions (Feynman diagrams)

French Computer
(yes, it exists !)

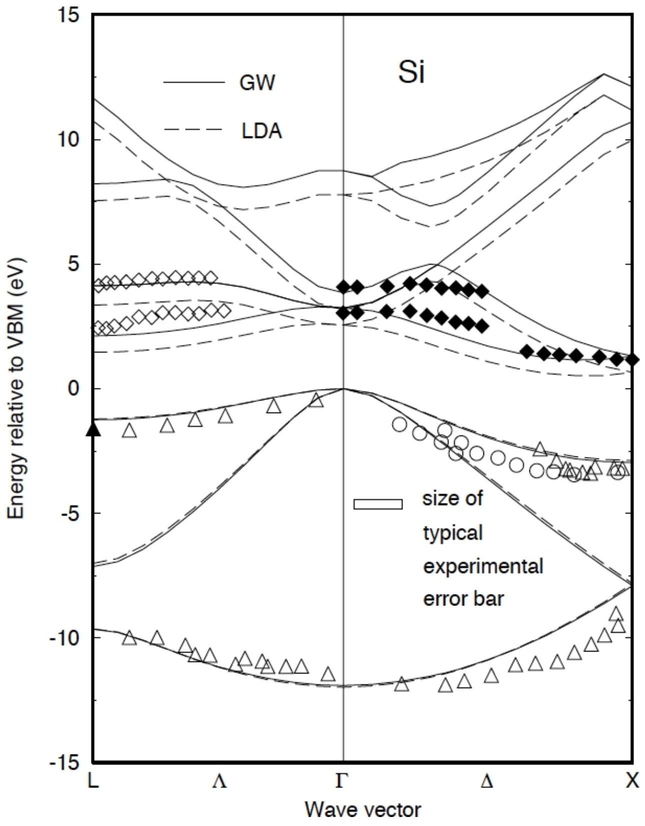


Electrons and holes moving in an organic solar cell

The answer is an unprecise « yes for many systems and many physical observables » but there is still much progress to be done !

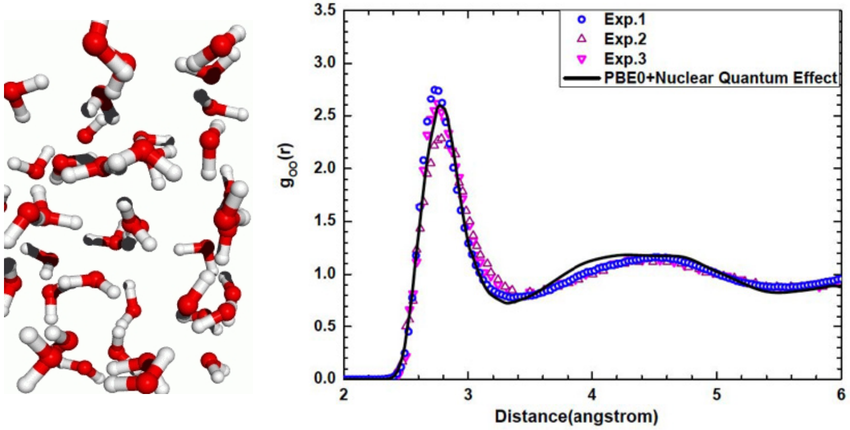
To start with the half-filled part of the glass:

Electronic band structure (silicon)

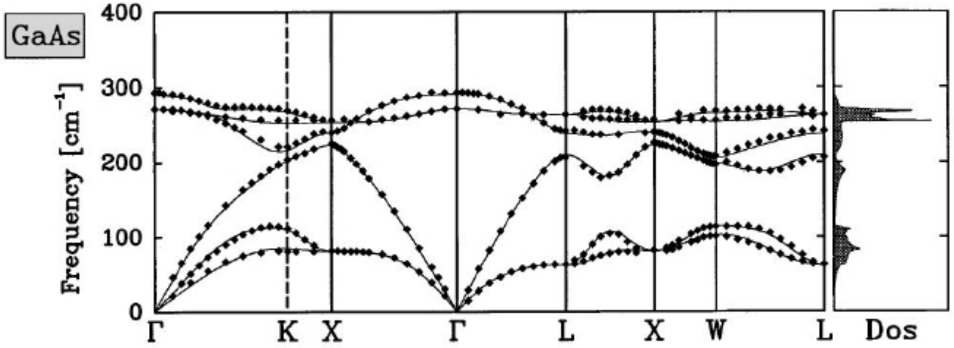


(symbols: photoemission experiments)

O-0 pair distribution in water (T=300 K)

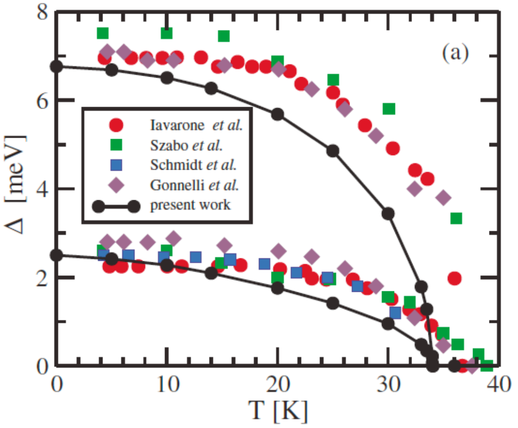


Phonon (vibrations) band structures



(points=experiment; Rev. Mod. Phys.**73**, 515 (2001)

Superconductivity



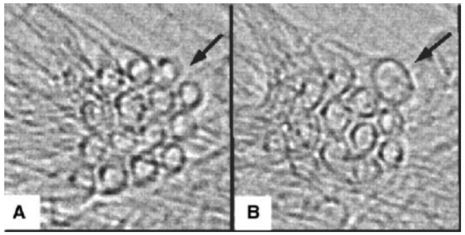
π and σ superconducting gaps in MgB_2: theory and experiments (PRL 94, 037004, 2005)

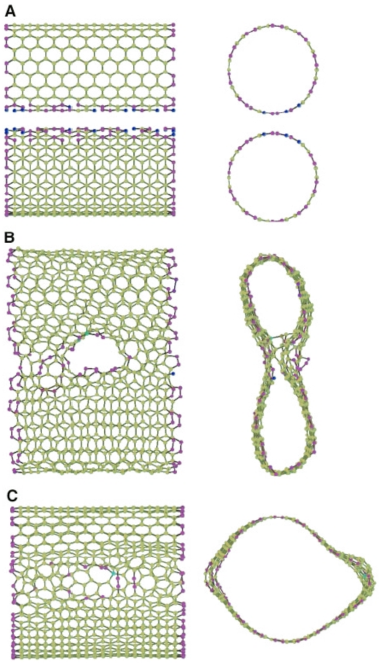
Coalescence of nanotubes under electronic irradiation

(Terrones et al. *Science* 2000)

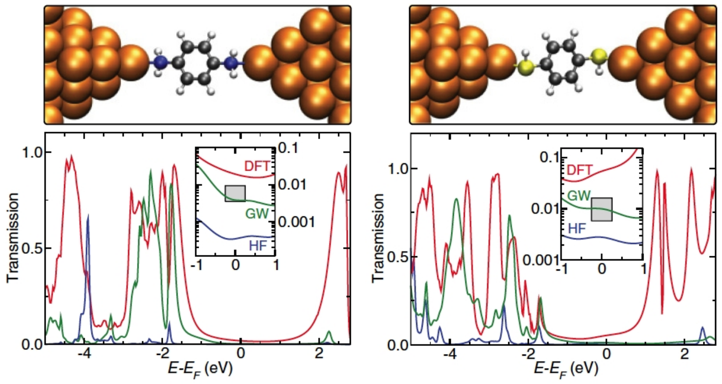
Experiment

Theory





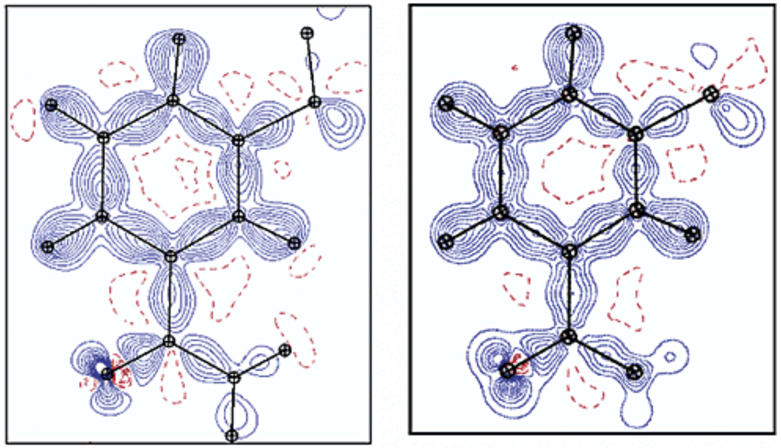
Electronic conductance in molecules



(PRB 83, 115108, 2011; Danemark)

