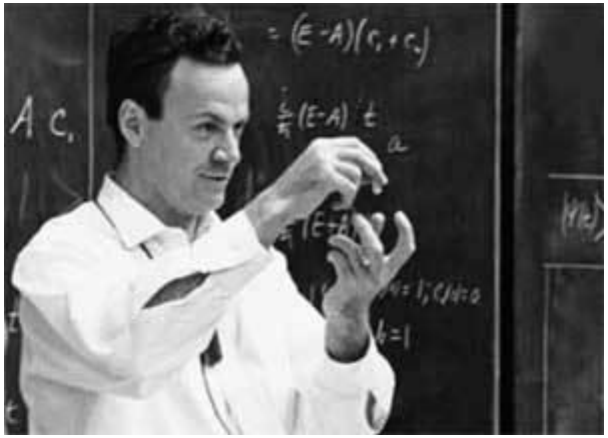
Computational materials science and sustainability

Ding Pan
Department of Physics and Department of Chemistry
Hong Kong University of Science and Technology
http://angstrom.ust.hk/

"If, in some cataclysm, all of scientific knowledge were to be destroyed, and only one sentence passed on to the next generation of creatures, what statement would contain the most information in the fewest words?"



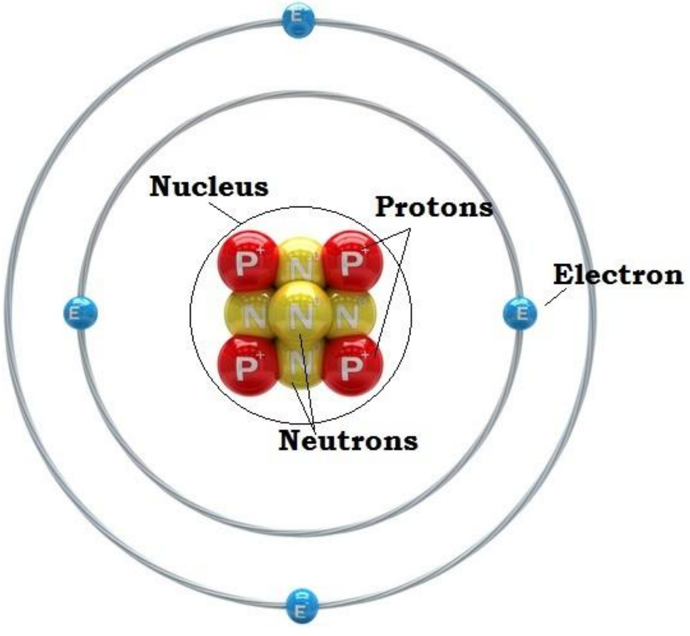
"all things are made of atoms"

--Richard Feynman

The Feynman Lectures on Physics

The structure of the atom

- “Atom”: invented by ancient Greek philosophers, originally denoted *a particle that cannot be cut into smaller particles*
- Scientific achievement in the 20th century: the atom is composed of various subatomic particles (electron, proton and neutron)



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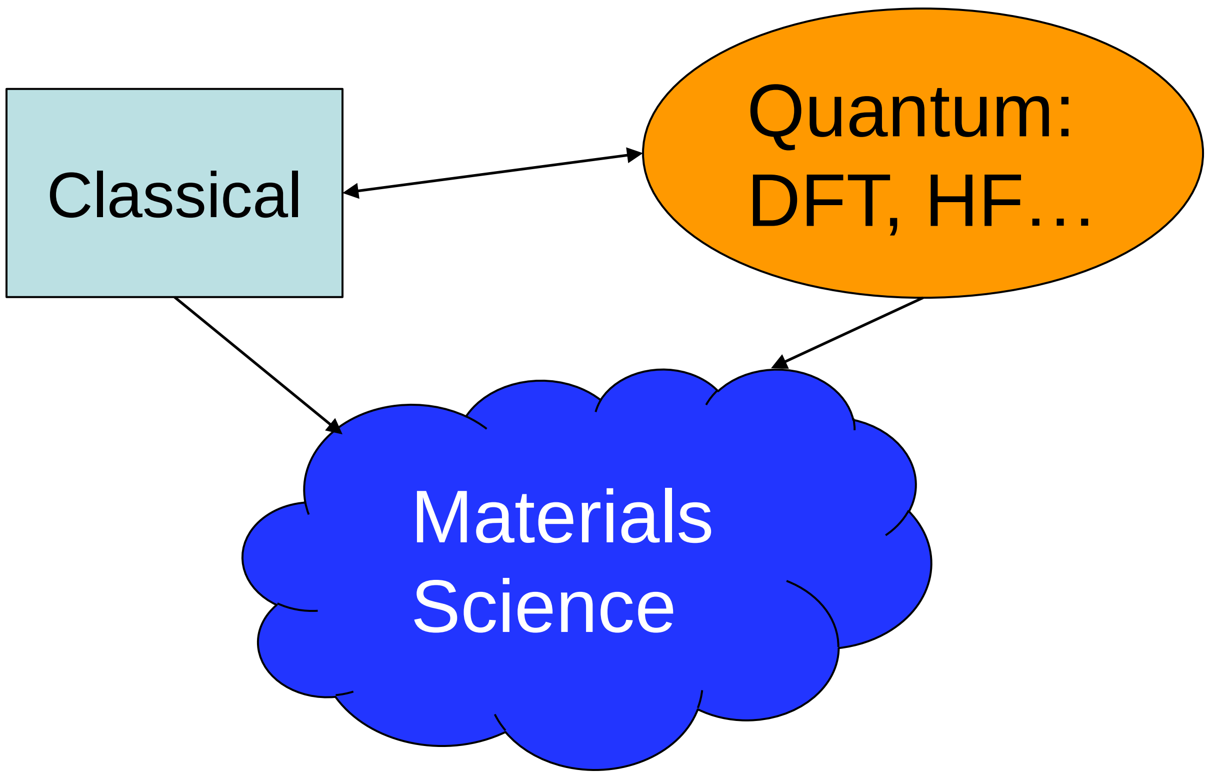
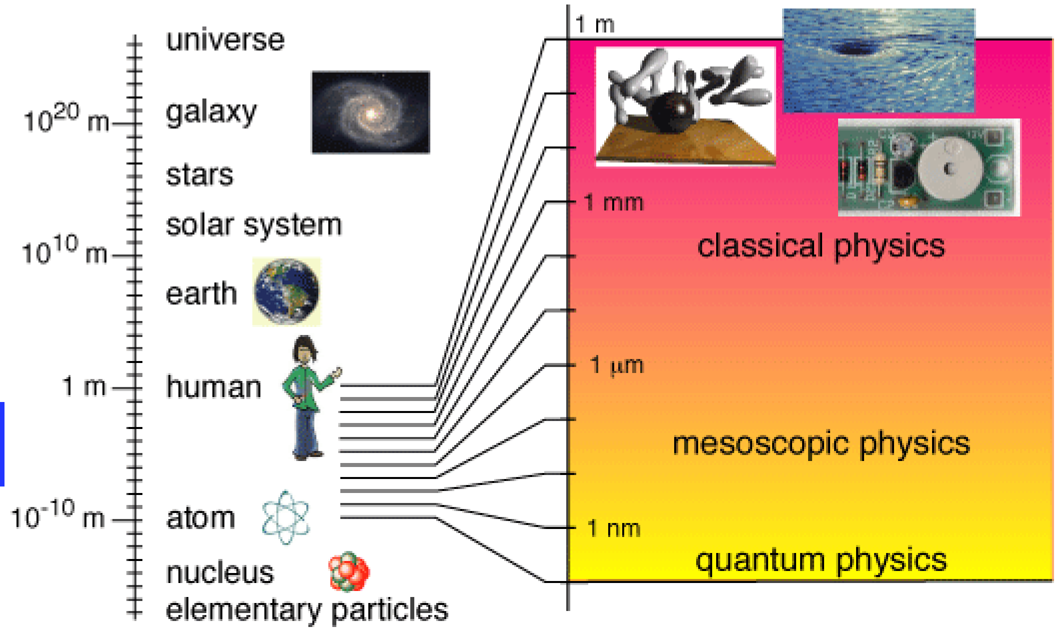


Quantum + Classical

Scale

Electromagnetic



Real materials

"I think I can safely say that nobody understands quantum mechanics". "The Character of Physical Law", -- Richard Feynman

"Shut up and calculate", -- David Mermin

What do we do?

