1.021, 3.021, 10.333, 22.00 Introduction to Modeling and Simulation
Spring 2012

Part II – Quantum Mechanical Methods

Brief Introduction to Part II

Lecture 0

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Content overview

I. Particle and continuum methods

1. Atoms, molecules, chemistry
2. Continuum modeling approaches and solution approaches
3. Statistical mechanics
4. Molecular dynamics, Monte Carlo
5. Visualization and data analysis
6. Mechanical properties – application: how things fail (and how to prevent it)
7. Multi-scale modeling paradigm
8. Biological systems (simulation in biophysics) – how proteins work and how to model them

II. Quantum mechanical methods

1. It's A Quantum World: The Theory of Quantum Mechanics
2. Quantum Mechanics: Practice Makes Perfect
3. The Many-Body Problem: From Many-Body to Single-Particle
4. Quantum modeling of materials
5. From Atoms to Solids
6. Basic properties of materials
7. Advanced properties of materials
8. What else can we do?

Computer Hardware Historical Milestones

1946: Eniac
Op/s: 5000
Sq. ft: 3000

1952: IBM SSEC
Op/s: 2000
Sq. ft: 1000

1951: MIT Whirlwind
Op/s: 200,000
Sq. ft: 3100

1964: CDC 6600
Op/s: 3,000,000
Sq. ft: 3100

1968: Apollo Guide
Apollo 7&11 missions

1971: Kenbak-1
First personal computer
256 Bytes of memory

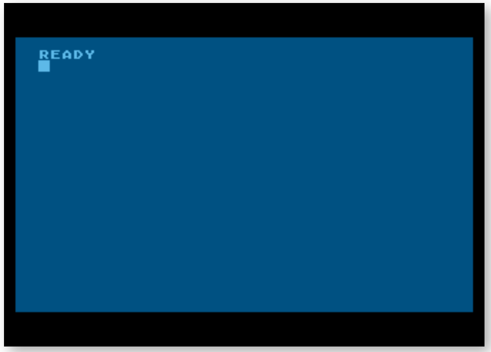
1974: Xerox Alto
Built-in mouse
Connect to network

JCG Personal Computer History

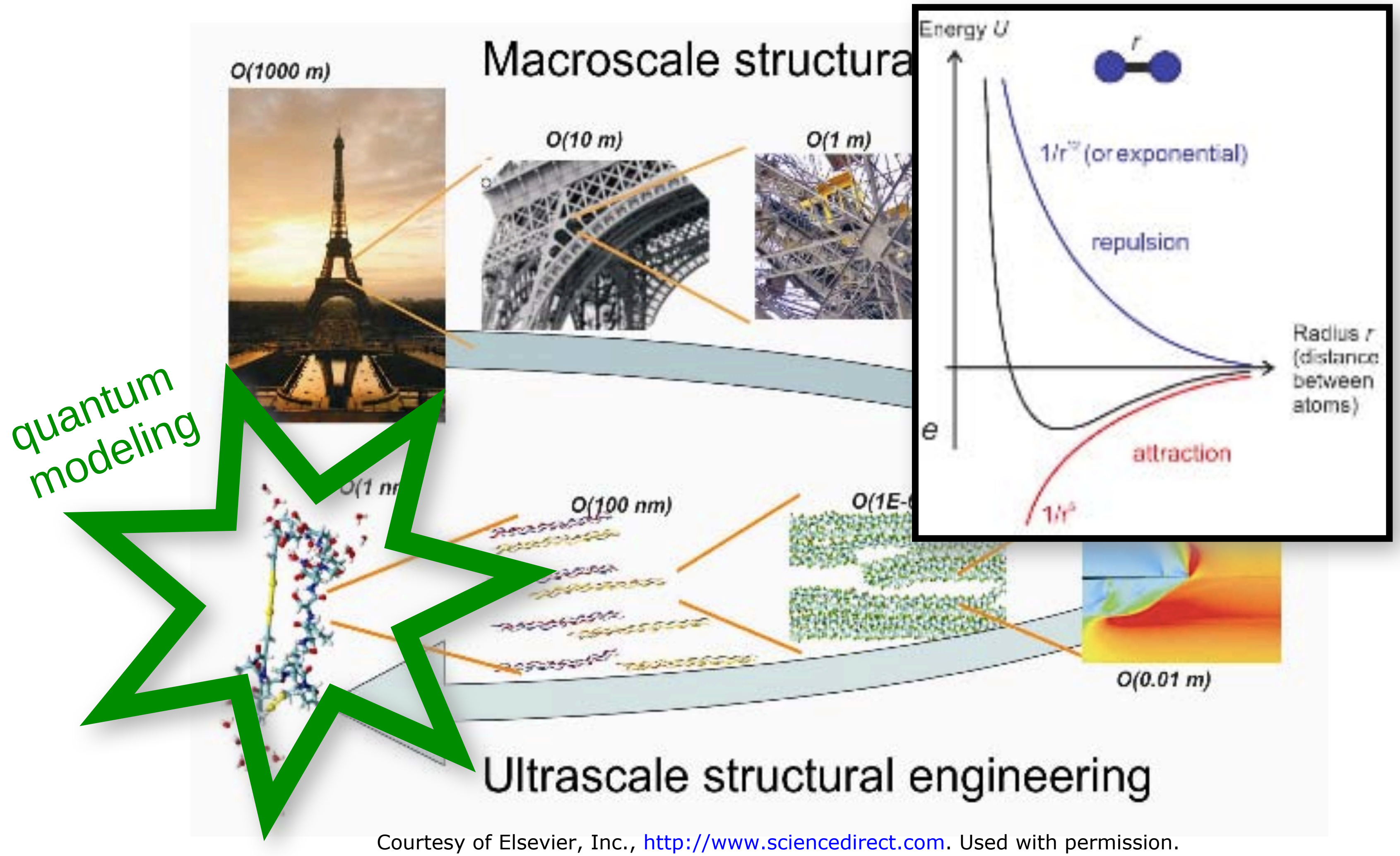
Tandy TRS-80 (a.k.a. “Trash-80”)

Atari 400 (note the stylish keyboard)