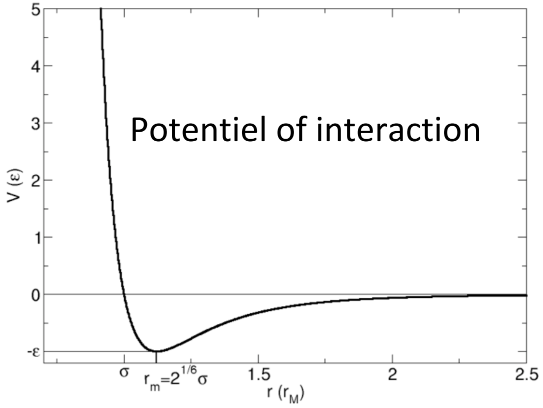
Charge density (electronic distribution)

Experiment Theory



Nicotinamide adenine dinucleotide cofactor (NAD^+) plays a major role in enzyme-catalyzed biological oxido-reduction processes.

Semi-empirical simulations: a quick rush through history



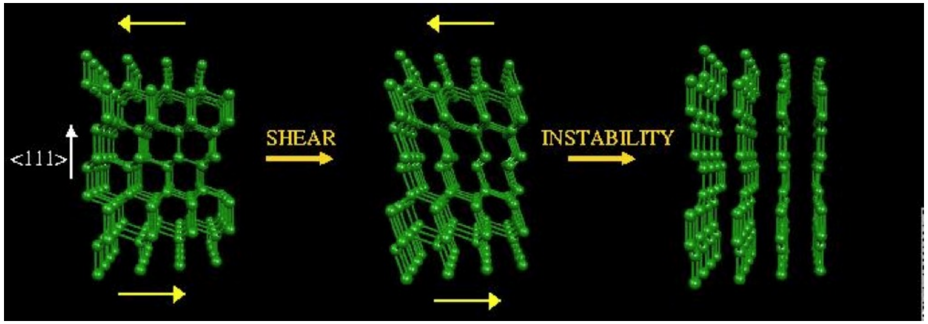
Historical studies: phase diagram of atoms/molecules interacting through a pair potential (ex: Lennard-Jones 1922):

$$V(r) = (A/r^{12} - B/r^{6})$$

A and B adjusted on experimental values for inter-atomic distances, frequencies, etc.

A universal potential for carbon?

Diamond: insulating and ultra-hard
Graphite: semi-metallic and sinterable

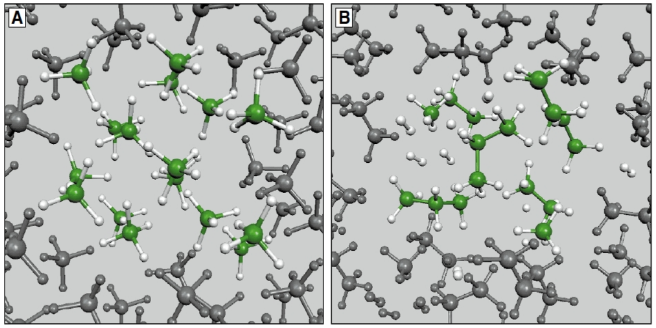


Diamond => graphite transformation under shear strain (90 Gpa)

What can we do when there is no experiment ?

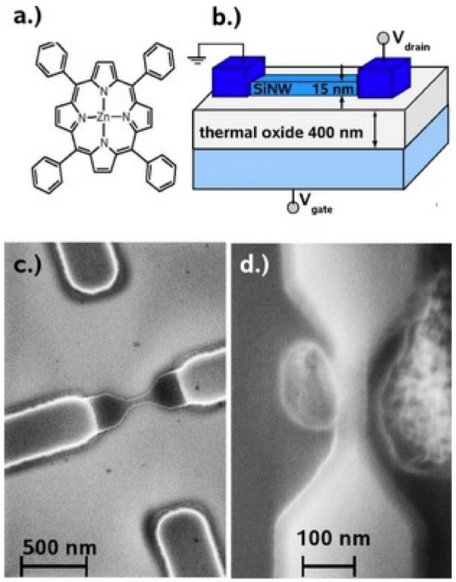
Physics of Iron at Earth's Core Conditions
Science 287 11 February 2000

Dissociation of Methane into Hydrocarbons at Extreme Planetary Pressure and Temperature
Science 275, 1288 (1997)

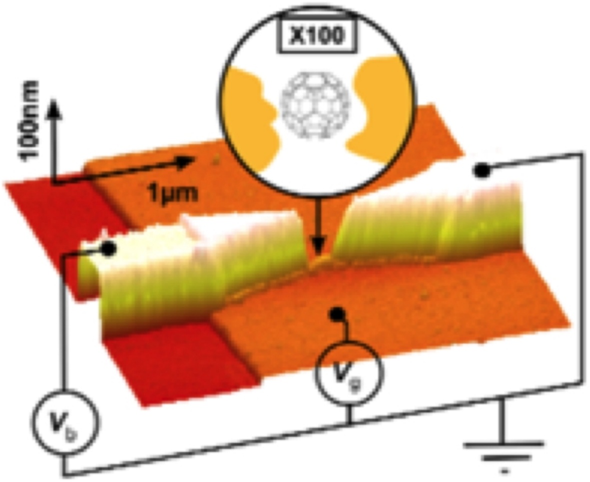


Nanosciences and nanotechnologies: the difficulty of measuring at the nano- and femto- scales

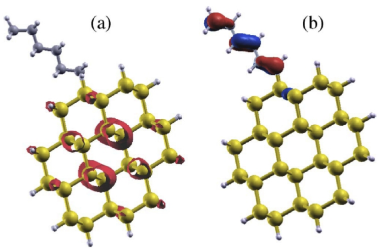
(V. Bouchiat et al.; W. Werndorfer et al.; Institut Néel, Grenoble)

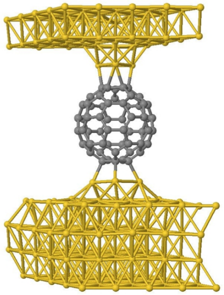


Functionalized wire ?



C_{60} contacted by gold electrodes ?





⇒ Correlate with theoretical « measurements » (conductance, optical absorption, etc.) on well defined (but simplified ??) systems.

Theory and experiments: the story of the blind and the paralytic

Emblem from Johann Theodor de Bry's Emblemata saecularia with the theme of mutual support (Wiki)

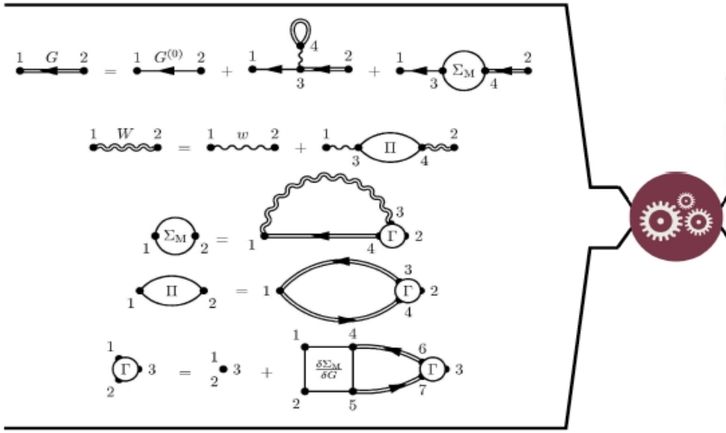
Experiments face difficulties to go down to the (spatial) nanoscale and the (time) femtosecond resolution !! (developments of STM, pump-probe femto lasers, etc.)

↕

Theory and « ab initio » computer modeling have difficulties going beyond the nano- and femtoseconds timescales.

Refined question: can we calculate the structural, optical, electronic, magnetic, superconducting, thermoelectric, *etc*. properties of condensed matter systems, including « nanoscaled » systems, using computers and numerical simulations **without any** *a priori* **experimental information (“***ab initio***”) ?**

Subsidiary question: if yes, with what accuracy and with which computers ?