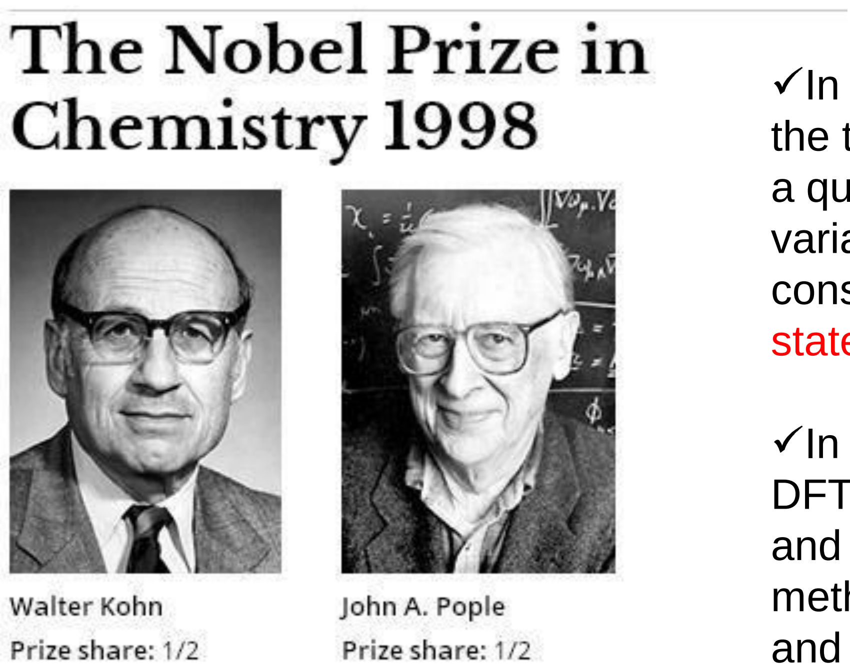
Apply the state-of-the-art methods to solve the Schrödinger equation numerically, in order to study the *real* materials, e.g., a glass of water:

$$H(t)\,|\,\psi(t)\rangle = i\hbar\frac{d}{dt}\,|\,\psi(t)\rangle$$

Exponential wall: the size of wave functions goes up exponentially

The workhorse of modern computational materials science

Density-functional theory (DFT): n(x, y, z)

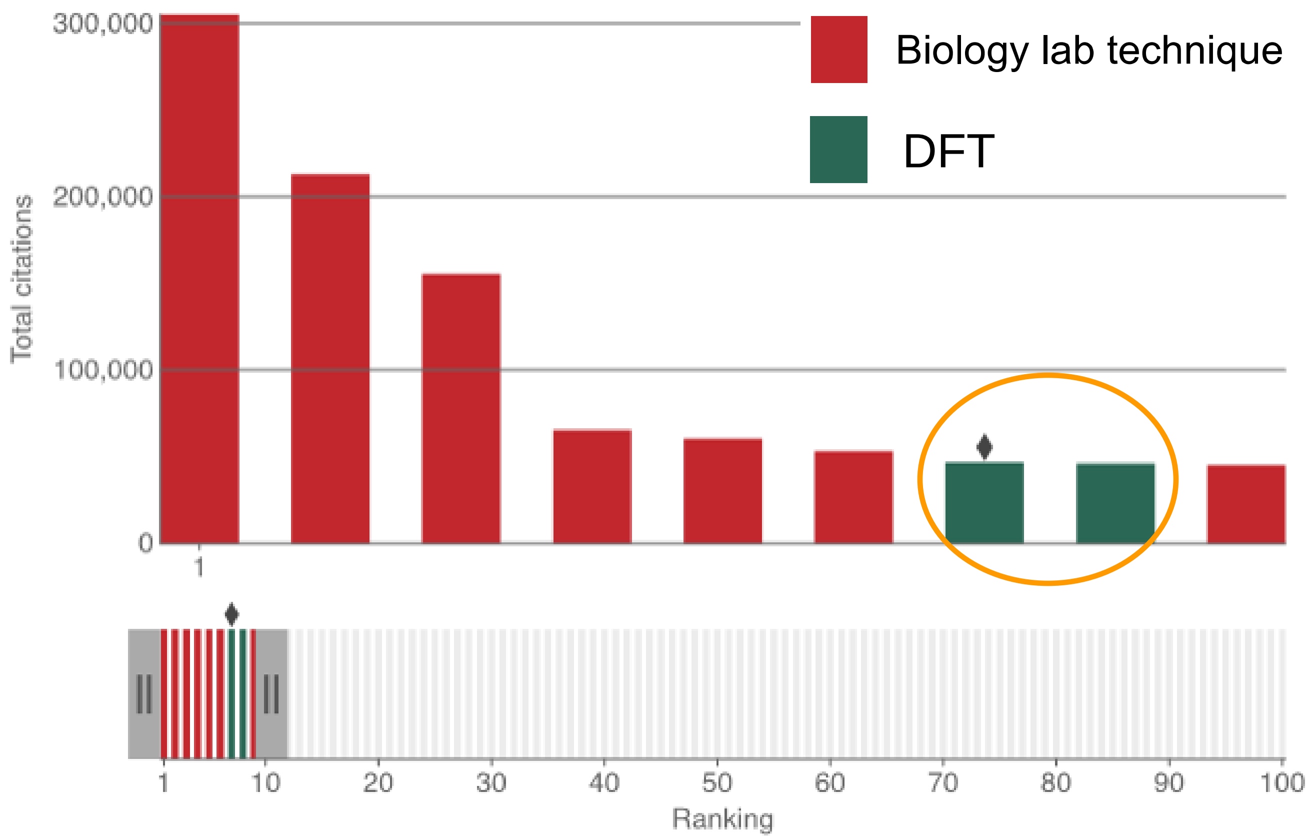


✓In 1964, Hohemberg and Kohn showed that the the density of particles in the ground state of a quantum many body system is a basic variable, i.e. all properties of the system can be considered unique functionals of the ground state density.

✓In 1965 Kohn and Sham (沈呂九) formulated DFT in terms of auxiliary single particles orbitals and laid the foundation of much of present day methods to treat electrons in atoms, molecules and solids!

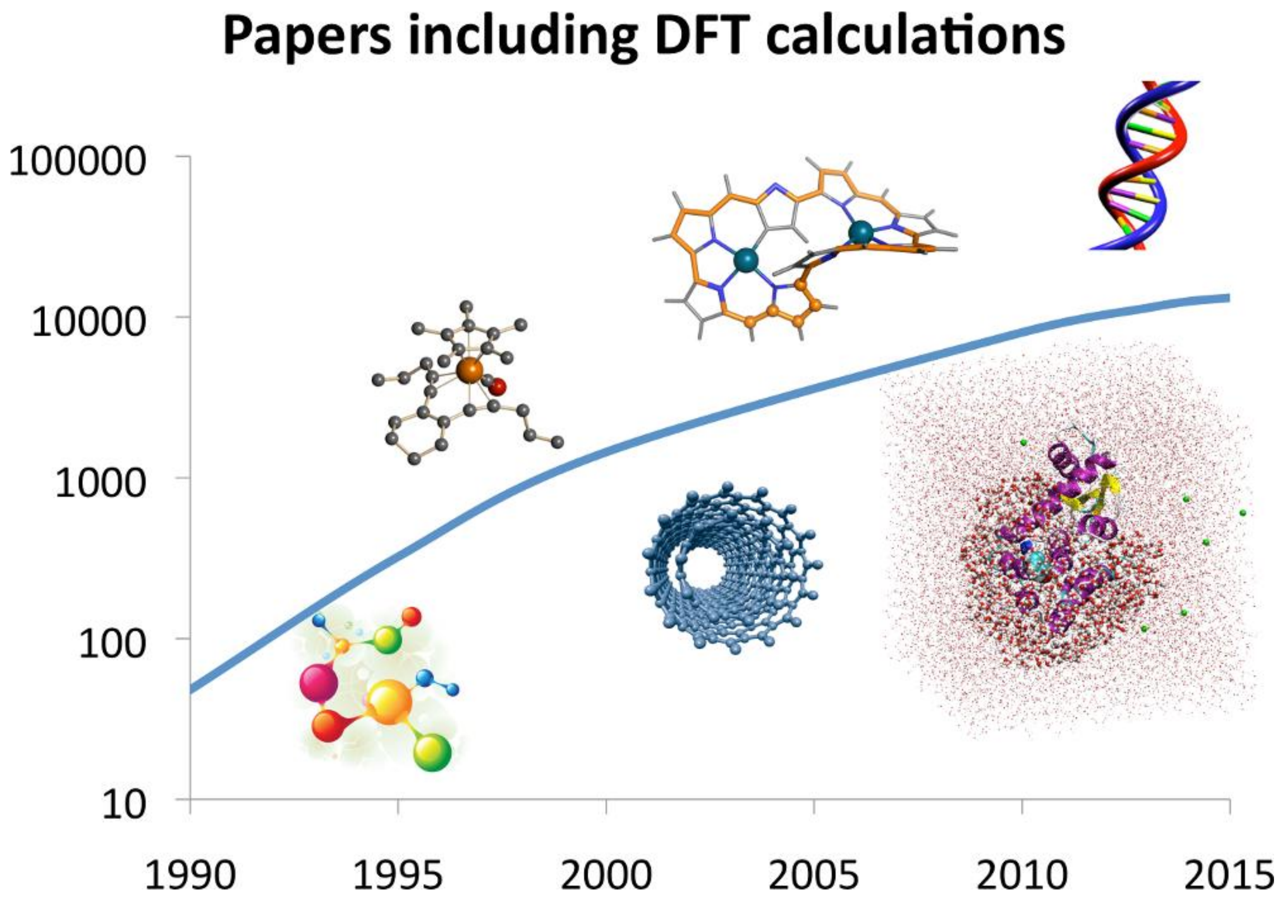
Impact

The most cited papers of all time



Nature 514, 550–553 (30 October 2014)

Impact



Papers including DFT calculations
100000
10000
1000
100
10
1990
1995
2000
2005
2010
2015