Start-up screens



Multi-scale modeling



Quantum mechanists

Werner Heisenberg, Max Planck,
Louis de Broglie, Albert Einstein,
Niels Bohr, Erwin Schrödinger,
Max Born, John von Neumann,
Paul Dirac, Wolfgang Pauli
(1900 - 1930)

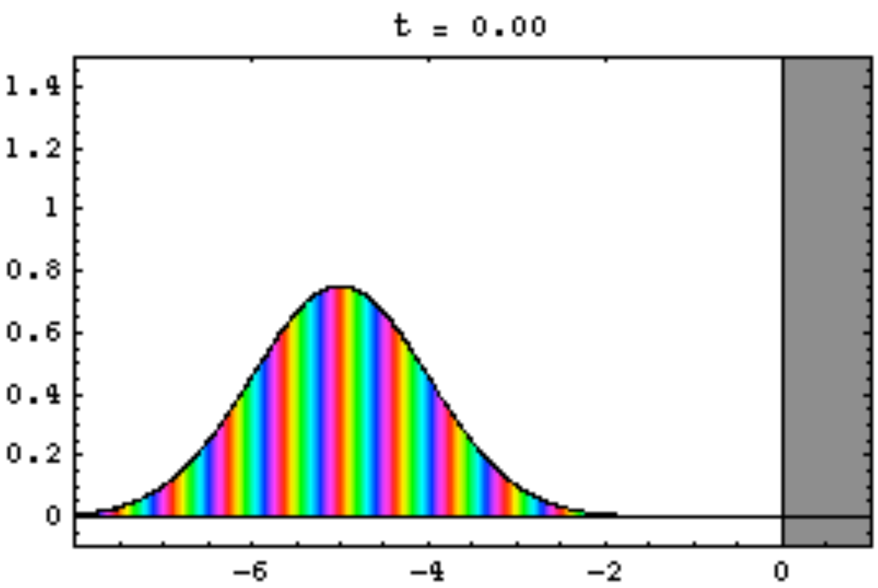
Why quantum mechanics?

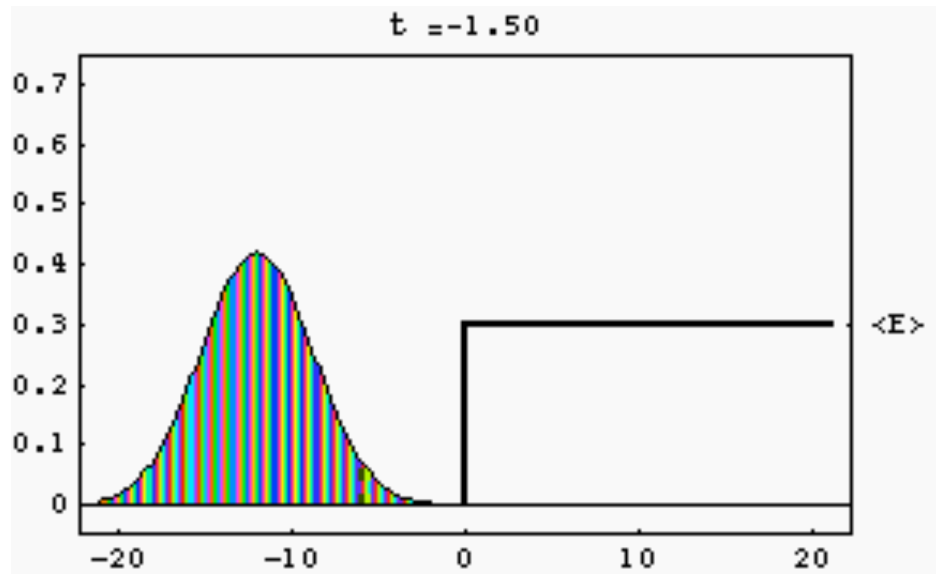
Classical mechanics

Newton's laws (1687) $$\vec{F} = \frac{d(m\vec{v})}{dt}$$

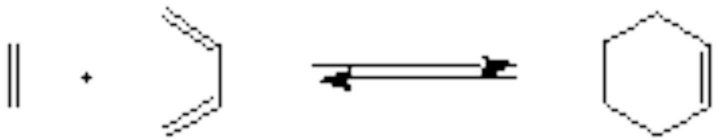
Problems?

Movies of a Quantum Ball Thrown into a Wall



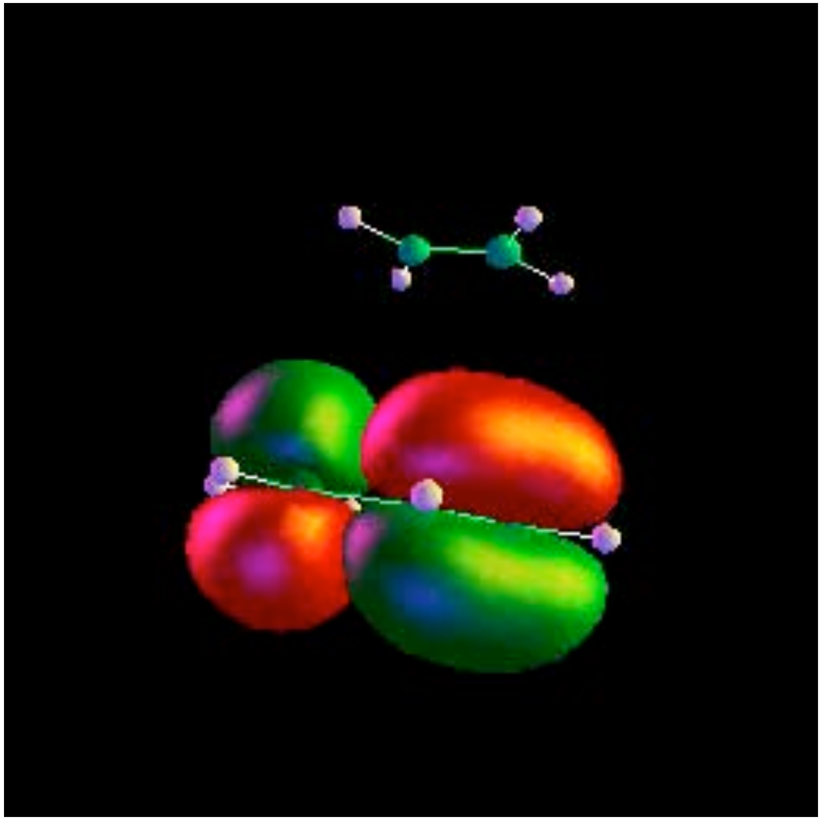


Example: Diels-Alder Reaction: 1,3-butadiene + ethylene → cyclohexene



Courtesy ChemWiki.