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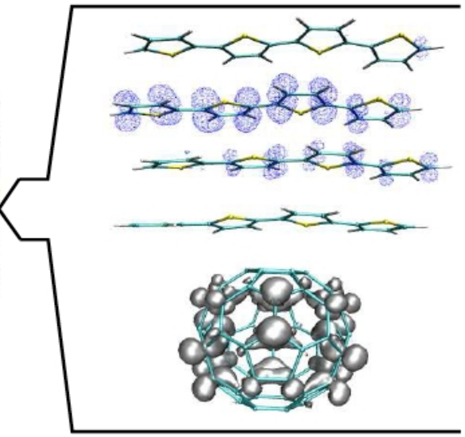


Electrons and holes moving in an organic solar cell

The answer is yes since the beginning of the 20th century and the rising of Quantum Mechanics that governs the behavior of electrons and atoms !


(Max Planck)


(Niels Bohr)


(Heisenberg)


(Paul Dirac)

...


(1927 Solvay conference in Brussels)

The wavefunction and the “Copenhagen interpretation” of electronic probability distribution:

The quantum state at the electronic level is described by a many-body wavefunction:

$$\Psi(r_1\sigma_1,\ldots,r_N\sigma_N) \equiv \Psi(\{r_i\}) \text{ such that } \left|\Psi(\{r_i\})\right|^2 dr_1\ldots dr_N$$

describes the probability of finding the electrons within the (dr_1, ..., dr_N) elementary volumes.

Any physical « observable » (total energy, forces on atoms, magnetization, etc.) results from averaging the corresponding « operator » with respect to this probability distribution:

$$\text{Energy and Hamiltonian } E = <\Psi\left|\hat{H}\right|\Psi> = \int\cdots\int dr_1\ldots dr_N \Psi^*(\{r_i\})\hat{H}(\{\nabla_i, r_i\})\Psi(\{r_i\})$$

The wavefunction is « just » the solution of the well-known Schrödinger equation

- The eigenstates are the solution of the Hamiltonian eigenvalue problem:

notations bra-ket: $\hat{H}|\Psi_n\rangle = E_n|\Psi_n\rangle$

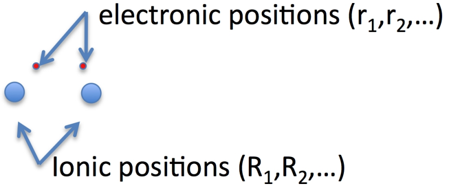
(Hamiltonien operator)

$$\hat{H} = \sum_i -\frac{\nabla_i^2}{2} + \sum_{i=1}^{N} v^{ions}(r_i) + \sum_{i<j}^{N} \frac{1}{r_{ij}}, \qquad v^{ions}(r_i) = -\sum_I \frac{Z_I}{|R_I - r_i|}$$

Kinetic energy $\hat{T}$

Ionic potentiel

Electron-electron interaction $\hat{V}^{ee}$



(atomic units : e=m_e= $4\pi\varepsilon_0$=1)

- For fermions, the wavefunction is totally anti-symmetric!

- By definition, the electronic charge density reads:

$$n(r) = N\int\cdots\int dr_2 \ldots dr_N |\Psi(r, r_2 \ldots r_N)|^2 \quad \text{with} \int dr\, n(r) = N \quad \text{since} \langle\Psi|\Psi\rangle = 1 \quad \text{(normalisatio}$$

n(r)dr =number of electrons in volume dr centered on r (must be positive)

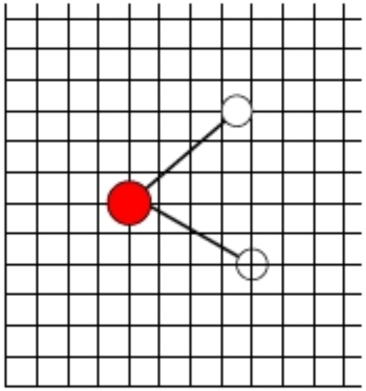
There is just a problem ...

There are typically 10^{22}-10^{23} electrons per cm^3 of matter !!

Supercalculators are « petaflopic »: 1 Petaflop = 10^{15} operations per second !

This is already quite scary, but the truth is even worse: let's take a small molecule with no more than 10 electrons ... and let's try to calculate its energy:

$$E = <\Psi|\hat{H}|\Psi> = \int \cdots \int dr_1 \ldots dr_N \Psi^*(\{r_i\})\hat{H}(\{\nabla_i, r_i\})\Psi(\{r_i\})$$

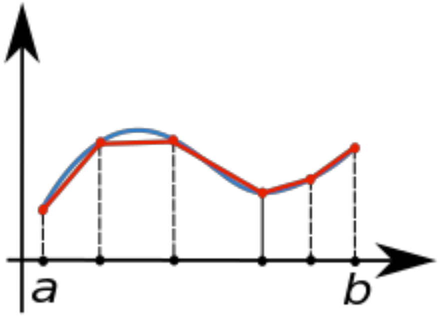


=> 3N=30 dimension integral (x_1,y_1,z_1, x_2,y_2,z_2, ...)

So if we represent each direction by a set of 10 grid points to evaluate the integral, this makes:

$$10^{30}$$

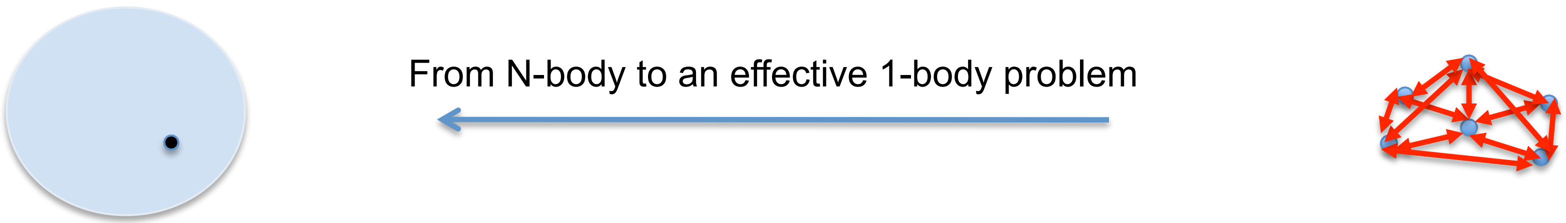
values to sum for getting the average (expectation) value.



A standard trapezoidal scheme for evaluating integrals in 1D

One need to do approximations to the many-body problem !

The mean-field idea: only one electron in the average field of the others !!



From N-body to an effective 1-body problem

Mean-field approaches

The « exact » many-body problem

Can we map the “interacting” N-body problem onto a “non-interacting” N-body problem in an « effective » potential so that the energy, charge density, etc. of this fictitious system is the same than that of the real system ?

In this non-interacting system, the electrons do not see each other: they are uncorrelated and they just see the effective potential $V^{eff}(r)$ => the Schrödinger equation is a « standard » 3D differential equation, NOT a N-body problem:

$$\left[-\frac{\nabla^2}{2}+\sum_{i=1}^{N} v^{ions}(r)+V^{eff}(r)\right]\varphi(r)=\varepsilon\,\varphi(r)$$

wavefunction of the non-interacting electrons (uncorrelated=> does not depend on other electrons position)

The density functional theory: an exact mean-field theory for the N-electron problem

P. Hohenberg and W. Kohn, PRB 1964
W. Kohn and L. Sham, PRB 1965

Walter Kohn,
Nobel 1998
(chemistry)

It was shown in 1964 by Hohenberg and Kohn that the many-body problem could be indeed recast into an independent electron problem subject to an effective V^{eff} potential that accounts for all electron-electron interactions.

A) This theorem is exact !!
B) It shows that V^{eff} only depends on the charge density of the system:

n(r) the charge density is a simple scalar field (not a 3N-dimension object) !
It is a mean-field quantity which averages over all electrons positions !!

BUT: We do not know how to write V^{eff} as a function of the charge density n(r)

Several approximations are used for this « functional » and the search for the universal and accurate fonctional is one of the most active field in « conceptual DFT ».