Materials:solids, liquids, nanostructures and combinations thereof

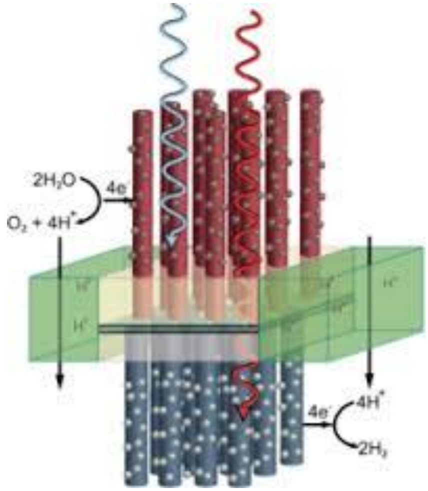
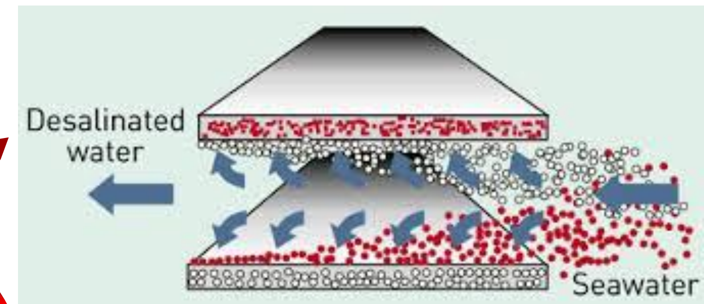
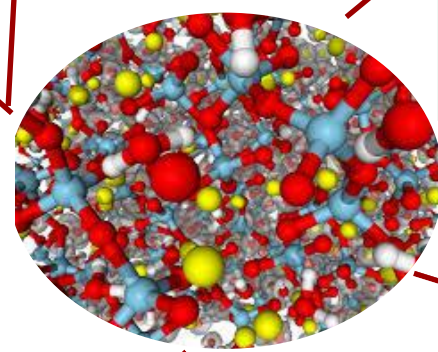
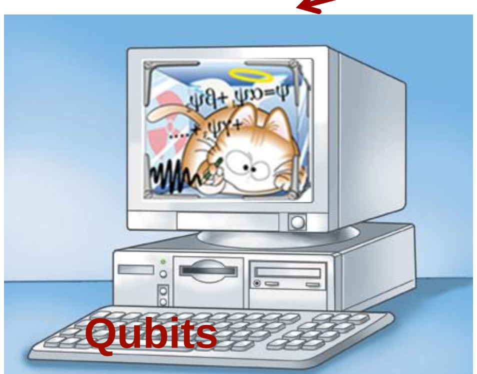


