

Alg-O-rithms that crack quantum mechanics:

from ATOMS to REAL MATERIALS

MATTIA FIORENTINI – KING'S COLLEGE LONDON | [THE LONDON BIG-O MEETUP](#)

OUTLINE

Discovering new materials with computational physics

- The concept of functional materials
- Challenges in materials science
- Current initiative: computers and material discovery

Algorithms and HPC

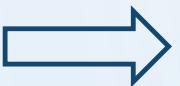
1. Quantum mechanics and the «first-principles» of matter
2. Telling life and death of electrons with FOURIER TRANSFORM: cracking the Schrödinger equation.
3. Following CONJUGATE GRADIENTS through electronic flows: the solution of the Boltzmann equation of transport
4. Do we really need all of this? HPC is expensive!

Application (my work) to thermoelectric materials

- The marvellous thermoelectric effect
- State-of-the-art of thermoelectric materials.
- Pathways for material engineering
- How I am contributing to this challenge.

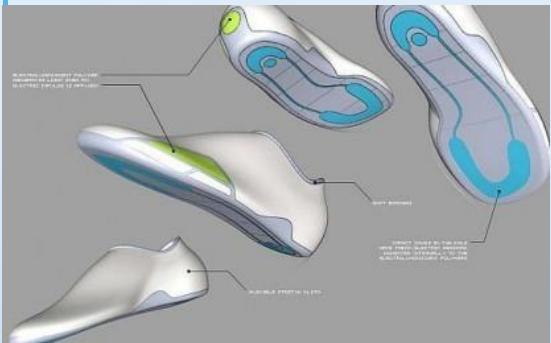
FUNCTIONAL MATERIALS

“FUNCTIONAL RESPONSE TO EXTERNAL STIMULUS”

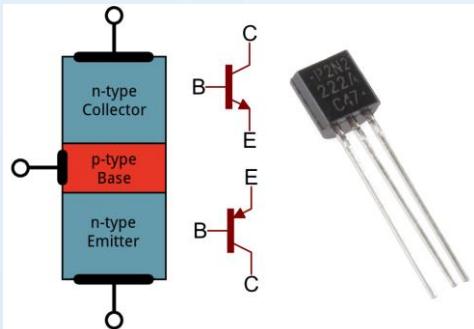


Reproduce the functionality of complex devices by engineering its physical features