Note: the demonstration of the Hohenberg-Kohn theorem at the Master level

Théorème de Hohenberg-Kohn (1964)

Soit $n(\vec{r})$ la densité de charge de l'état fondamental. Alors il existe un seul potentiel extérieur $v^{ext}(\vec{r})$ qui "réalise" $n(\vec{r})$

$$\hat{H} = \hat{T} + V^{ee} + \sum_i v^{ext}(\vec{r}_i) \longrightarrow \underbrace{\psi_0 \longrightarrow n(r)}_{\text{état fondamental}}$$

Par l'absurde Supposons qu'il existe 2 potentiels

$$\begin{tikzcd} v_1^{ext}(\vec{r}) \arrow[r] & \hat{H}_1 \arrow[r] & \psi_1^{(0)} \arrow[dr] & \\ & & & n(r) \\ v_2^{ext}(\vec{r}) \arrow[r] & \hat{H}_2 \arrow[r] & \psi_2^{(0)} \arrow[ur] & \end{tikzcd}$$

m̂ densité de charge

Principe variationnel

$$\langle \psi_1 | \hat{H}_1 | \psi_1 \rangle < \langle \psi_2 | \hat{H}_1 | \psi_2 \rangle$$

état fondamental non-dégénéré

$$\Downarrow$$

$$\langle \psi_2 | \hat{H}_2 | \psi_2 \rangle + \langle \psi_2 | \hat{H}_1 - \hat{H}_2 | \psi_2 \rangle$$

$$\Rightarrow E_1^{(0)} < E_2^{(0)} + \int d\vec{r} \left[v_1^{ext}(r) - v_2^{ext}(\vec{r}) \right] n(r) \quad Ⓐ$$

fondamental de $\hat{H}_1$ et $\hat{H}_2$

on peut inverser (1) et (2)

$$Ⓑ \quad E_2^{(0)} < E_1^{(0)} + \int d\vec{r} \left[v_2^{ext} - v_1^{ext} \right](r)\, n(r)$$

$$Ⓐ + Ⓑ \Longrightarrow E_1^{(0)} + E_2^{(0)} < E_2^{(0)} + E_1^{(0)}$$

$$\boxed{\text{Impossible}}$$

Donc $n(r) \xrightarrow{\text{univoque}} v^{ext}(\vec{r})$

La réciproque est évidente

$$v^{ext}(\vec{r}) \longrightarrow \hat{H} \longrightarrow \underbrace{\psi_0 \longrightarrow n(r)}_{\text{fondamentale}}$$

$\Rightarrow$ relation biunivoque entre

$$\begin{tikzcd} v^{ext}(r) \arrow[r, leftrightarrow] \arrow[dr, leftrightarrow] & \psi_0(r) \arrow[d, leftrightarrow] \\ & n(r) \end{tikzcd}$$

$\Rightarrow$ La densité de charge détermine l'état fondamental et toutes les informations

$$E^0[\psi] \longrightarrow E^0[n(r)]$$

fonctionnelle de ψ

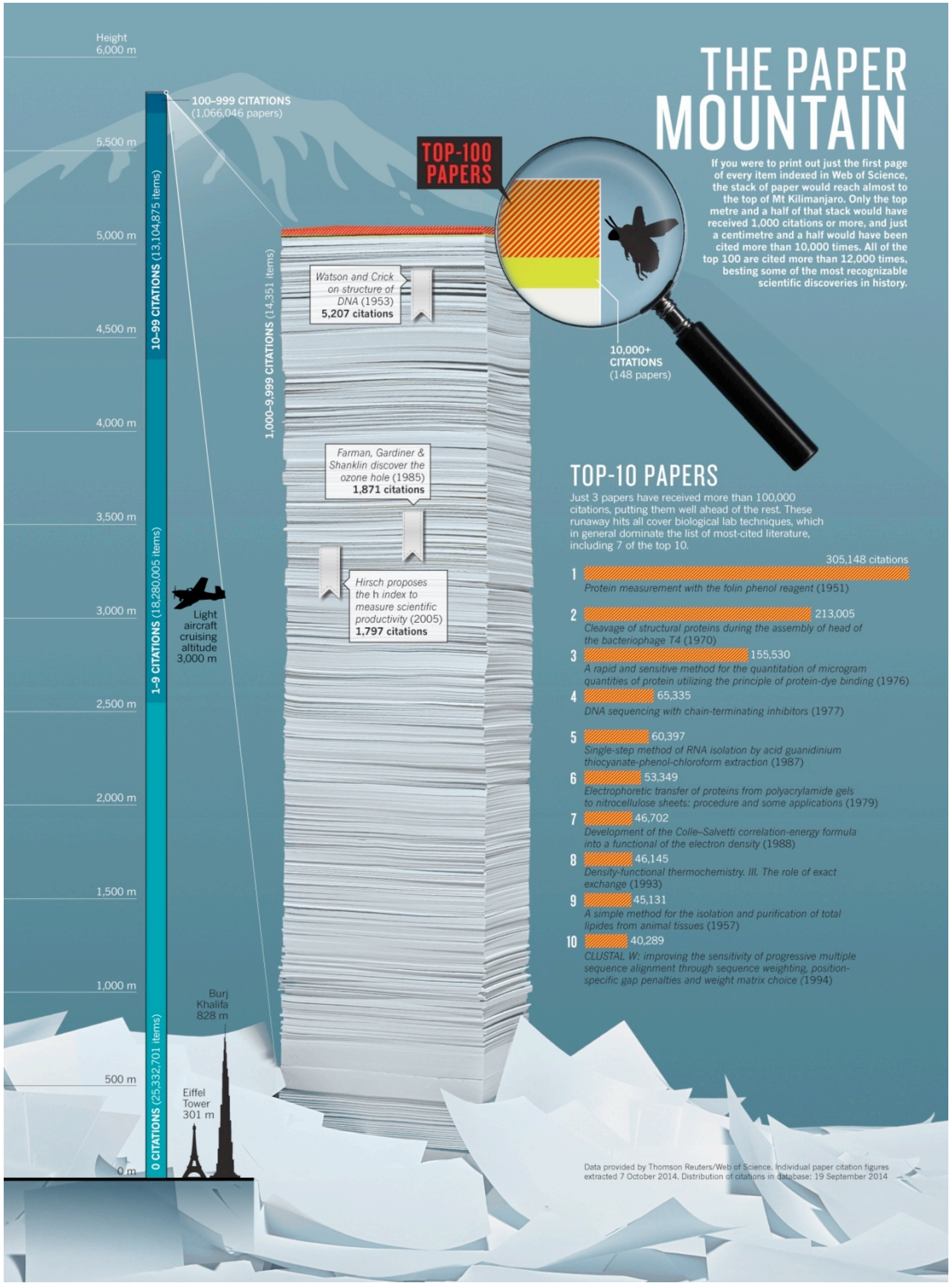
fonctionnelle de $n(\vec{r})$ (champ scalaire à 3D)

Théorie de champ moyen exact

on écrit en général

$$E^0[n] = \underbrace{[T + V^{ee}](n)}_{F_{HK}[n]} + \int v^{ext}(\vec{r})\, n(\vec{r})\, d\vec{r}$$

fonctionnelle universelle de Hohenberg et Kohn



THE PAPER MOUNTAIN

If you were to print out just the first page of every item indexed in Web of Science, the stack of paper would reach almost to the top of Mt Kilimanjaro. Only the top metre and a half of that stack would have received 1,000 citations or more, and just a centimetre and a half would have been cited more than 10,000 times. All of the top 100 are cited more than 12,000 times, besting some of the most recognizable scientific discoveries in history.

TOP-10 PAPERS

Just 3 papers have received more than 100,000 citations, putting them well ahead of the rest. These runaway hits all cover biological lab techniques, which in general dominate the list of most-cited literature, including 7 of the top 10.

