Computational materials science and sustainability

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“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)
Contents

Classical

Quantum: DFT, HF...

Materials Science

Quantum + Classical
“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:

\[ H(t) \psi(t) = i\hbar \frac{d}{dt} \psi(t) \]

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, Hohenberg and Kohn showed that 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!
The most cited papers of all time

Nature 514, 550–553 (30 October 2014)
Materials: solids, liquids, nanostructures and combinations thereof

- Solar cells
- Clean Water
- Photo-electrochemical cells
- Thermoelectric generators
- Qubits
- Carbon in the Earth
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.

Theoretical challenge of modeling aqueous solutions: static dielectric constant, $\varepsilon_0$

- The static dielectric constant, $\varepsilon_0$, determines the solvation properties of water:
  - At ambient conditions, $\varepsilon_0$ of water is unusually large: 78
  - At the vapor-liquid supercritical point, $\varepsilon_0$ is $\sim 6$

Figure courtesy of Nicholas Brawand Fernández et al., J. Phys. Chem. Ref. Data. 26, 1125 (1997)
The dielectric constant, $\varepsilon_0$, monotonically increases with pressure at fixed $T$.

DFT-PBE predicts larger values of $\varepsilon_0$ than the water model SPC/E, but the difference between DFT-PBE and SPC/E is smaller at 2000 K than at 1000 K.
Water-rock interaction: Solubility of carbonates in the Earth’s upper mantle

Equilibrium constant

\[ \Delta G_0^\circ (\varepsilon_0) = -RT \ln K \]

The solubility product constant, \( K_{sp} \), activities of ions, \( a_i \), activity coefficients, \( \gamma_i \) and concentrations \( m_i \):

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

\( \text{MgCO}_3 \): An important mineral stable up to 80 GPa in the mantle; insoluble in water at ambient conditions

\text{MgCO}_3 \) (magnesite) becomes at least slightly soluble at the bottom of the upper mantle \((T = 1000 \text{ K})\).
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 with increasing temperature.

Water in the mantle can help transport significant quantities of 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 Earth Water (DEW) Model
http://www.dewcommunity.org/
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?

$\text{CO}_2\text{(aq)} + \text{H}_2\text{O} = \text{HCO}_3^- + \text{H}^+$

$\text{HCO}_3^- = \text{CO}_3^{2-} + \text{H}^+$

What is the form of dissolved carbon present at HP-HT, molecular \(\text{CO}_2\text{(aq)}\), bicarbonate \((\text{HCO}_3^-)\), carbonate \((\text{CO}_3^{2-})\) ions or other species?

$\text{Na}_2\text{CO}_3$ in water at $\sim 10$ GPa, 1000 K, Time: 0.24 ps

$\sim 2.5$ atm, 300 K

From wikipedia.org

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.

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

L. Pauling discovered in 1935:

By density-functional theory (DFT) calculations, we found that ice surface is proton ordered by a study conducted by D. Pan et al. in Phys. Rev. Lett. 101, 155703 (2008). This conclusion is supported by computational models that demonstrate its validity. Additionally, there is a large variation of vacancy formation energies in the surface of crystalline ice, as reported by Watkins et al. in Nature Materials. The role of proton ordering in adsorption preference of polar molecules on ice surface is also explored, as detailed in a study by Sun et al. in PNAS.
Outline

- Water science
- Deep carbon cycle
- Clean energy
Convert the energy we receive from the sun

New materials

Catalysts

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

Defective photo-absorber (oxide)

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

Defective liquid (solvated ions in water)

Finite T processes
Photoelectron spectra of salts in water


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

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

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.

Summary

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

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