Photo-electrochemical cells

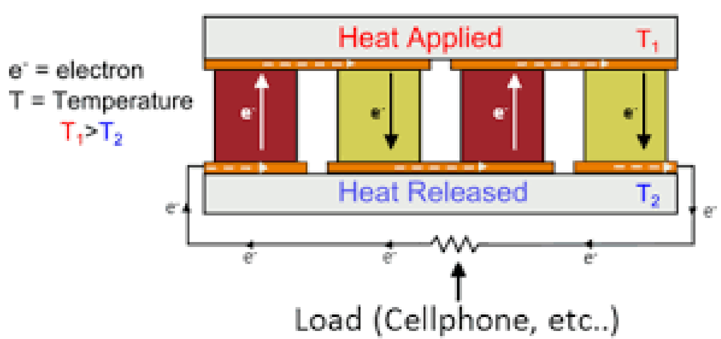
Clean Water

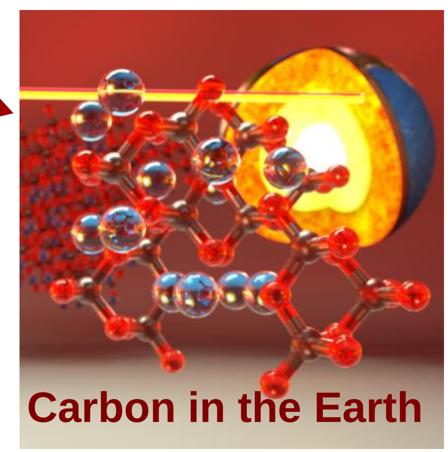






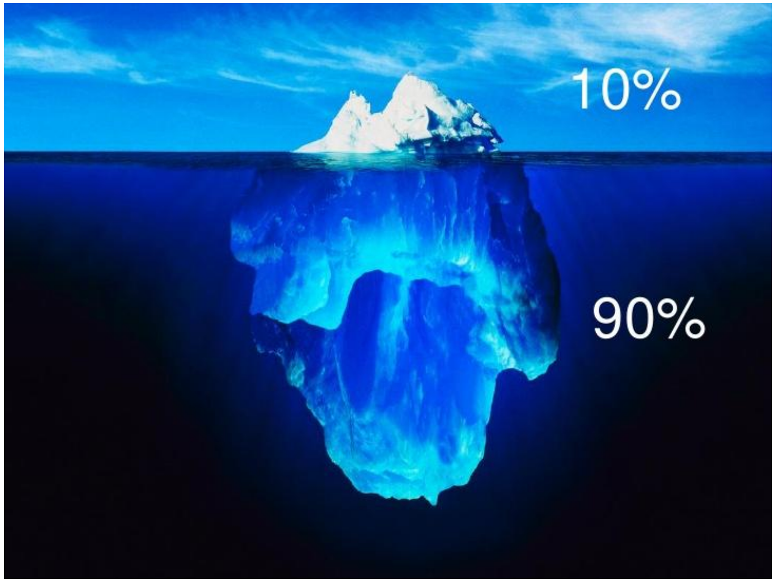
Thermoelectric generators





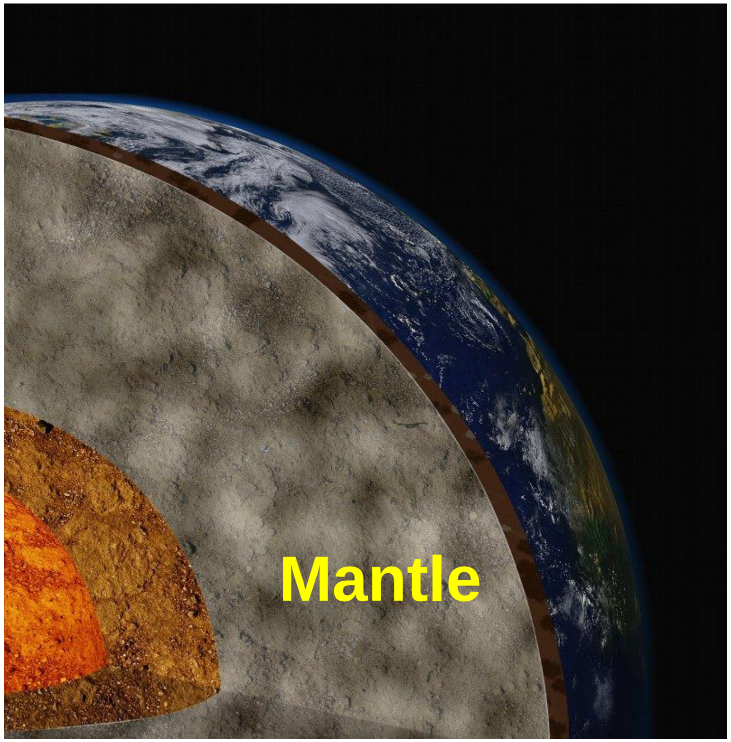
Outline

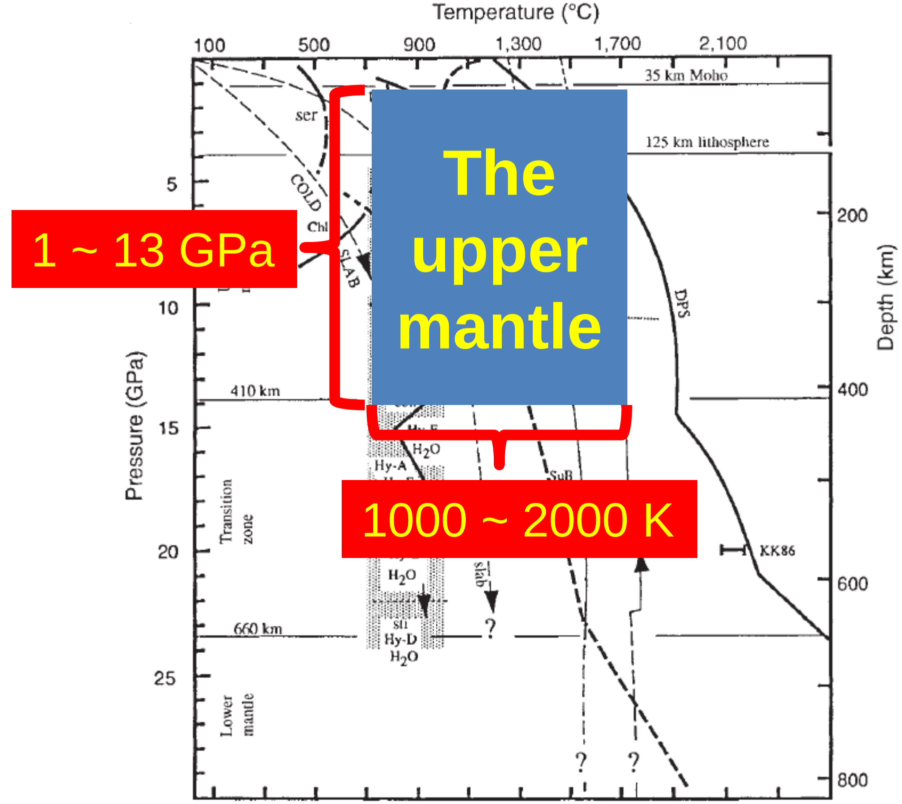
- Water science



Van der Waals interactions make ice float on water

Water is a major component of fluids in the Earth's mantle





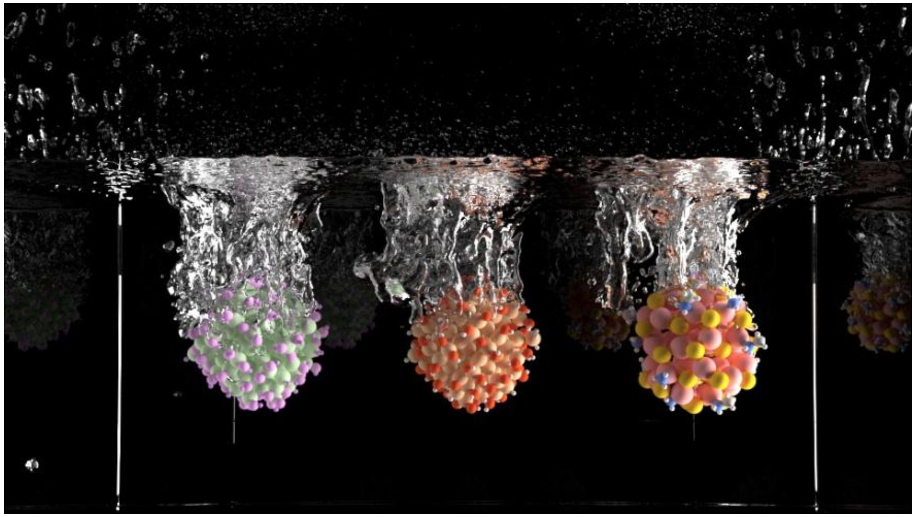
- Water is present in all magmas and mantle rocks
- Green chemistry: supercritical water used to dispose human waste
- The upper mantle: Pressure (P): 1 ~ 13 GPa; Temperature (T): 1000 ~ 2000 K
- The vapor-liquid supercritical point of water: 647 K, 22 MPa

A.B. Thompson, Nature 358, 295 (1992); M. Murakami et al., Science 295, 1885(2002); M. Hirschmann & D. Kohlstedt, Phys. Today 65, 40 (2012)

Theoretical challenge of modeling aqueous solutions: static dielectric constant, ε_0

Vacuum

$$F = \frac{q_+ q_-}{r^2}$$



Water

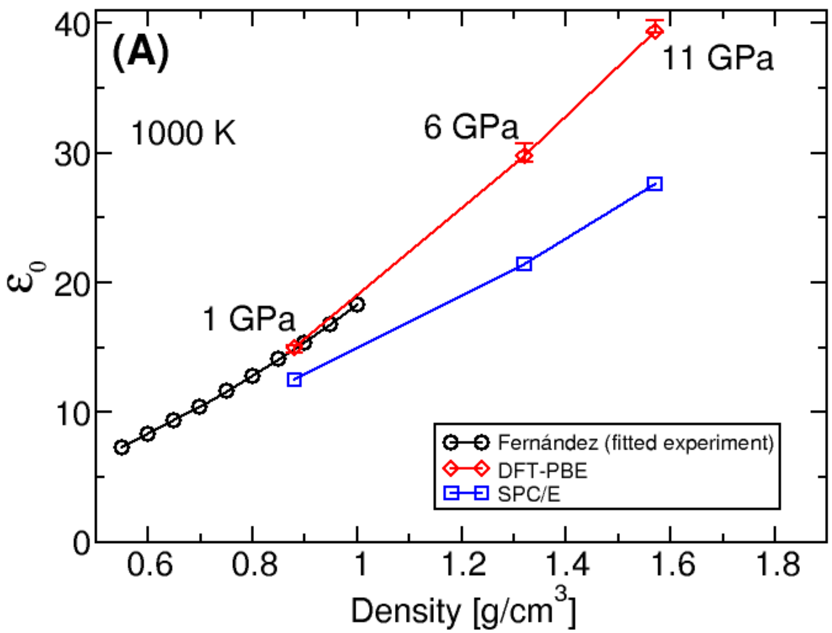
$$F = \frac{q_+ q_-}{\varepsilon_0 r^2}$$

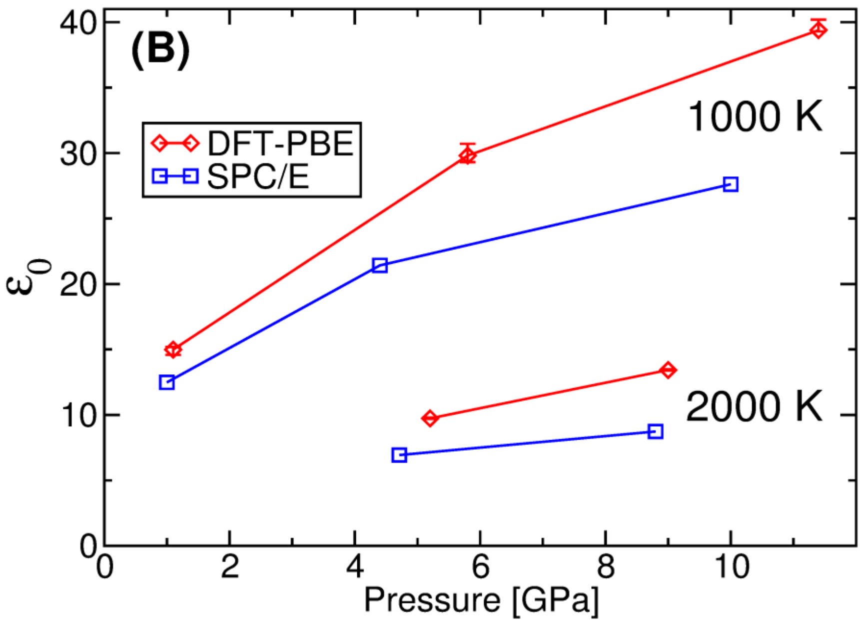
- The static dielectric constant, ε_0, determines the solvation properties of water:
  - At ambient conditions, ε_0 of water is unusually large: 78
  - At the vapor-liquid supercritical point, ε_0 is ~ 6

Figure courtesy of Nicholas Brawand

Fernández et al., J. Phys. Chem. Ref. Data. 26, 1125 (1997)

Pressure and temperature dependence of ε_0





- The dielectric constant, ε_0, monotonically increases with pressure at fixed T
- DFT-PBE predicts larger values of ε_0 than the water model SPC/E, but the difference between DFT-PBE and SPC/E is smaller at 2000 than at 1000 K

Water-rock interaction: Solubility of carbonates in the Earth's upper mantle

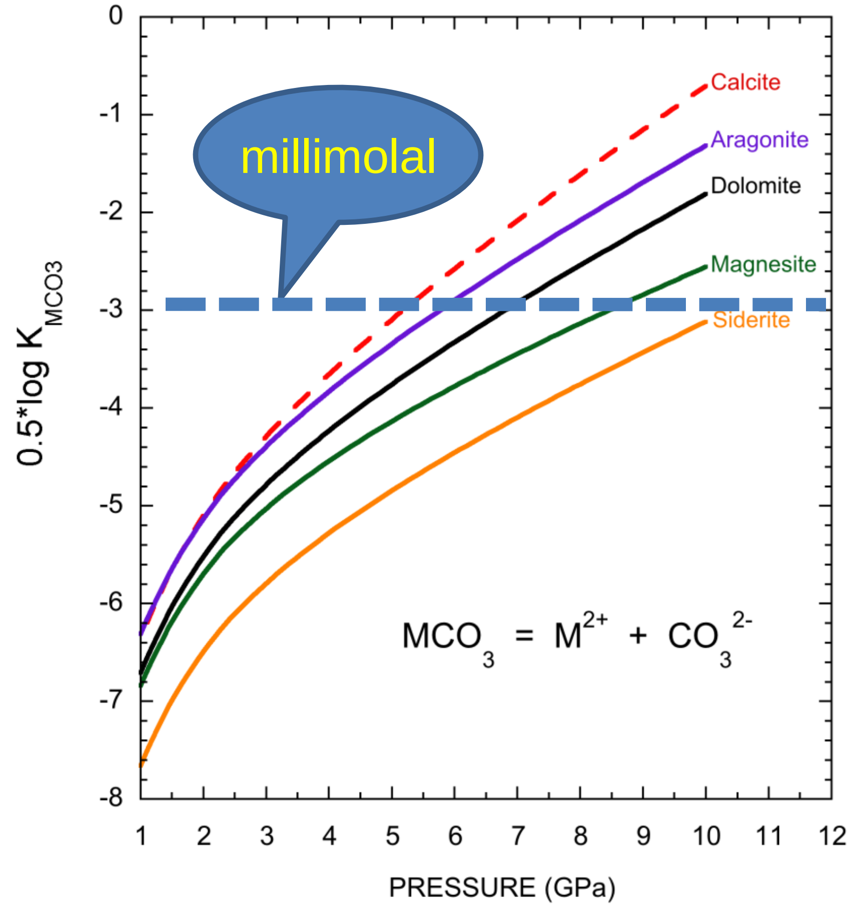
Equilibrium constant

$$\Delta G_0(\varepsilon_0) = -RT \ln K$$

The solubility product constant, K_{sp}, activities of ions, a_i, activity coefficients, γ_i and concentrations m_i:

$$K_{sp} = a_{M^{2+}} a_{CO_3^{2-}} \quad (a_i = \gamma_i m_i)$$

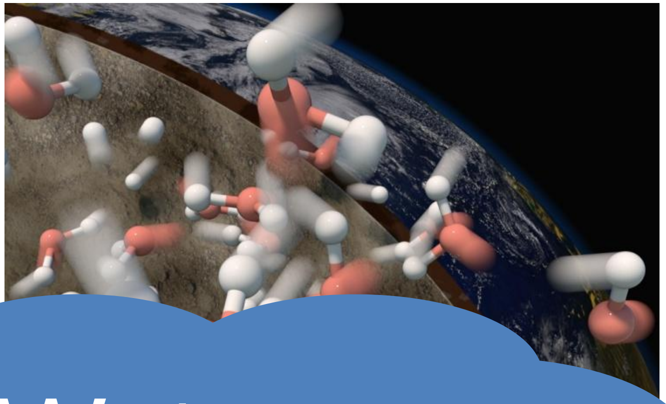
$MgCO_3$: An important mineral stable up to 80 GPa in the mantle; insoluble in water at ambient conditions



$MgCO_3$ (magnesite) becomes at least slightly soluble at the bottom of the upper mantle (T = 1000 K).