1 305,148 citations
Protein measurement with the folin phenol reagent (1951)

2 213,005
Cleavage of structural proteins during the assembly of head of the bacteriophage T4 (1970)

3 155,530
A rapid and sensitive method for the quantitation of microgram quantities of protein utilizing the principle of protein-dye binding (1976)

4 65,335
DNA sequencing with chain-terminating inhibitors (1977)

5 60,397
Single-step method of RNA isolation by acid guanidinium thiocyanate-phenol-chloroform extraction (1987)

6 53,349
Electrophoretic transfer of proteins from polyacrylamide gels to nitrocellulose sheets: procedure and some applications (1979)

7 46,702
Development of the Colle–Salvetti correlation-energy formula into a functional of the electron density (1988)

8 46,145
Density-functional thermochemistry. III. The role of exact exchange (1993)

9 45,131
A simple method for the isolation and purification of total lipides from animal tissues (1957)

10 40,289
CLUSTAL W: improving the sensitivity of progressive multiple sequence alignment through sequence weighting, position-specific gap penalties and weight matrix choice (1994)

Data provided by Thomson Reuters/Web of Science. Individual paper citation figures extracted 7 October 2014. Distribution of citations in database: 19 September 2014

Rank 7:
Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density,
Chengteh Lee, Weitao Yang, and Robert G. Parr (1988)

Rank 8:
Density-functional thermochemistry
(3) The role of exact exchange,
A.D.Becke (1993)

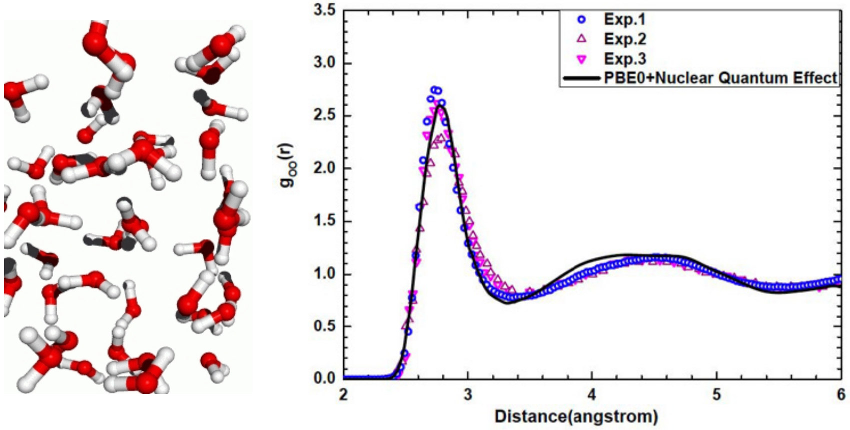
Rank 34:
Inhomogeneous Electron Gas
P. Hohenberg and W. Kohn (1964)

Rank 39:
Self-Consistent Equations Including Exchange and Correlation Effects
W. Kohn and L. J. Sham (1965)

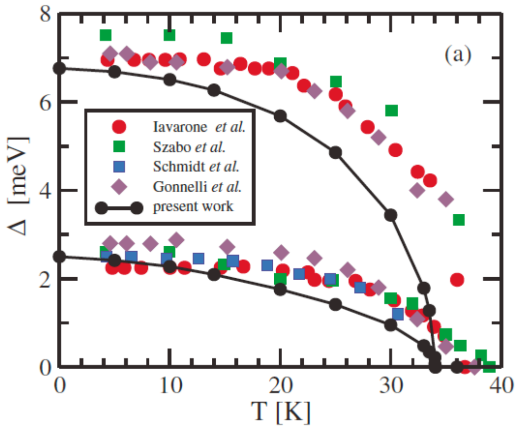
How accurate is the DFT and its approximate effective potential V^{eff} ?

We have already an answer to that question:

O-0 pair distribution in water (T=300 K)

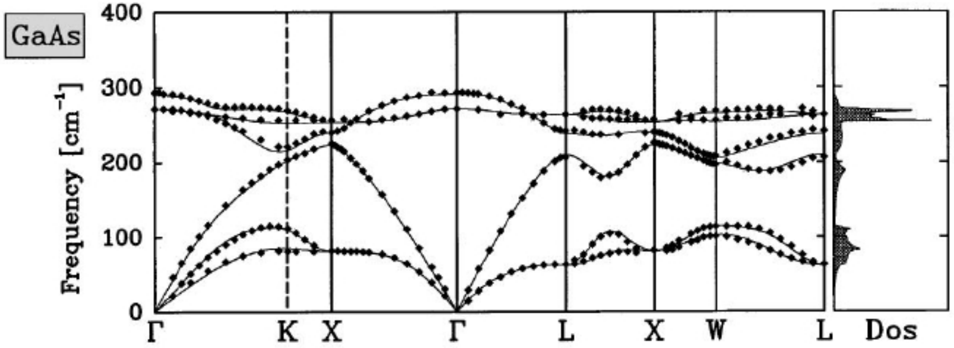


Superconductivity



π and σ superconducting gaps in MgB_2

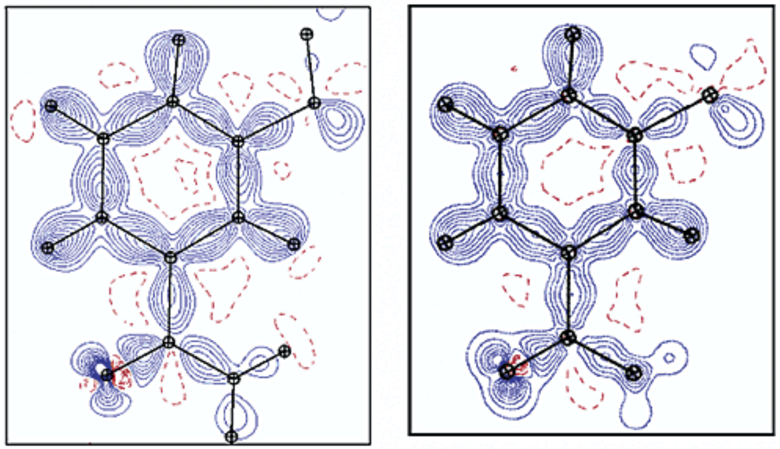
Phonon (vibrations) band structures



(points=experiment; Rev. Mod. Phys.**73**, 515 (2001))

Charge density (electronic distribution)

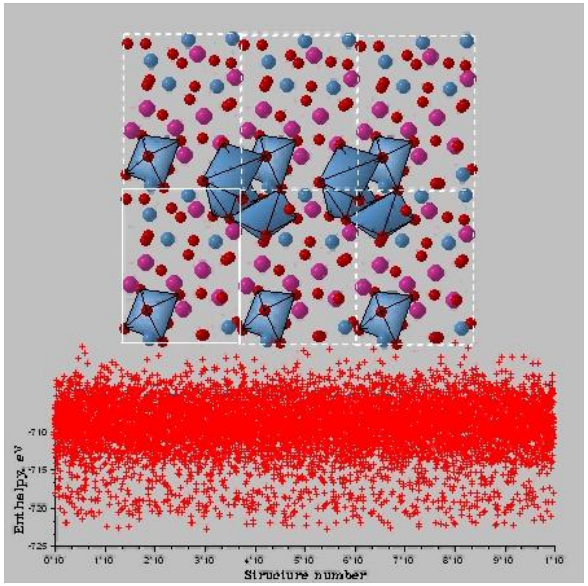
Experiment Theory



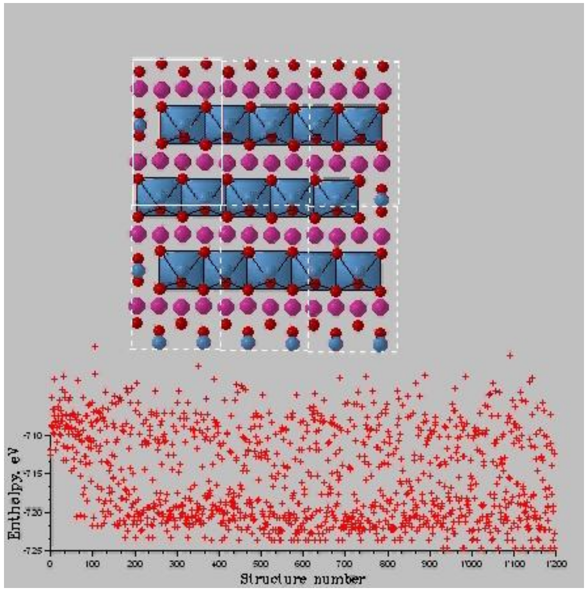
The search for novel materials

Since *ab initio* simulations do not need any experimental input and provide very reasonable properties of materials with a moderate cost within the DFT formalism, one can search for novel materials in the computer: this is called computational alchemy.

Exercice: for a given atomic stoichiometry (that of perovskite MgSiO3)
what are the most stable structures ?



Random search: 120 000 explored structures before finding the known $MgSiO_3$ compound.



Genetic algorithm guided search: less than 1000 explored structures before finding the known $MgSiO_3$ compound.