Predicting what these electrons do is what gives us those much-needed energy curves – quantum mechanics is key!



See Lecture 1 video for animation.

A Little Bit of Schrödinger

Written out explicitly, the Schrödinger equation looks like this:

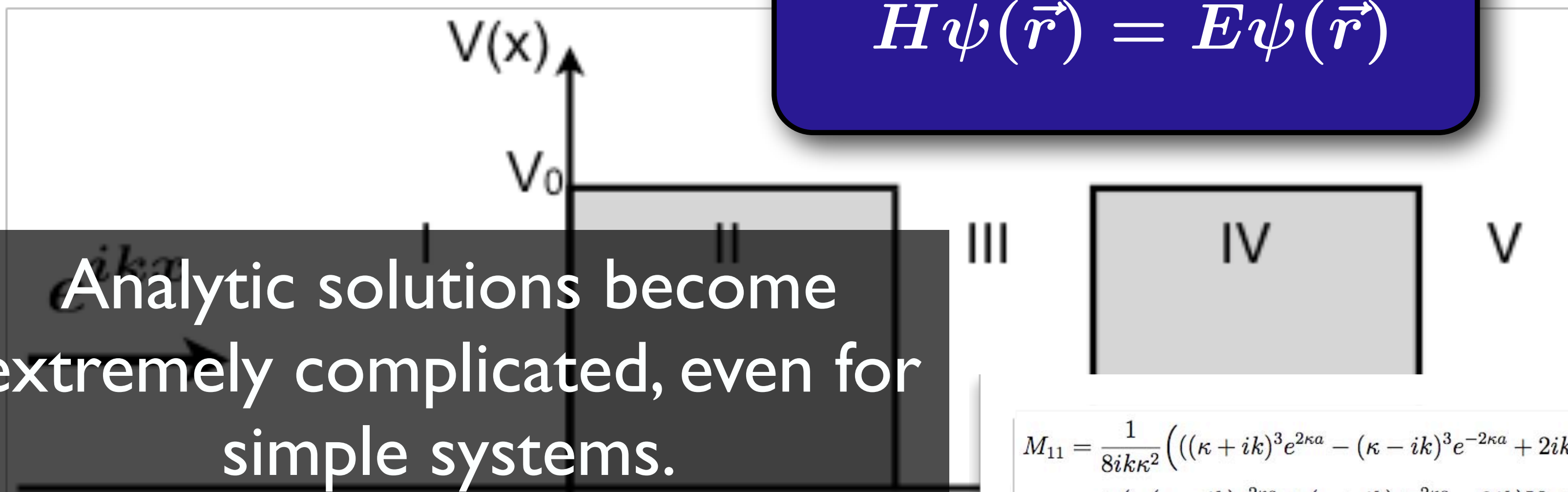
$$\left\{-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)+V\right\}\Psi(\mathbf{r},t)=i\hbar\frac{\partial\Psi(\mathbf{r},t)}{\partial t}$$

- $\Psi(\mathbf{r},t)$ is the wavefunction for the system of particles, which characterizes the particle's motion. One can derive all properties of the system of particles from its wavefunction.

- We no longer ask "Where is/are the particle(s)?", but instead ask "What is the probability distribution governing the positions?"

Solving the Schrodinger Equation

$$H\psi(\vec{r}) = E\psi(\vec{r})$$



Analytic solutions become extremely complicated, even for simple systems.

$$\begin{aligned}
x = 0: &\quad & 1 + R &= A + B \\
& & ik - ikR &= \kappa A - \kappa B \\
x = a: & & Ae^{\kappa a} + Be^{-\kappa a} &= Ce^{ika} + De^{-ika} \\
& & \kappa Ae^{\kappa a} - \kappa Be^{-\kappa a} &= ikCe^{ika} - ikDe^{-ika} \\
x = a + b: & & Ce^{ik(a+b)} + De^{-ik(a+b)} &= Fe^{\kappa(a+b)} + Ge^{-\kappa(a+b)} \\
& & ikCe^{ik(a+b)} - ikDe^{-ik(a+b)} &= \kappa Fe^{\kappa(a+b)} - \kappa e^{-\kappa(a+b)} \\
x = 2a + b: & & Fe^{\kappa(2a+b)} + Ge^{-\kappa(2a+b)} &= Te^{ik(2a+b)} \\
& & \kappa Fe^{\kappa(2a+b)} - \kappa Ge^{-\kappa(2a+b)} &= ikTe^{ik(2a+b)}.
\end{aligned}$$

$$M_{11} = \frac{1}{8ik\kappa^2}\Big(\big((\kappa+ik)^3e^{2\kappa a} - (\kappa-ik)^3e^{-2\kappa a} + 2ikV_1\big)e^{ikb} + \big(-(\kappa-ik)e^{2\kappa a} + (\kappa+ik)e^{-2\kappa a} - 2ik\big)V_1e^{-ikb}\Big)$$

$$M_{12} = \frac{1}{8ik\kappa^2}\Big(\big((\kappa+ik)e^{2\kappa a} - (\kappa-ik)e^{-2\kappa a} - 2ik\big)V_1e^{ikb} + \big(-(\kappa-ik)^3e^{2\kappa a} + (\kappa+ik)^3e^{-2\kappa a} + 2ikV_1\big)e^{-ikb}\Big)$$

$$M_{21} = \frac{1}{8ik\kappa}\Big(\big((\kappa+ik)^3e^{2\kappa a} + (\kappa-ik)^3e^{-2\kappa a} - 2\kappa V_1\big)e^{ikb} - \big((\kappa-ik)e^{2\kappa a} + (\kappa+ik)e^{-2\kappa a} - 2\kappa\big)V_1e^{-ikb}\Big)$$

$$M_{22} = \frac{1}{8ik\kappa}\Big(\big((\kappa+ik)e^{2\kappa a} + (\kappa-ik)e^{-2\kappa a} - 2\kappa\big)V_1e^{ikb} + \big(-(\kappa-ik)^3e^{2\kappa a} - (\kappa+ik)^3e^{-2\kappa a} + 2\kappa V_1\big)e^{-ikb}\Big)$$

Year 1929…

The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble.