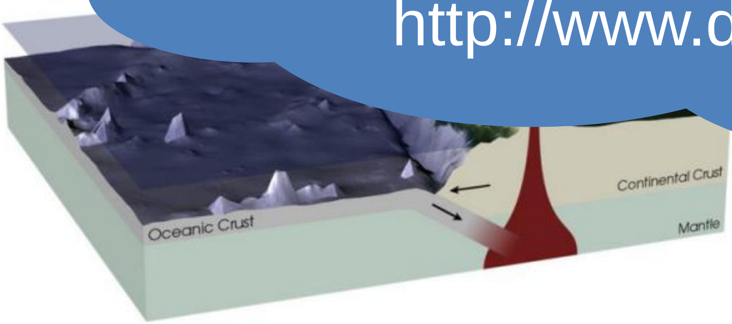
Summary and implications for the deep carbon transport

- In the Earth's mantle, the static dielectric constant of water can vary from < 10 to ~ 38
- The static dielectric constant monotonically depends on pressure, and decreases dramatically increasi



Deep Earth Water (DEW) Model

http://www.dewcommunity.org/

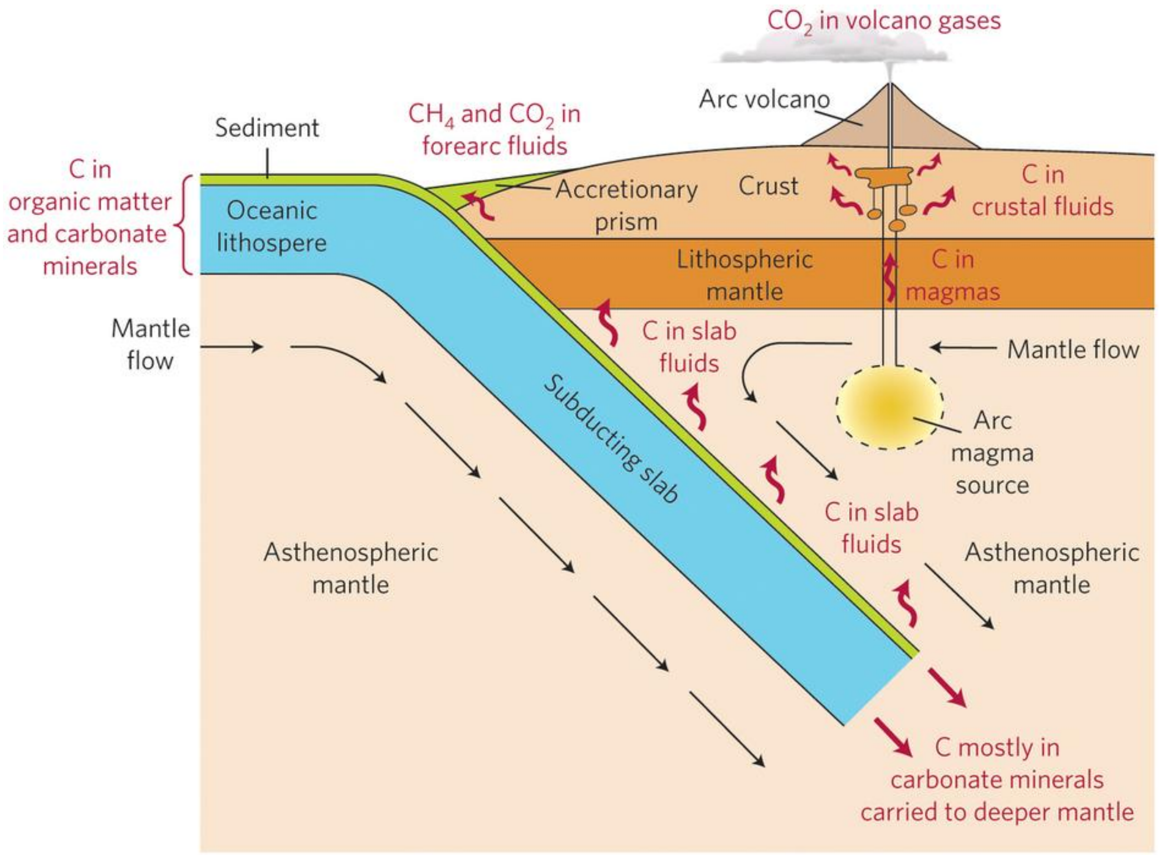


transport
oxidized carbon

- With the help of ab initio calculations on the dielectric constant of water, we can model the water-rock interactions under the Earth's mantle conditions

D. Pan, et al., PNAS 110, 6646 (2013)
C. E. Manning, PNAS 110, 6616 (2013)

DEEP CARBON OBSERVATORY



“a global research program to transform our understanding of carbon **in** Earth”

Many interesting questions:

- ❑ Formation of diamonds
- ❑ Abiogenic petroleum origin
- ❑ **Dissolved carbon in the deep *fluids***

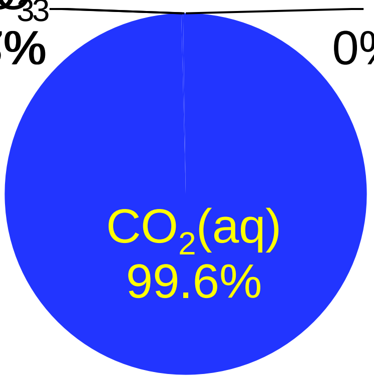
…

C. E. Manning, Nature Geosci. 7, 333 (2014)

Carbon in water: in what form?

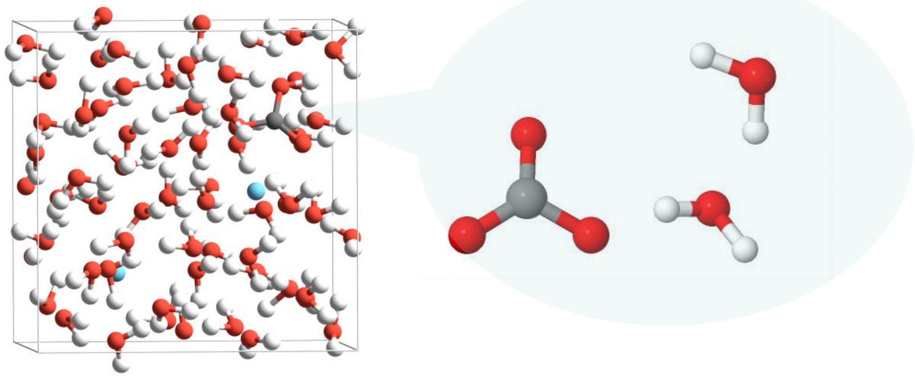
$$CO_{2,aq} + H_2O = HCO_3^- + H^+ \qquad HCO_3^- = CO_3^{2-} + H^+$$

~2.5 atm,
300 K



From *wikipedia.org*

Na_2CO_3 in water at ~ 10 GPa, 1000 K,
Time: 0.24 ps



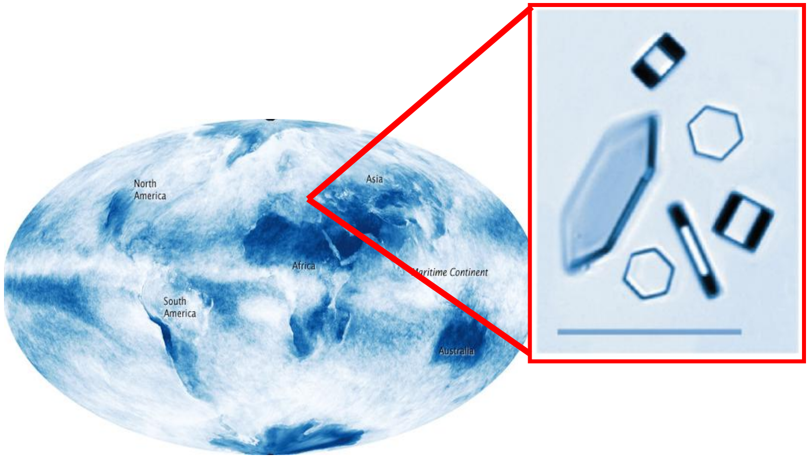
What is the form of dissolved carbon present at HP-HT, molecular CO_2(aq), bicarbonate (HCO_3^-), carbonate (CO_3^{2-}) ions or other species?