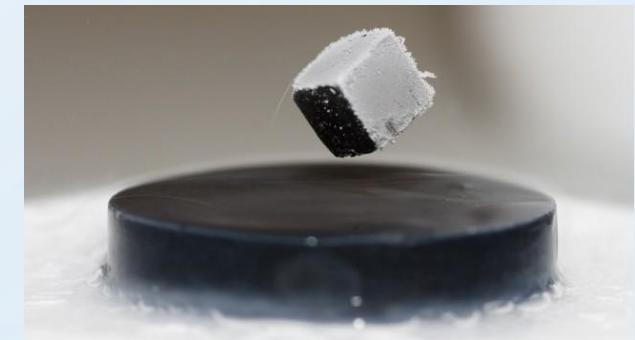
Piezoelectric



Semiconductors



Superconductors



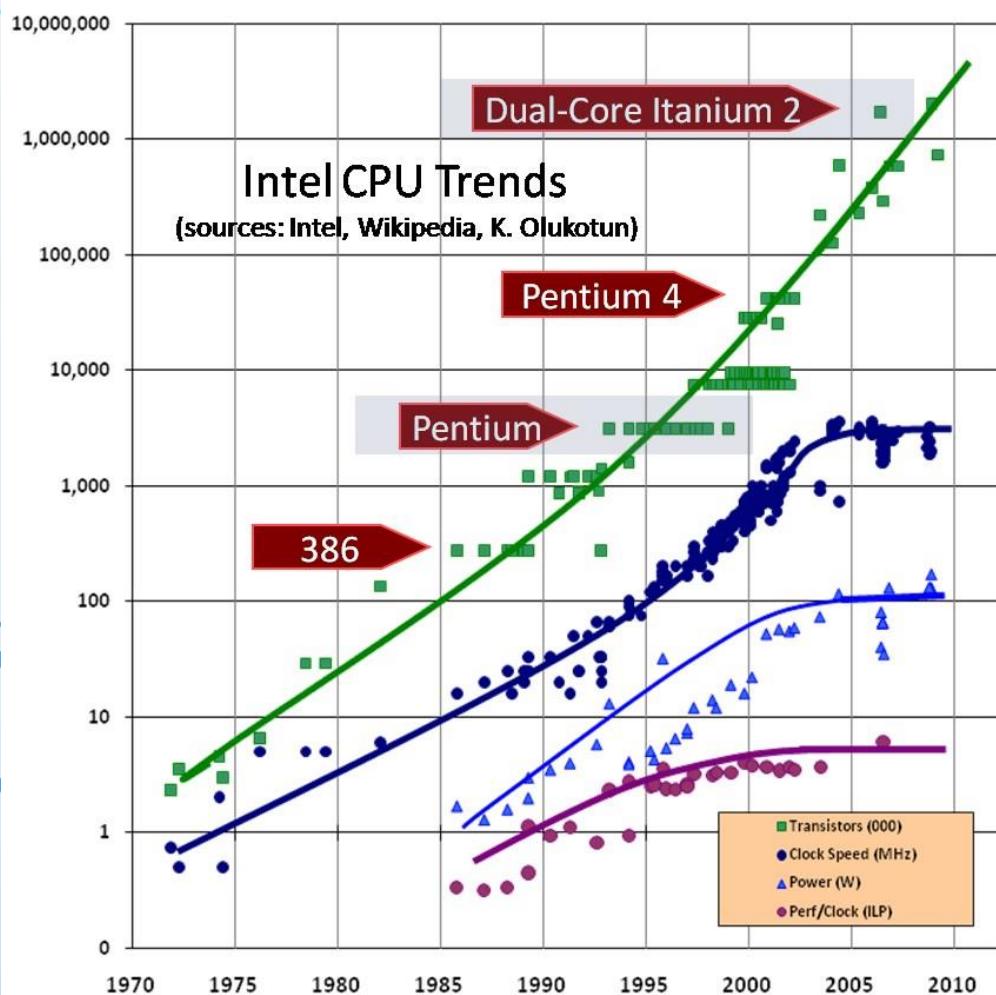
Ferromagnets



FUNCTIONAL MATERIALS

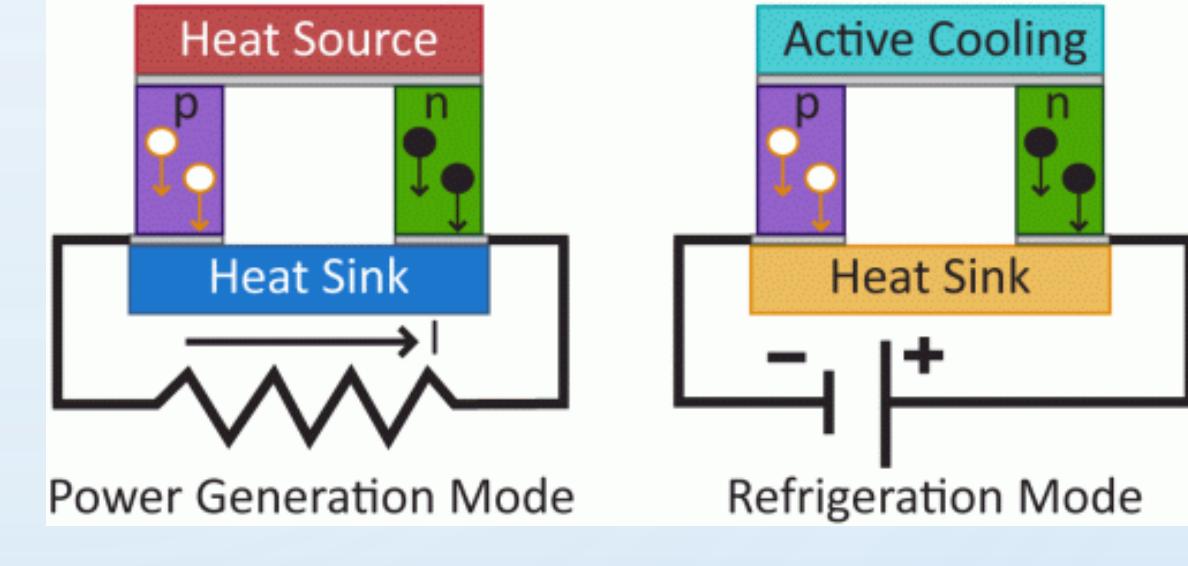
CHALLENGES

Silicon-based electronics



UNEXPLOITED OPPORTUNITIES

Thermoelectric devices



Quest for more efficient batteries

CURRENT INITIATIVES IN MATERIAL DISCOVERY

www.mgi.org

The screenshot shows the homepage of the Materials Genome Initiative (MGI) website. At the top, there's a navigation bar with links to 'BRIEFING ROOM', 'ISSUES', 'THE ADMINISTRATION', 'PARTICIPATE', '1600 PENN', and a search bar. Below the navigation, a banner features the MGI logo and the text 'Materials Genome Initiative'. A quote from President Obama is displayed: "To help businesses discover, develop, and deploy new materials twice as fast, we're launching what we call the Materials Genome Initiative. The invention of silicon circuits and lithium-ion batteries made computers and iPods and iPads possible -- but it took years to get those technologies from the drawing board to the marketplace. We can do it faster." The quote is attributed to President Obama, June 2011 at Carnegie Mellon University. To the right of the quote is a photograph of President Obama and a woman in a lab setting, examining a long, glowing white light panel.