P.A.M. Dirac, Proc. Roy. Soc. 123, 714 (1929)

…and 1963

If there is no complete agreement […] between the results of one's work and the experiment, one should not allow oneself to be too discouraged […]

P.A.M. Dirac, Scientific American, May 1963

Density functional theory

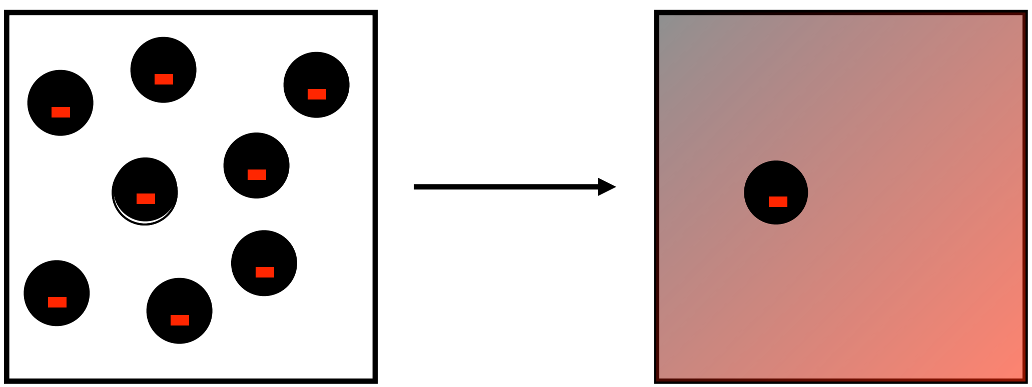
Energy ⟷ Electron density

$$E_0 = E[n_0]$$

Hohenberg & Kohn, 1964

Interacting ⟶ Non-interacting

Image of Walter Kohn receiving Nobel prize removed due to copyright restrictions.

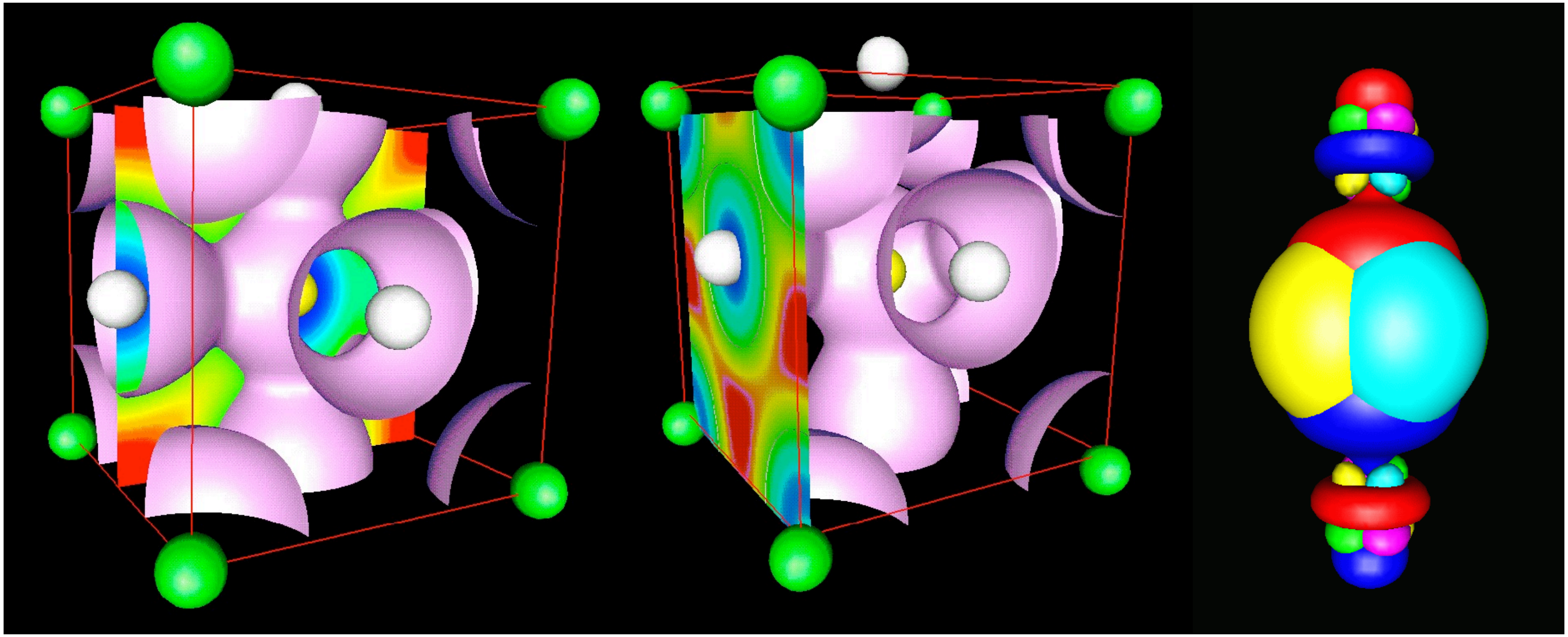


Kohn & Sham, 1965

Walter Kohn (left), receiving the Nobel prize in chemistry in 1998.

Why do we need quantum mechanics ?