Ding Pan, and Giulia Galli Science Advances 2, e1601278 (2016)

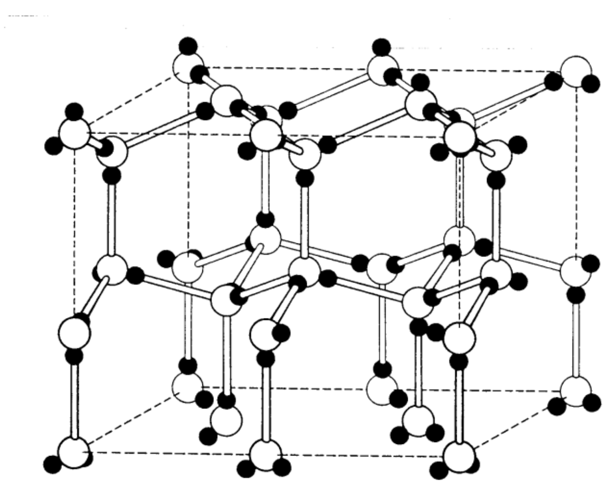
Ice surface

Motivations

- ✓ More than 50% of Earth surface is covered by clouds, which consist of ice particles
- ✓ Many critical atmospheric reactions, e.g., the ozone depletion, happen on ice surfaces.

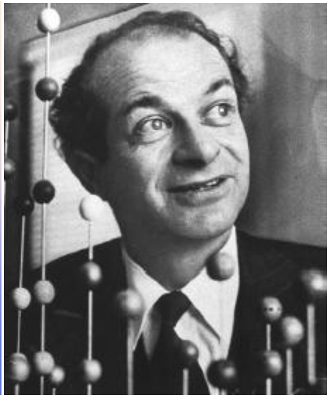


Strictly speaking, the crystalline ice is not a crystal



Ice Ih

In the bulk of ice Ih, proton distribution is disordered, obeying the ice rule



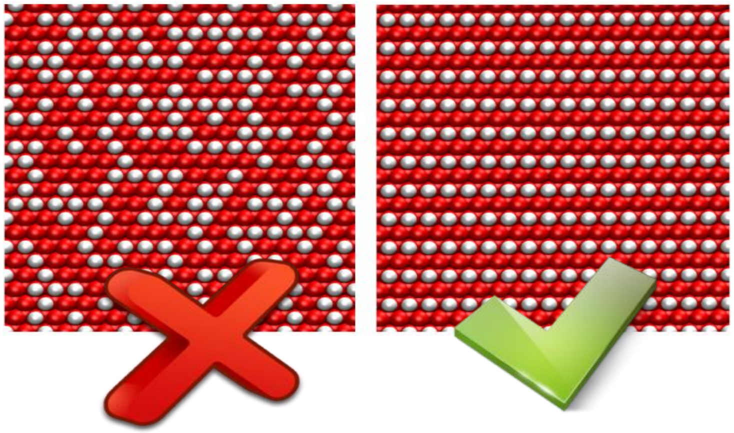
L. Pauling discovered in 1935

L. Pauling, J. Am. Chem. Soc. 57, 2680 (1935)

Ice surface is proton ordered

By density-functional theory (DFT) calculations, we found

1. Ice surface is proton ordered: **D. Pan** et al. Phys. Rev. Lett. 101, 155703 (2008)



2. **Large variation of vacancy formation energies in the surface of crystalline ice**

nature materials

M. Watkins[1,2,3], D. Pan[4], E. G. Wang[5], A. Michaelides[1,2,3], J. VandeVondele[6] and B. Slater[1,3]★

3. **Role of proton ordering in adsorption preference of polar molecule on ice surface**

PNAS

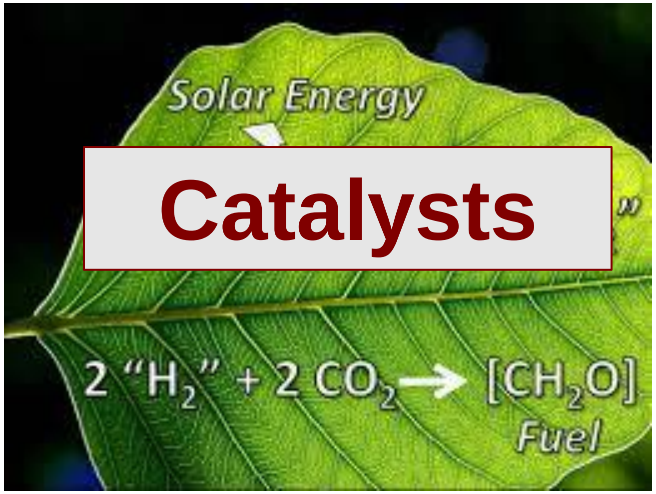
Zhaoru Sun[a], Ding Pan[b], Limei Xu[a,1], and Enge Wang[a,1]

[a]International Center for Quantum Materials, Peking University, No. 5 Yiheyuan Road, Haidian District, Beijing 100871, People's Republic of China; and [b]Department of Chemistry, University of California, Davis, CA 95616

Outline

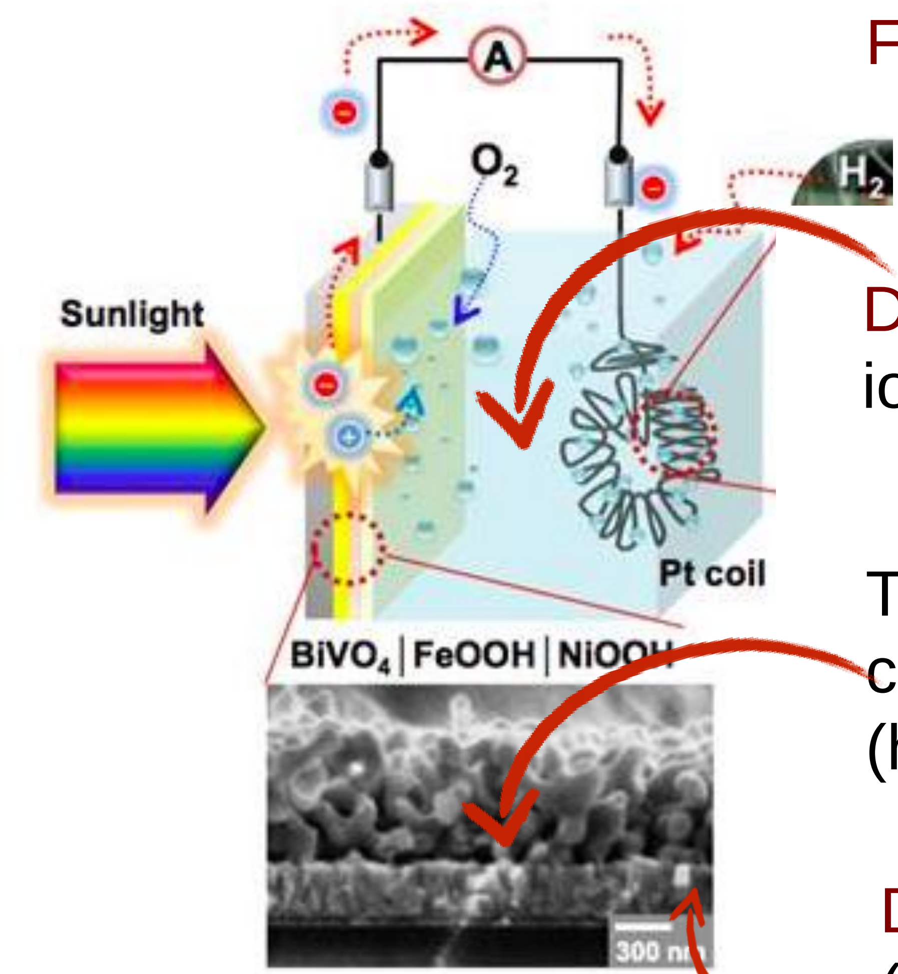
- Water science
- Deep carbon cycle
- Clean energy

Convert the energy we receive from the sun



The availability (and/or creation) of earth- abundant materials and the control of specific chemical processes are key to **scientific & technological advances** in solar energy conversion

Artificial photosynthesis



Finite T processes

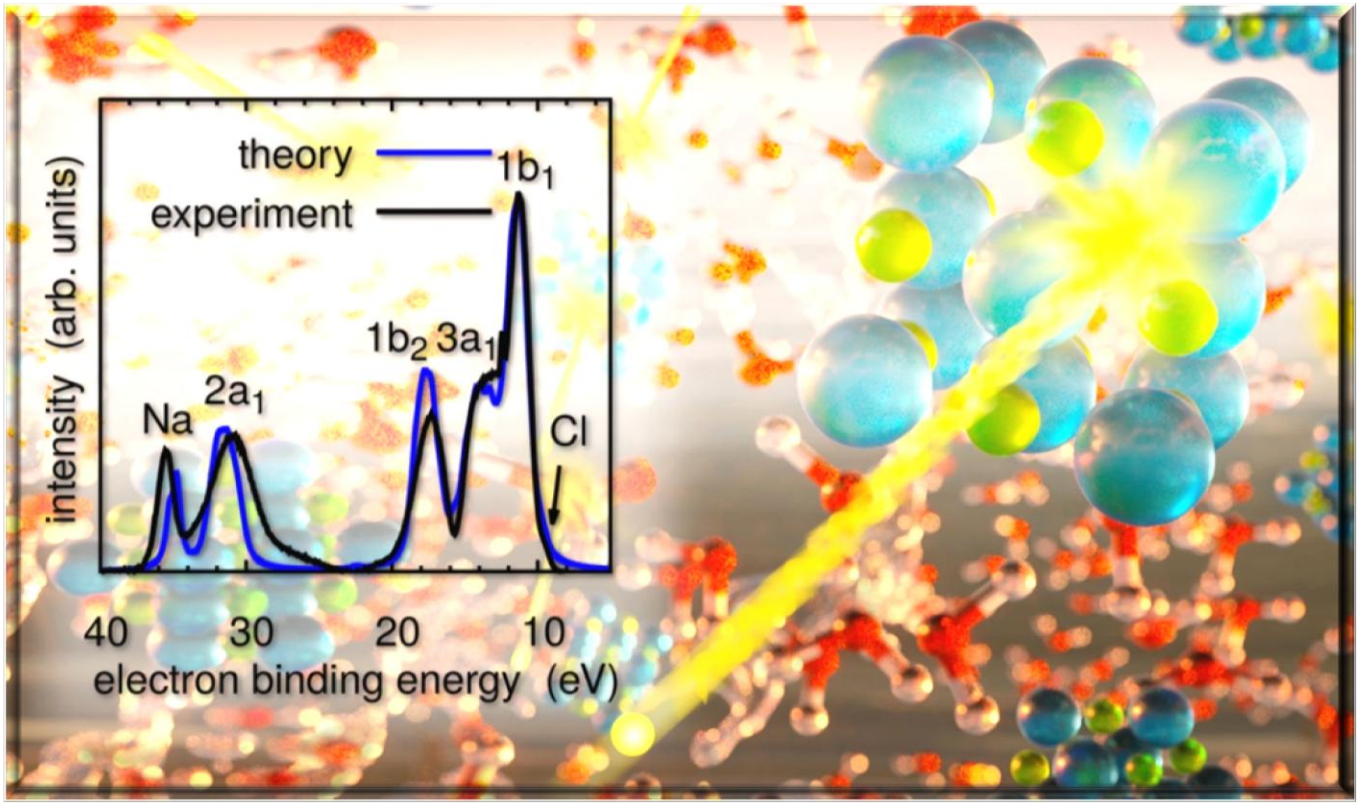
Defective liquid (solvated ions in water)