(page web code USPEX: **Universal Structure Predictor: Evolutionary Xtallography)**

The materials project@Harvard

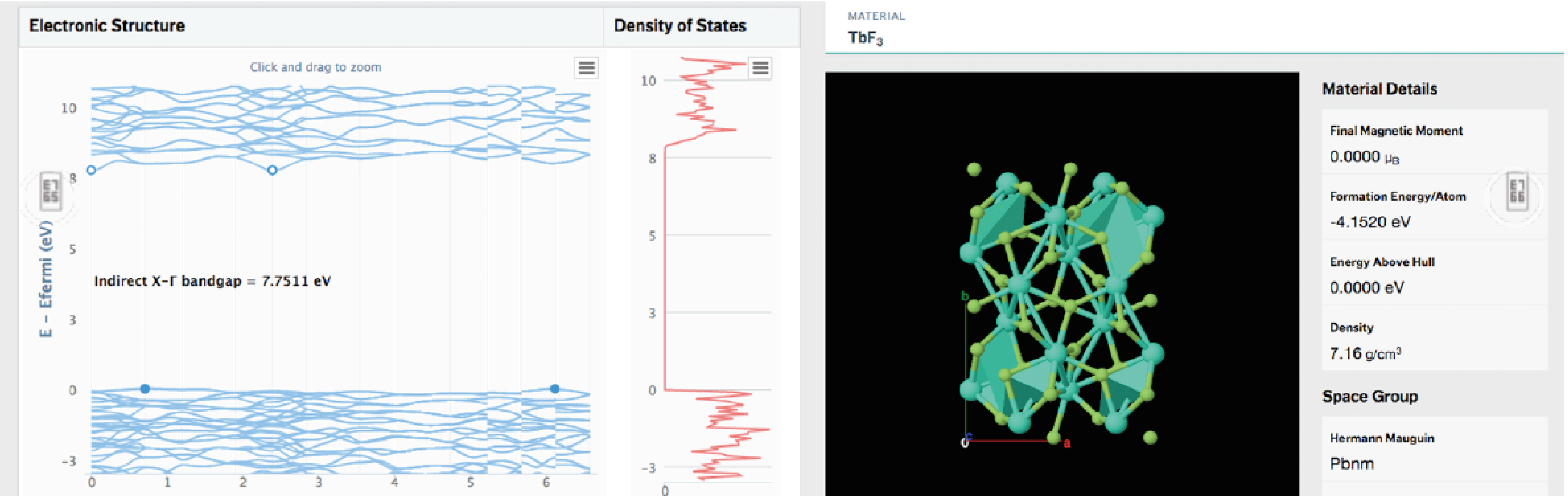
The Materials Project

Harnessing the power of supercomputing and state of the art electronic structure methods, the Materials Project provides open web-based access to computed information on known and predicted materials as well as powerful analysis tools to inspire and design novel materials.

Learn more (/about)

a **Tutorials (https://www.youtube.com/playlist?list=PLTjFYVNE7LTjHJwV994iQHS-bIkh3UXKJ)**

Sign In or Register (/janrain/loginpage/?next=/) to start using



Indirect X-Γ bandgap = 7.7511 eV

MATERIAL

TbF_3

Material Details

Final Magnetic Moment
0.0000 μ_B

Formation Energy/Atom
-4.1520 eV

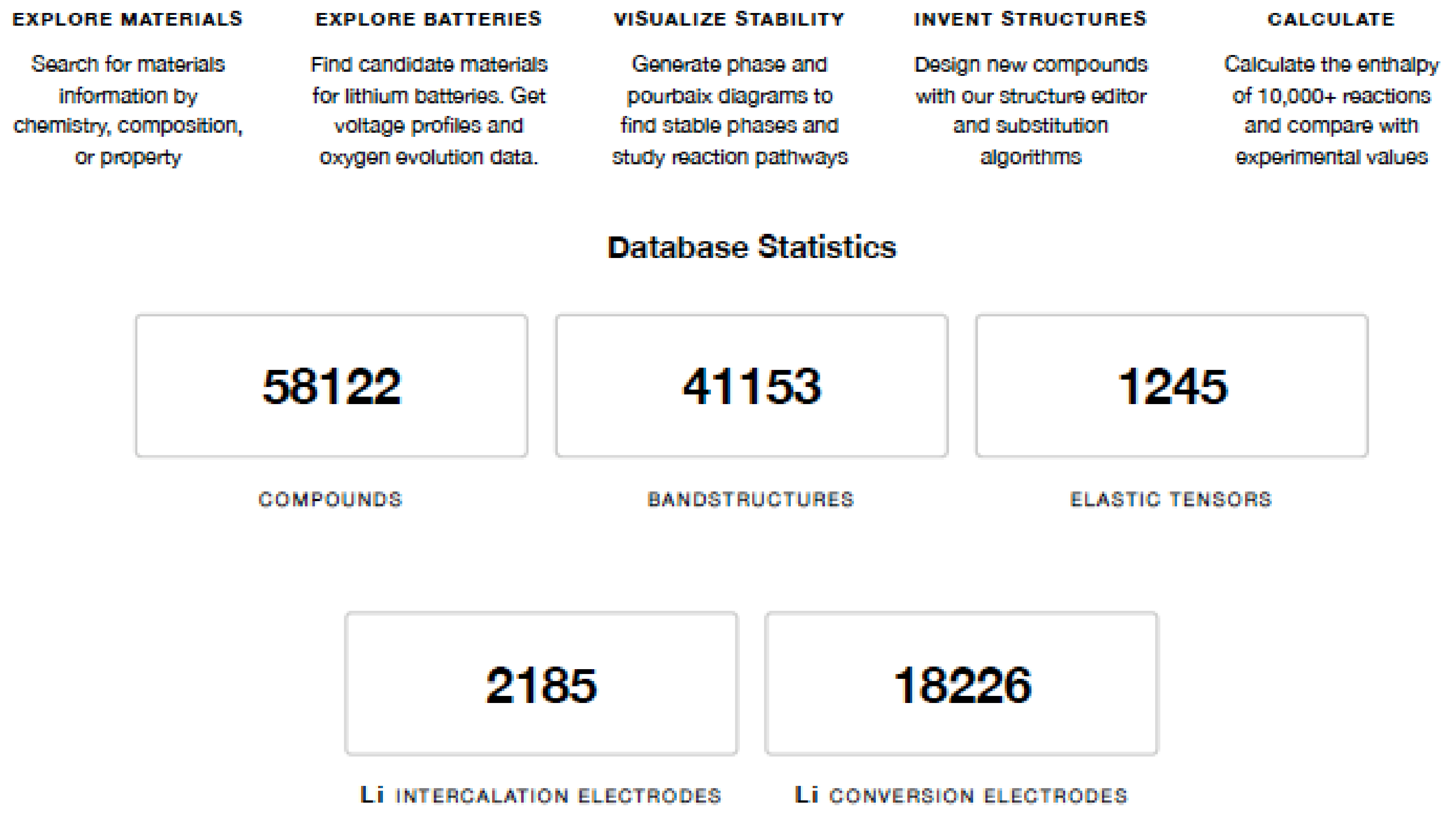
Energy Above Hull
0.0000 eV

Density
7.16 g/cm^3

Space Group

Hermann Mauguin
Pbnm

The materials project@Harvard (continued)



EXPLORE MATERIALS

Search for materials information by chemistry, composition, or property

EXPLORE BATTERIES

Find candidate materials for lithium batteries. Get voltage profiles and oxygen evolution data.

VISUALIZE STABILITY

Generate phase and pourbaix diagrams to find stable phases and study reaction pathways

INVENT STRUCTURES

Design new compounds with our structure editor and substitution algorithms

CALCULATE

Calculate the enthalpy of 10,000+ reactions and compare with experimental values

Database Statistics

58122	41153	1245
COMPOUNDS	BANDSTRUCTURES	ELASTIC TENSORS

2185	18226
Li INTERCALATION ELECTRODES	Li CONVERSION ELECTRODES

Computational alchemy (II)

Design of a Surface Alloy Catalyst for Steam Reforming

F. Besenbacher, I. Chorkendorff, B. S. Clausen, B. Hammer,
A. M. Molenbroek, J. K. Nørskov,* I. Stensgaard

Detailed studies of elementary chemical processes on well-characterized single crystal surfaces have contributed substantially to the understanding of heterogeneous catalysis. Insight into the structure of surface alloys combined with an understanding of the relation between the surface composition and reactivity is shown to lead directly to new ideas for catalyst design. The feasibility of such an approach is illustrated by the synthesis, characterization, and tests of a high–surface area gold-nickel catalyst for steam reforming.