Example: Bonding and Structure

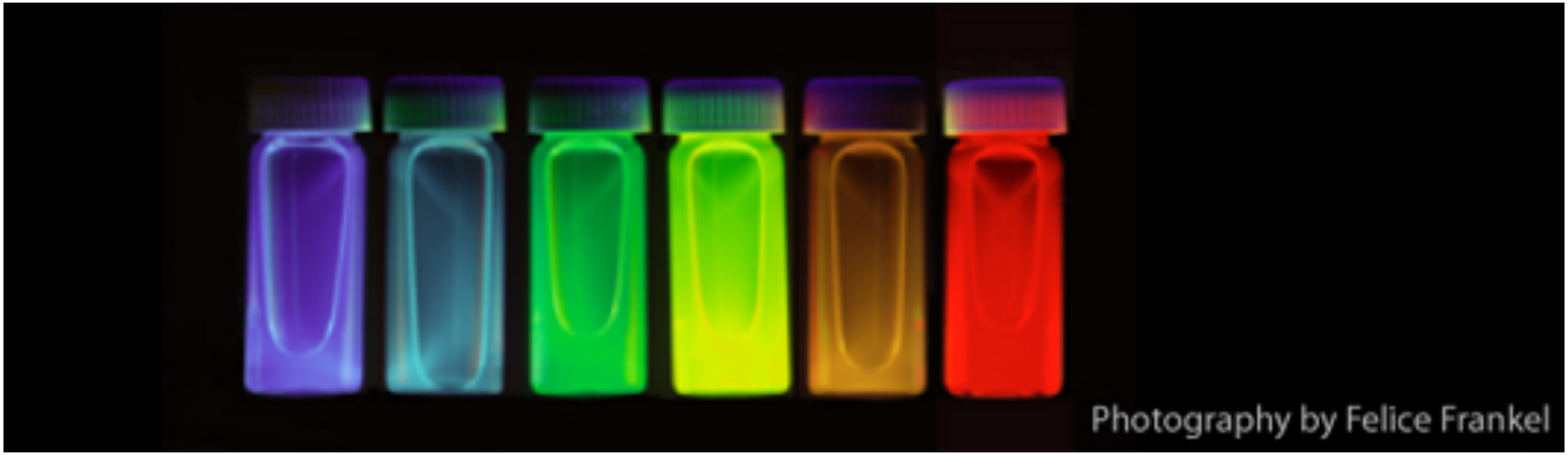


Figures by Nicola Marzari.

Photo courtesy of Nicola Marzari and David Vanderbilt/Rutgers University.

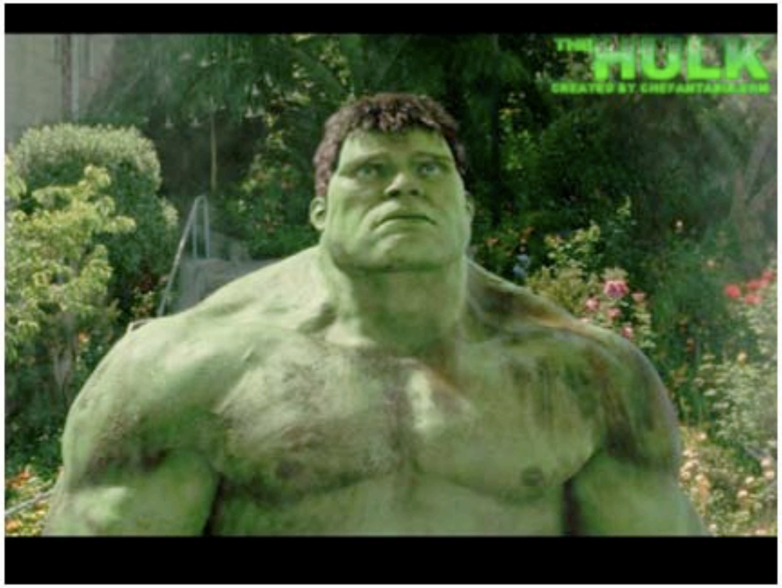
Paraelectric (cubic) and ferroelectric (tetragonal) phases of $PbTiO_3$

Example: Electronic, optical, magnetic properties



Example: Nanotechnology

Nanotechnology Scientist in *Spiderman*



Nanotechnology created *The Hulk*

How small is nano?

10^0 m = 1m

10^{-9} = 1 nanometer

10^9 m = 1 million km

10^0 m = 1m

Images from Eames Power of Ten film removed due to copyright restrictions. See http://www.powersof10.com/.

Nanotechnology Definition

"How Super-Cows and Nanotechnology will Make Ice Cream Healthy"

telegraph.co.uk, August 21, 2005

In a field somewhere in County Down, Northern Ireland, is a herd of 40 super-cows that could take all the poisonous guilt out of bingeing on ice cream. Unilever, the manufacturer of Persil and PG Tips, is sponsoring a secret research project by a leading British agricultural science institution into how to reduce the levels of saturated fat in cow's milk.

It is also experimenting with nanotechnology, or the science of invisibly tiny things. Unilever believes that by halving the size of particles that make up the emulsion - or fatty oil - that it uses to make ice cream, it could use 90 per cent less of the emulsion.

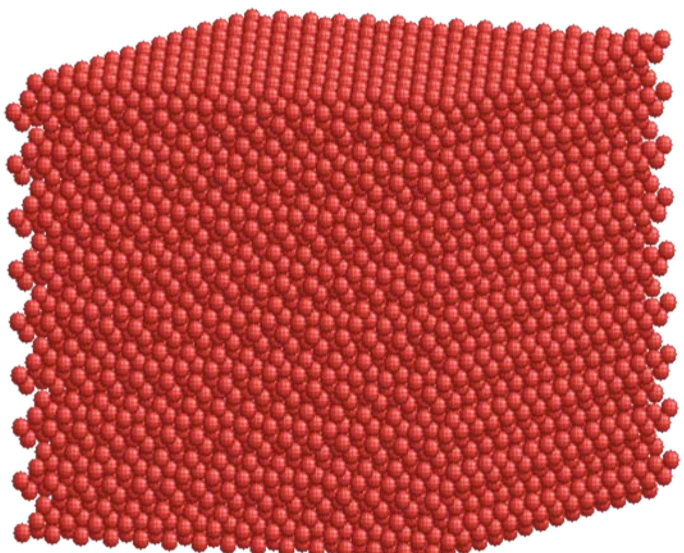
New Optical Properties

Quantum Dots

optically boring

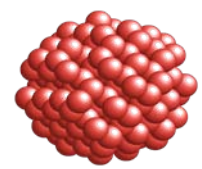
Courtesy of Felice Frankel. Used with permission.