Three-way interface: catalyst/photo-absorber/water (hard/soft-matter interfaces)

Defective photo-absorber (oxide)

K.S.Choi's group, UW Madison, Science 2014; T.W.Kim, Y. Ping, GG & KS Choi Nat. Comm. 2015

Photoelectron spectra of salts in water



A.Gaiduk, M.Govoni, J.K. Skone, R.Siedel, B.Winter and and GG JACS Comm. 2016

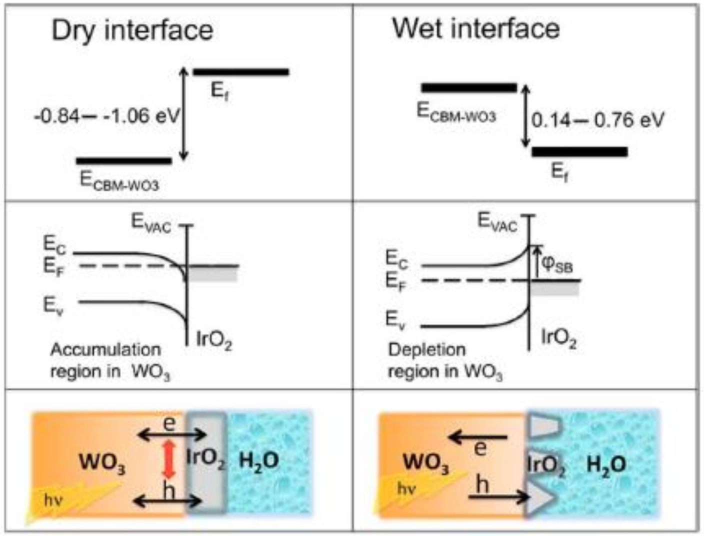
First principles MD w/hybrid fcntls GW calculations of electronic energies and intensities; absolute energy positions

Photoelectrode/catalyst interface

Ohmic contact or Schottky barrier?

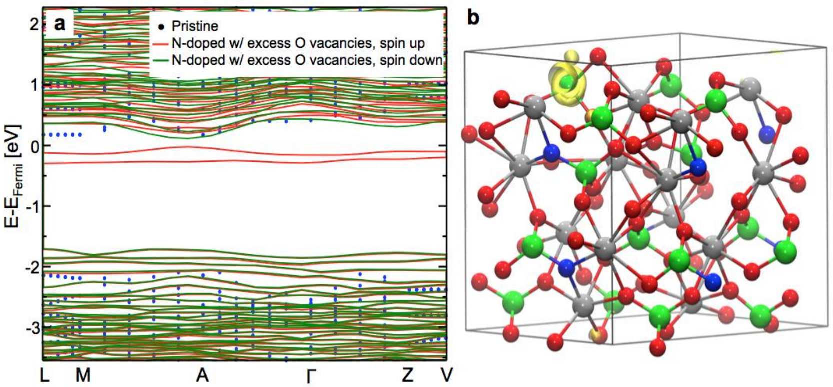
It depends on whether the interface is dry or wet, which in turns depends on the catalyst morphology

- Determined WO_3/IrO_2 model and compared surface and interface stability with experiments
- Determined level alignment to determine whether charges will recombine or cross the interface

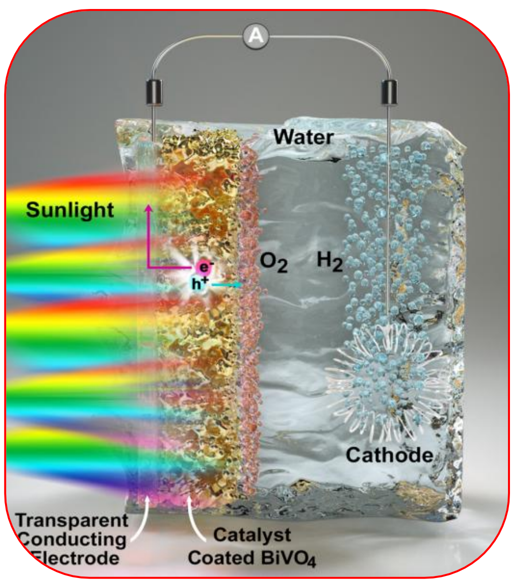


Y.Ping, W.A.Goddard III and GG JACS Comm 2015

Defects play a leading role: $BiVO_4$



$BiVO_4$: Charge transport occurs via polarons. Control of defects is key: increasing concentration of O vacancies increases mobilities for 2 reasons: # of charge carriers increase and polaron hopping activation energy decreases T.W. Kim, Y. Ping, GG & KS Choi Nat. Comm. 2015

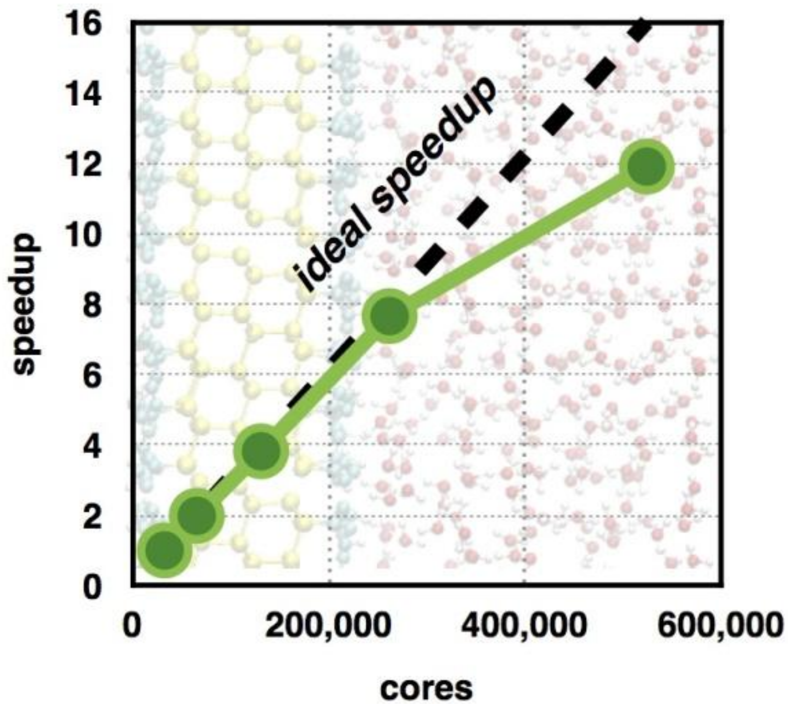


$$\frac{1}{\varepsilon_p} = \frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon_0}, \quad W_H = \frac{e^2}{4\varepsilon_p}\left(\frac{1}{r_p} - \frac{1}{R}\right) \quad \mu \propto \frac{1}{T} \exp\left(\frac{-W_H}{kT}\right)$$

Material optimization: Bismuth vanadate photo-anodes simultaneous improvement of band gap and charge transport

High-performance computing

Our computer code can make full use of huge supercomputers



Parallel performance of the WEST code (http://west-code.org), which uses one of the most accurate methods to calculate the electronic excited state properties. Quantifying how electrons are excited is of great use in the sustainable energy development, e.g., **next-generation solar energy conversion**. The WEST code can use up to 0.5 million CPU cores.