www.sciencemag.org • SCIENCE • VOL. 279 • 20 MARCH 1998

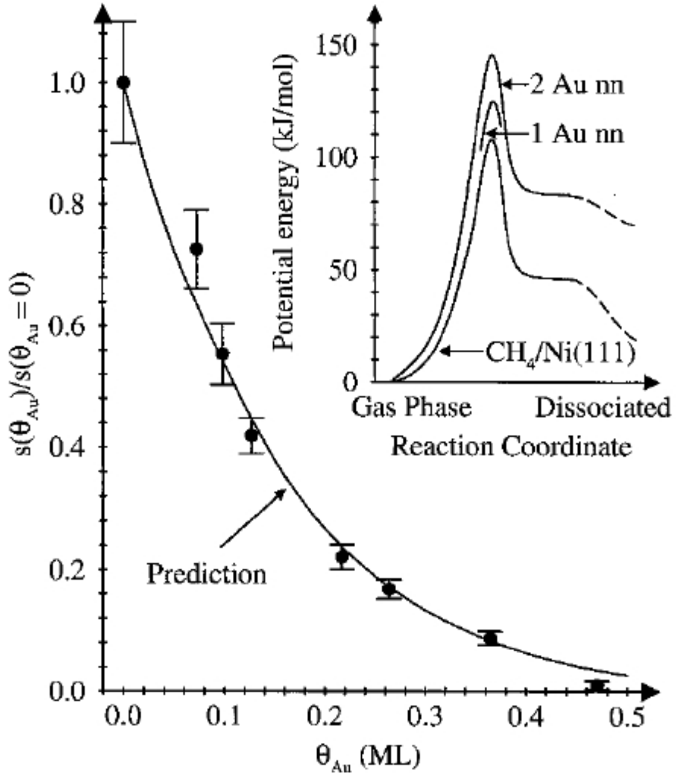
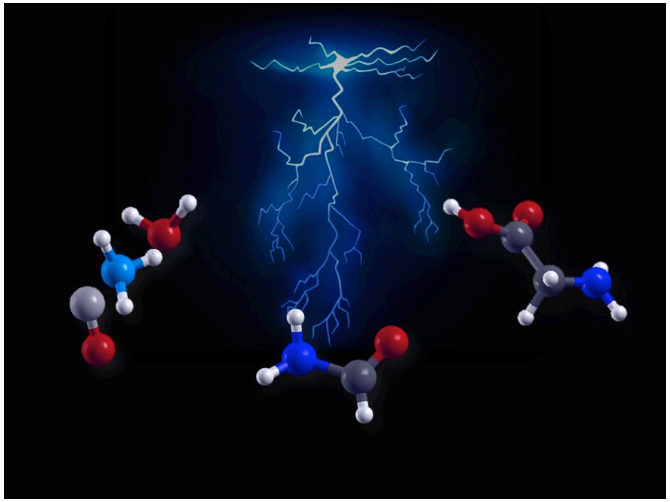


Fig. 2. The measured dissociation probability $s(\theta_{Au})$ for CH_4 on Ni(111) as a function of the Au coverage θ_{Au}. The dissociation probability has been normalized to the value for $\theta_{Au} = 0$. The full curve is the prediction of the model described in the text. (**Inset**) The calculated energy along the minimum-energy path for CH_4 dissociation over a clean Ni(111) surface and over a Ni atom in a Ni(111) surface with one or two nearest-neighbor (nn) Au atoms.

The search of better catalysts for very large scale industrial synthesis processes is a very active field in computational chemistry !!

Computational alchemy (III): revisiting Miller's experiment

« In 1953, Miller reported the surprising results he had achieved by the application of an electric discharge on a mixture of the gases CH_4, NH_3, H_2O, and H_2 that simulated what was considered at the time as a model atmosphere for the primordial Earth. The result of this experiment was a substantial yield of a mixture of amino acids. » (from: Saitta and Saija, PNAS 2014)



(H_2O, CO,NH_3) => formamide => glycine

Computer simulations have shown that indeed under a large electric field the transformation of simple molecules into simple aminoacides is possible. The reaction pathway could be identified and the needed strength and catalytic role of the electric field could be understood.

As expected, this « in silico » story about the « origin of life » attracted much coverage ..

DER SPIEGEL

Libération

Le Scienze
EDIZIONE ITALIANA DI SCIENTIFIC AMERICAN

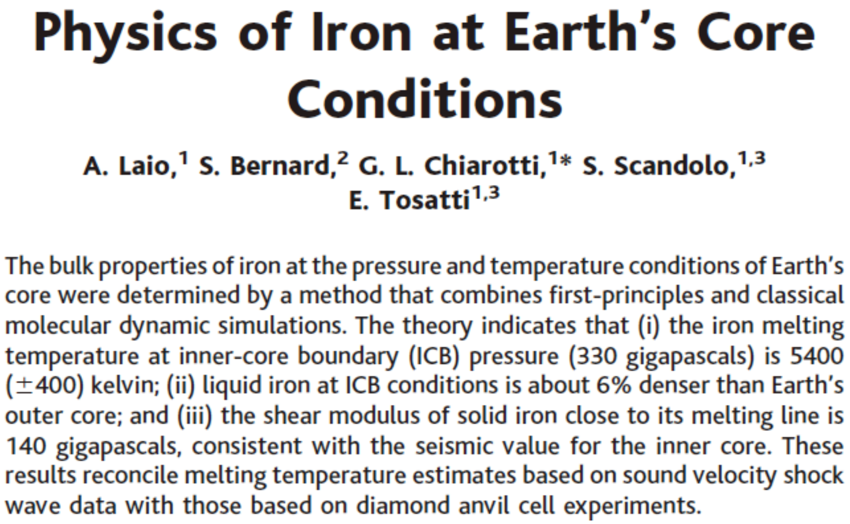
la Repubblica

Computational geophysics

Wikipedia

" ... according to seismological studies, [the Earth's inner core] is primarily a solid ball with a radius of about 1220 kilometers. It is believed to consist primarily of an iron-nickel alloy and to be approximately the same temperature as the surface of the Sun approximately 5700 K."

Getting information on the Earth solid inner core and liquid outer core, and/or reproduce experimentally the pressure/temperature conditions, is extremely difficult. Reproducing the PT phase diagram (structure, viscosity, electronic properties, etc.) of pure or alloyed metallic systems is starting to be within reach of *ab initio* simulations. The Earth magnetic field and its relation with convection in the outer core, are important related questions.



Physics of Iron at Earth's Core Conditions

A. Laio,[1] S. Bernard,[2] G. L. Chiarotti,[1]* S. Scandolo,[1,3]
E. Tosatti[1,3]

The bulk properties of iron at the pressure and temperature conditions of Earth's core were determined by a method that combines first-principles and classical molecular dynamic simulations. The theory indicates that (i) the iron melting temperature at inner-core boundary (ICB) pressure (330 gigapascals) is 5400 (±400) kelvin; (ii) liquid iron at ICB conditions is about 6% denser than Earth's outer core; and (iii) the shear modulus of solid iron close to its melting line is 140 gigapascals, consistent with the seismic value for the inner core. These results reconcile melting temperature estimates based on sound velocity shock wave data with those based on diamond anvil cell experiments.

Science 287 11 February 2000

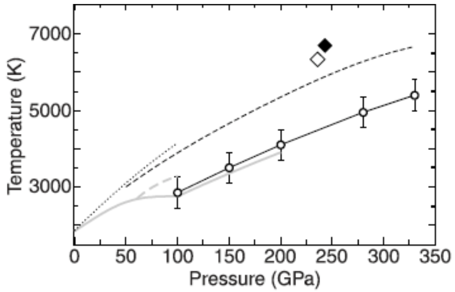
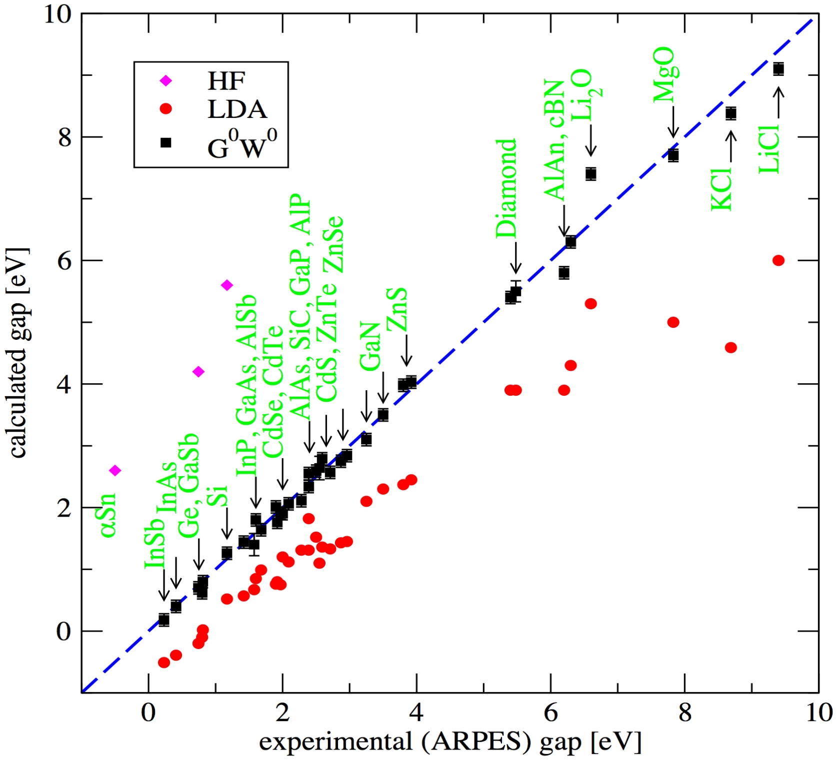