optically exciting



+

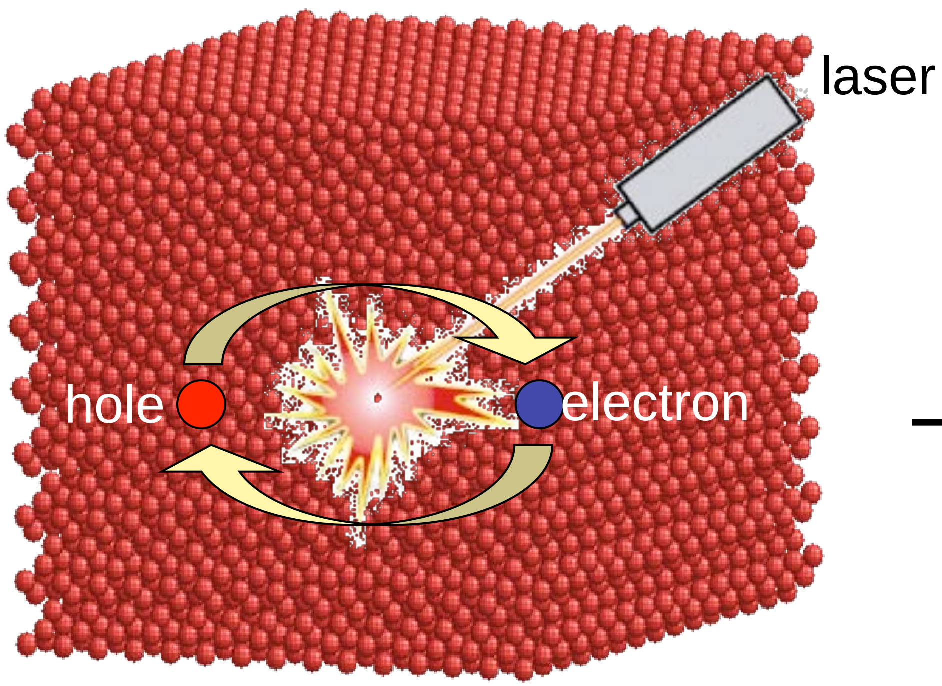
nano scooper



quantum dot

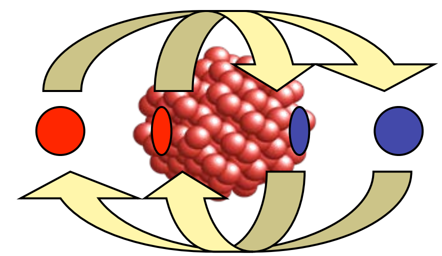
bulk semiconductor

Quantum Confinement



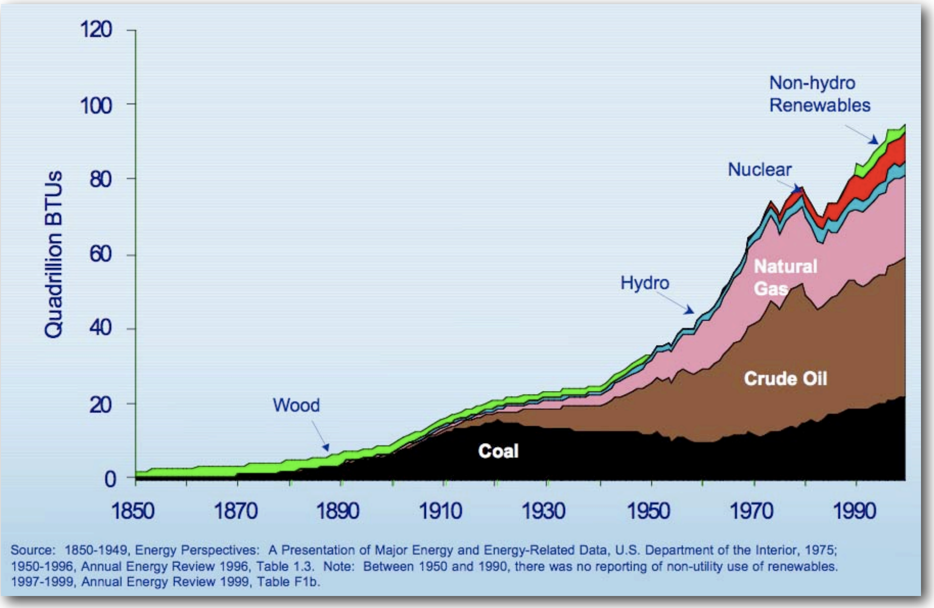
bulk semiconductor

quantum confinement

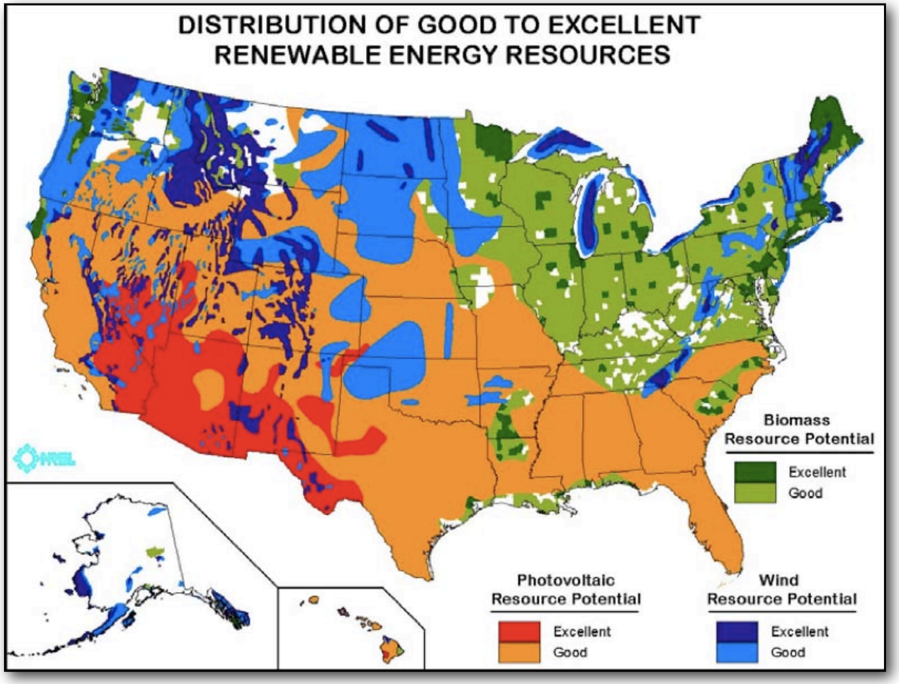


quantum dot

Physical confinement of excited state leads to unique **quantum effect**: light emitted depends on size.