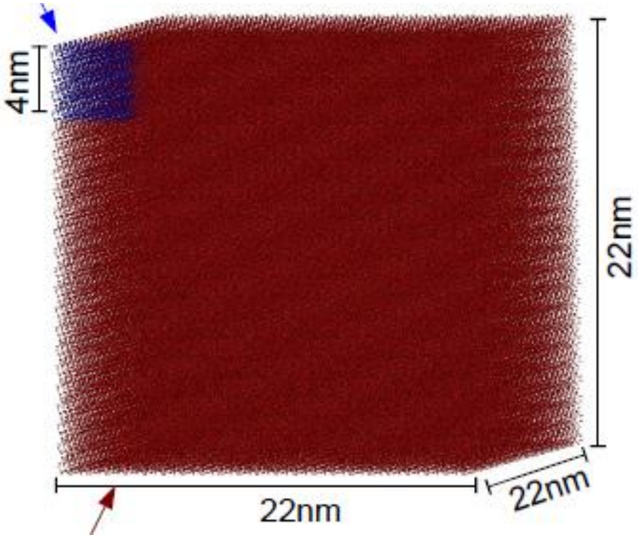
Speedup quantifies how well the multiple CPU cores accelerate calculations

M. Govoni and G. Galli J. Chem. Theory Comput. 11, 2680-2696 (2015).

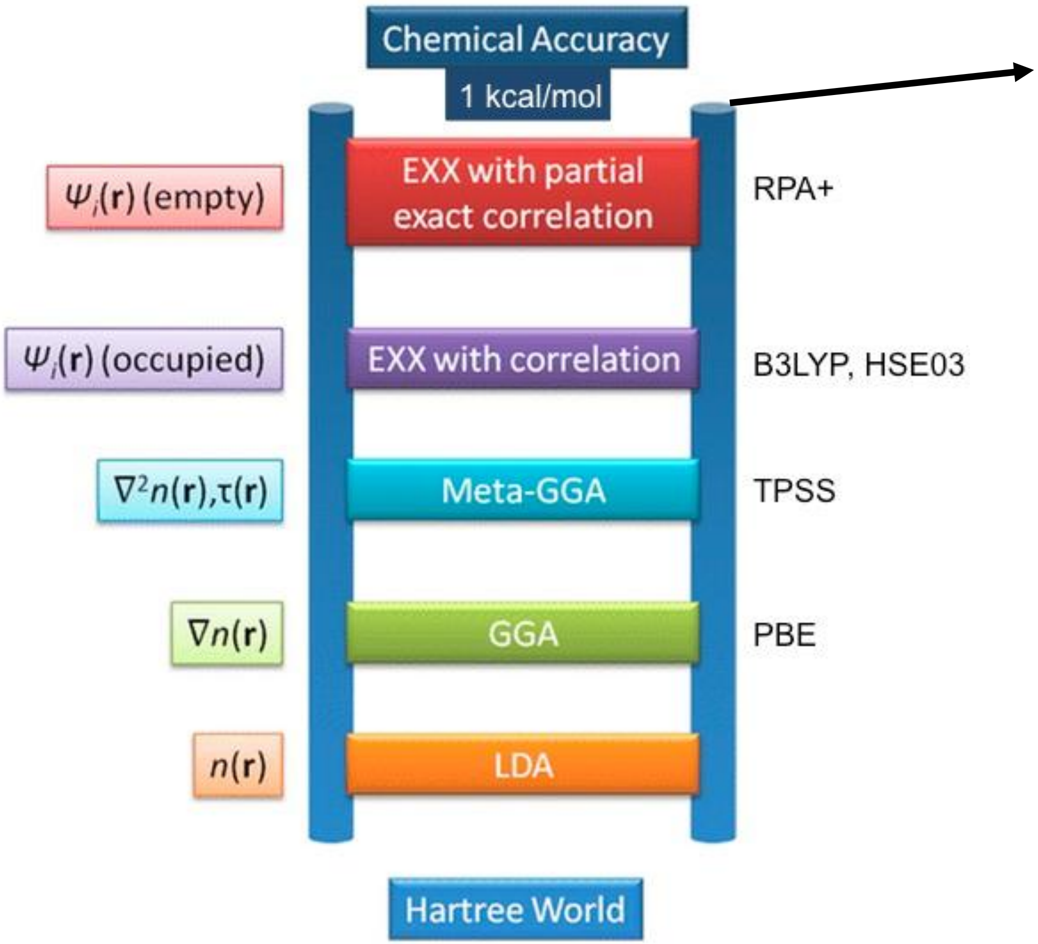
Outline

- Water science
- Deep carbon cycle
- Clean energy
- Current developments

Large scale



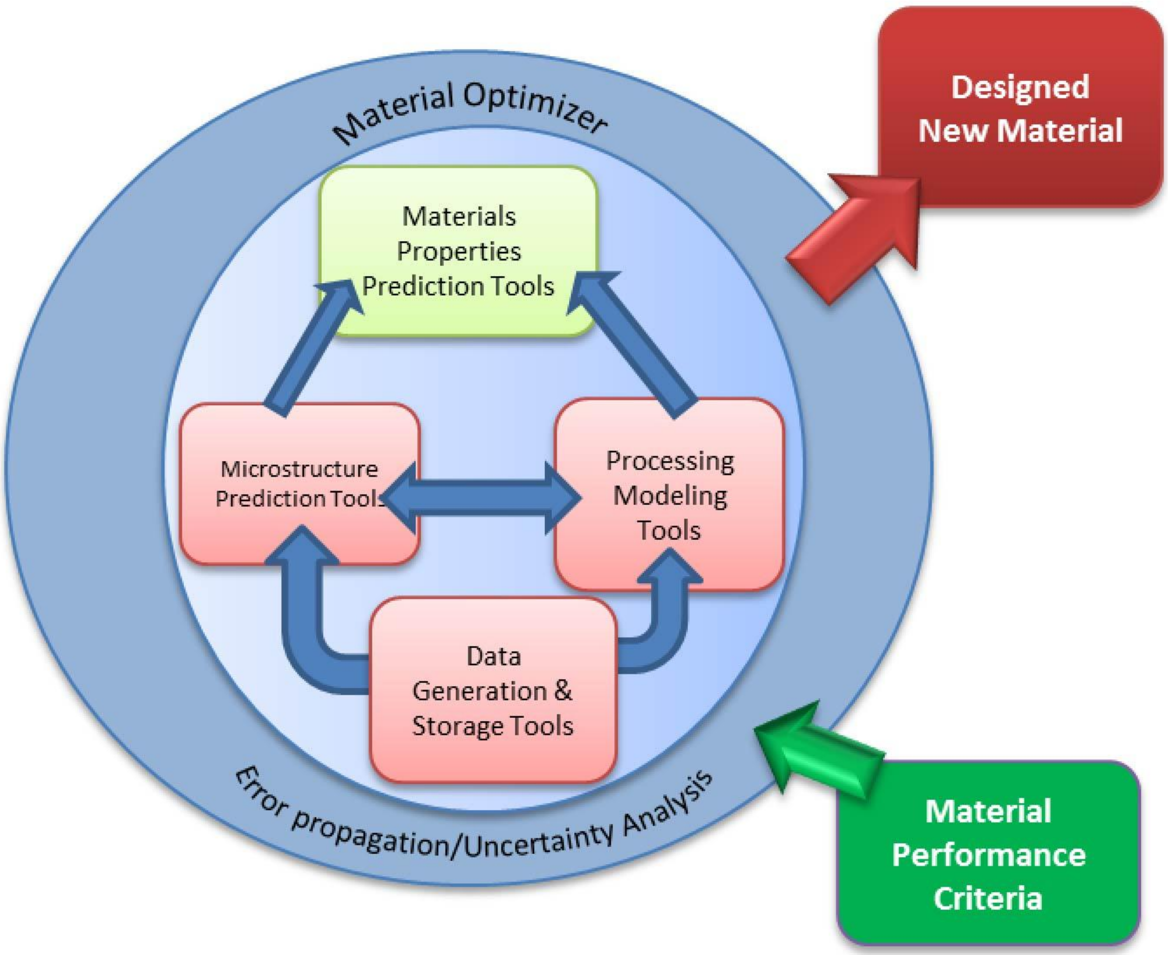
High accuracy



Van der Waals

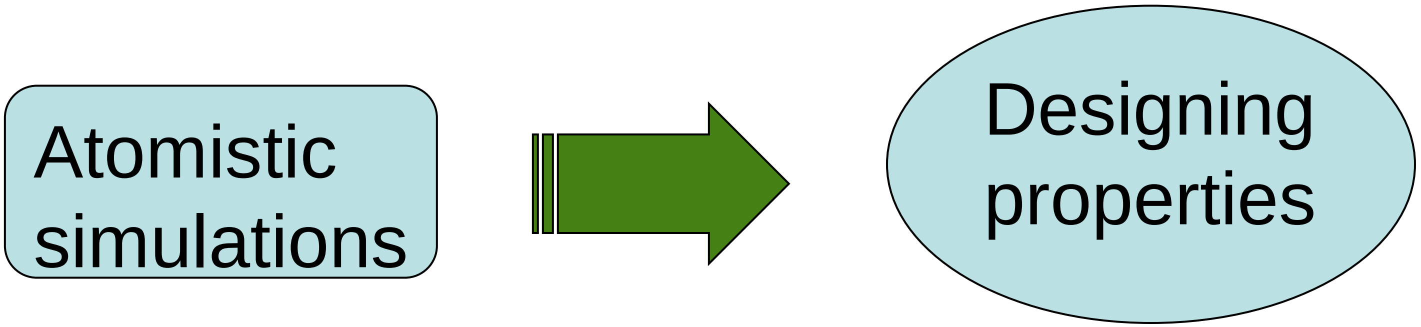
Exchange-correlation functional

Materials genome and big data



Computation: theory or experiment?

- ✓There are still many things experiments can do better (e.g faster and more accurately) than computations
- ✓Modeling rarely is "Simulation of Reality". Rather it is the accurate computation of quantities that are essential to prove/disprove a theory, or guarantee a property



Gerbrand Ceder, and Nicola Marzari. 3.320 Atomistic Computer Modeling of Materials (SMA 5107). Spring 2005. Massachusetts Institute of Technology: MIT openCourseWare, https://ocw.mit.edu

Summary

- Water science
- Deep carbon cycle
- Clean energy
- Current developments

Acknowledgements

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