Fig. 2. High-pressure melting curve of Fe. Our results are given by open circles with error bars (bars in Figs. 2 and 5 represent errors discussed in text). The gray solid curve shows DAC data by Boehler (*3*) and data (up to ~150 GPa) by Saxena *et al.* (*5*); the gray dashed curve shows DAC data by Shen *et al.* (*6*). The dotted line indicates DAC data by Williams *et al.* (*2*); the dashed line indicates theoretical results by Alfè *et al.* (*25*). The open diamond shows shock wave datum by Yoo *et al.* (*4*), and the solid diamond shows shock wave datum by Williams *et al.* (*2*).

Back to fundamental research (why do we still need to explore fundamental formalisms ?)

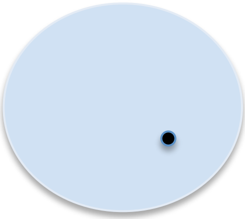
The previous slides focused on « success » stories. However, there are still many questions and « physical observables » that the standard density functional theory (DFT) cannot tackle with enough accuracy !!

The approximate V^{eff} potentials we know are designed for getting good structural, vibrational, etc. properties. But they are not built for getting e.g. very good electronic properties (« band structures »):

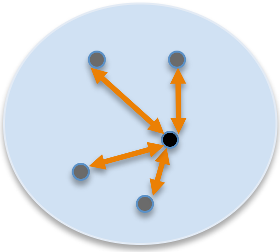


Theoretical versus experimental band gap of semiconductors and insulators. The red dots are the « DFT » data with the « LDA » functional, the pink dots are the Hartree-Fock data. The black dots are DFT data corrected by a « few-body » correction (GW formalism, see next slide).

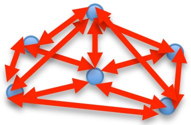
The *ab initio* zoo: from mean-field to many-body perturbation theory



Mean-field approaches
(DFT, Hartree-Fock, *etc.*)

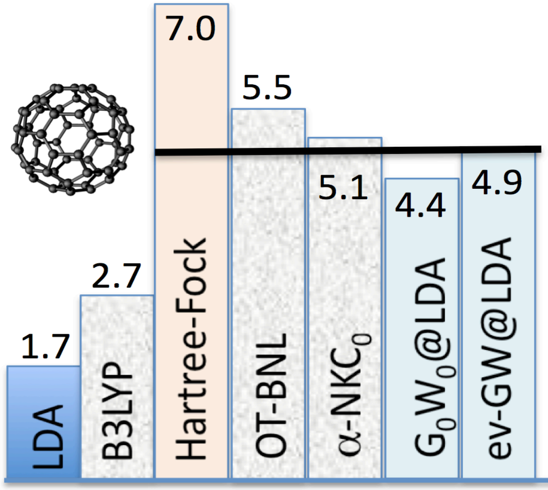


Many-body perturbation theory
(GW, Bethe-Salpeter, etc.)

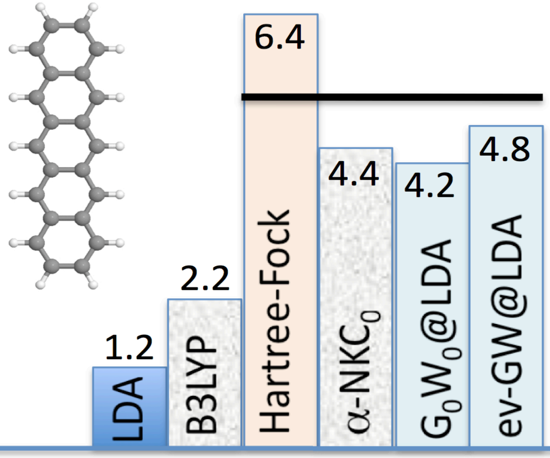


The « exact » many-body problem
(QMC, CI, coupled-cluster, etc.)

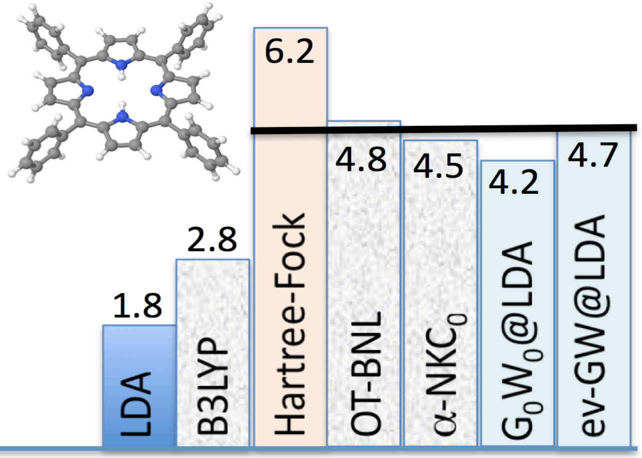
Example: HOMO-LUMO gap of molecules of interest for organic electronics or photovoltaics



Exp. HOMO-LUMO gap : 4.9 eV



Exp. HOMO-LUMO gap : 5.2 eV



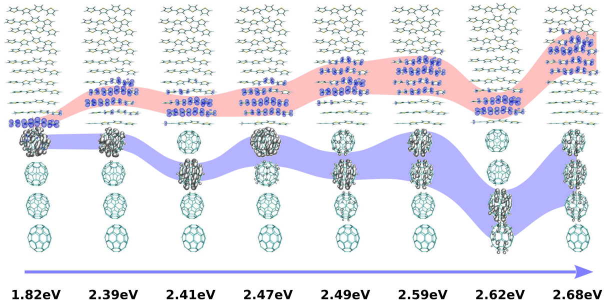
Exp. HOMO-LUMO gap : 4.7 eV

α-KNC$_0$: enforcing linearity of E(N) for N fractional (Dabo et al., PCCP 2013) <= DFT world
ev-GW@LDA: self-consistency on the eigenvalues (Blase et al., PRB 2012) <= Many-Body world

Organic photovoltaics (OPV): screening of novel molecules

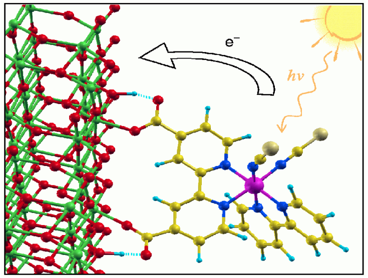
The Harvard Clean Energy Project: Large-Scale Computational Screening and Design of Organic Photovoltaics on the World Community Grid

Understanding the origin of organic cells efficiency

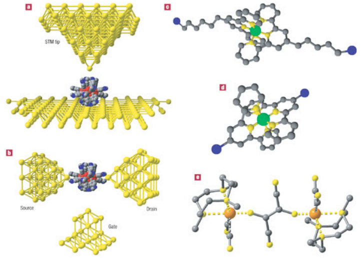


Electron-hole dissociation at a molecular donor/acceptor interface (collab. U Mons et CEA/INAC)

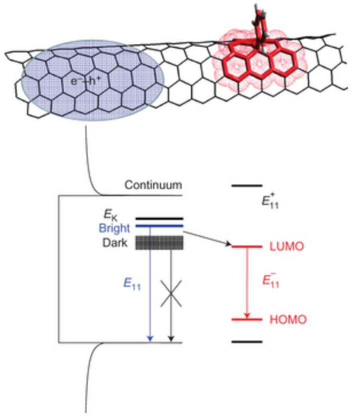
Explore novel systems and architectures



DSSCs



Molecular (spin)tronique



Functionalized tubes

Merci pour votre attention
Vielen Dank für Ihre Aufmerksamkeit
Tack för din uppmärksamhet
Bedankt voor uw aandacht