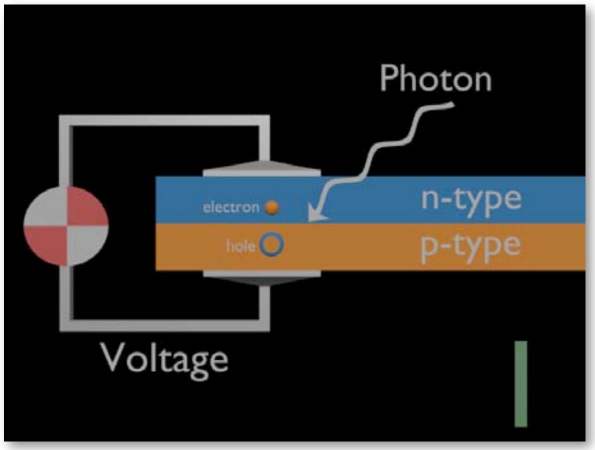


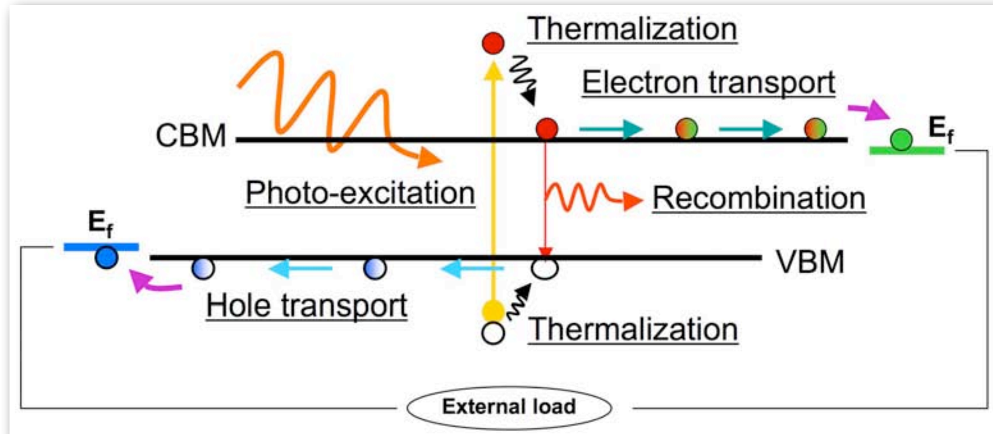
In order to keep CO_2 emissions in check, we will need to consume half of our electricity through renewable sources by the year 2050.



Need major improvements in efficiency and cost in order to take advantage of these resources.

Example: make solar cells cheaper and more efficient



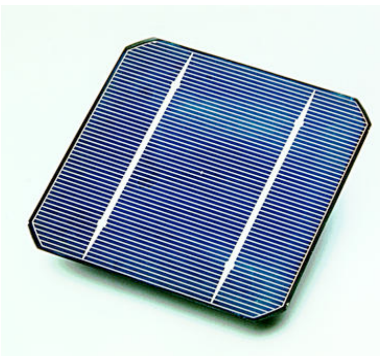


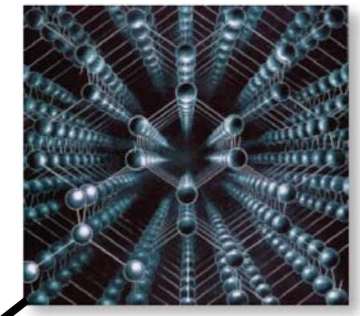
Understand, predict, and tailor these key fundamental processes.

Four Basic Steps:

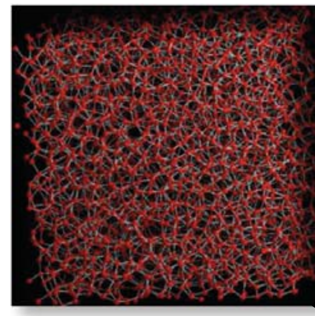
1) Convert a photon into an electron and a hole
2) Electron and hole "thermalize"
3) The electron-hole pair diffuses
4) Electron and hole are separated and taken out

Amorphous vs. Crystalline Silicon Solar Cells





crystalline



amorphous

Crystalline

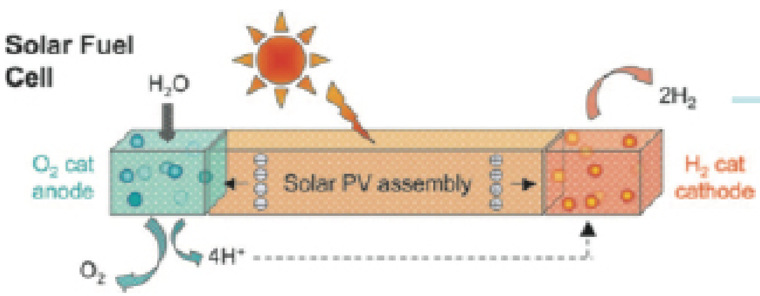
- Gap: 1.12 eV
- Lower absorption coefficient, device ~100 µm
- Mobilities:
  - electron: 250 µm in 1 ns
  - hole: 250 µm in 3 ns

Amorphous

- Gap: 1.6-1.8 eV
- High absorption coefficient, device ~1 µm
- Mobilities:
  - electron: 0.25 µm in 1 ns
  - hole: 0.25 µm in 200 ns

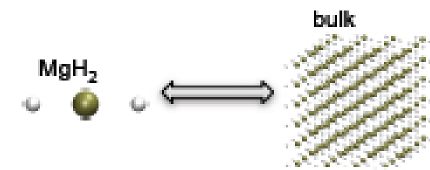
Example: Energy Storage Materials

solar fuels, hydrogen storage

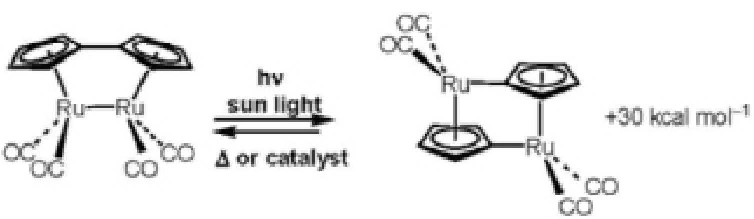


Quantum chemistry methods, reaction path energetics, excited states.

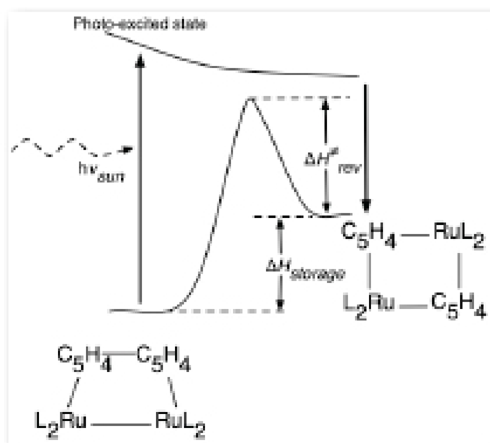
Image is in the public domain.



Tunable thermodynamics for H desorption.



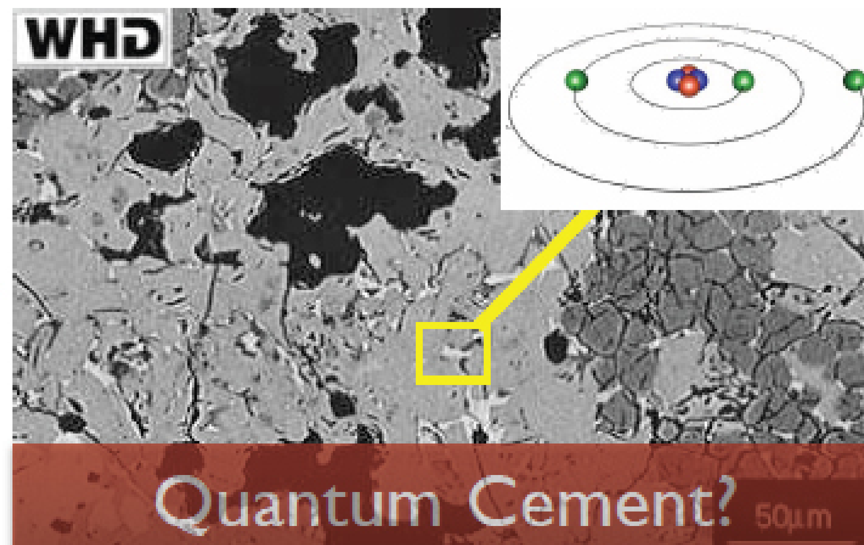
sunlight → stored heat energy.



Pushing electrons up a hill takes quantum mechanics

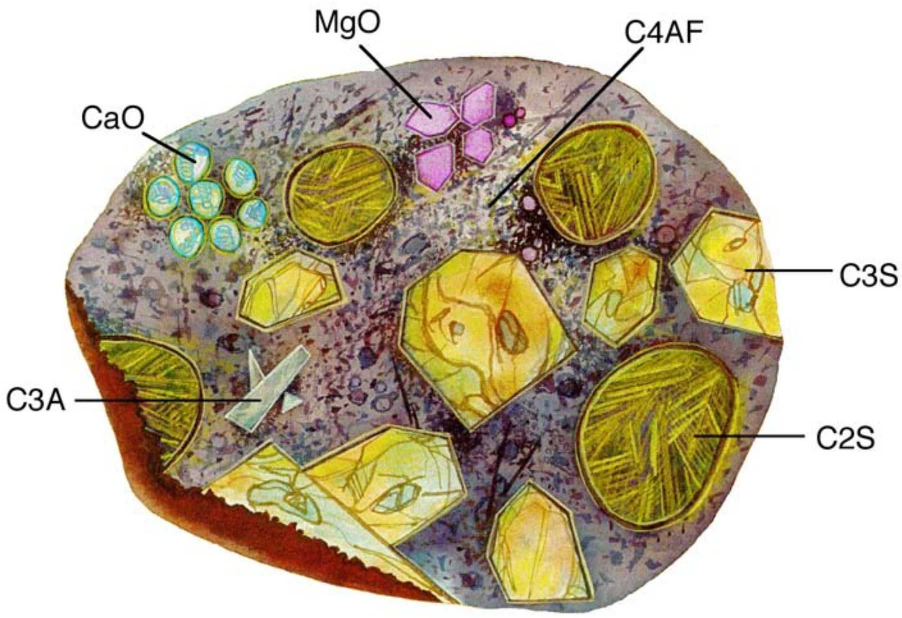
Example: Concrete Science

- Cement accounts for 5-10% of global CO_2 Emissions
- Cement is mainly made of synthetic rock : Clinker
- 4 major phases: Alite (Ca3SiO5), Belite (Ca2SiO4), Aluminate (Ca3Al2O6), Ferrite (Ca2AlFeO5)
- Many different polymorphisms, not fully understood



Surface Reactivity is Key Problem

- Alite (C3S)
  - 7 polymorphs
  - Constitutes 50-70 %
  - Reaction with water : Fast
- Belite (C2S)
  - 3 polymorphs
  - Constitutes 15-30 %
  - Reaction with water : Slow



Adapted from Cement Microscopy, Halliburton Services, Duncan, OK.

- Why? How?
- Can we tune the Belite reaction rate?

It's a quantum world!

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