~ 250 M\$ since 2011 jus from US Gov.

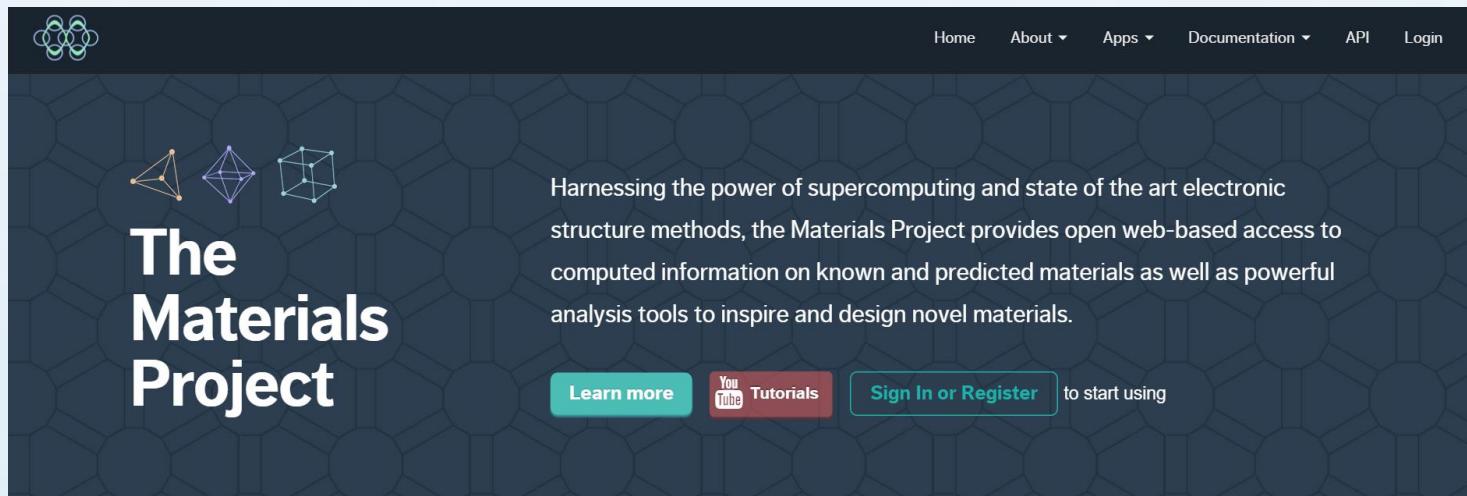
STRATEGIC GOALS:

1. Enable a paradigm shift in material development
2. Integrate experiment, computation and theory
3. Facilitate access to data

COMPUTATIONAL PHYSICS IN MATERIAL DISCOVERY

www.materialsproject.org

“Free-access database of properties of novel materials”



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

58251

41688

2176

COMPOUNDS

BANDSTRUCTURES

ELASTIC TENSORS

2185

18226

Li INTERCALATION ELECTRODES

Li CONVERSION ELECTRODES

COMPUTATIONAL PHYSICS IN MATERIAL DISCOVERY

www.materialsproject.org

The screenshot shows the Materials Project's website with a dark header bar containing the logo, Home, About, Apps, Documentation, API, and Login links. Below the header, there are navigation links for About, Database Stats, Founders, Partners & Support, Open APIs, and Contact.

About the Materials Project

software

By computing properties of all known materials, the Materials Project aims to remove guesswork from materials design in a variety of applications. Experimental

supercomputers

Supercomputing clusters at the Lawrence Berkeley National Laboratory's NERSC Scientific Computing Center and Computational Research Division provide

screening

Computational materials science is now powerful enough that it can predict many properties of materials before those materials are ever synthesized in the lab.

Implementation

HPC

Material discovery

COMPUTATIONAL PHYSICS IN MATERIAL DISCOVERY

Quote “If the US Gov is funding this, it must be really interesting/useful” - anon

About computational physics

Theory Select promising theories / equations:
QUANTUM MECHANICS

Implementation Develop computational methods to solve them:
Software and **HPC**

Results Compare the calculation with experiments:
UNDERSTAND and/or **IMPROVE** THEORY

OUTLINE

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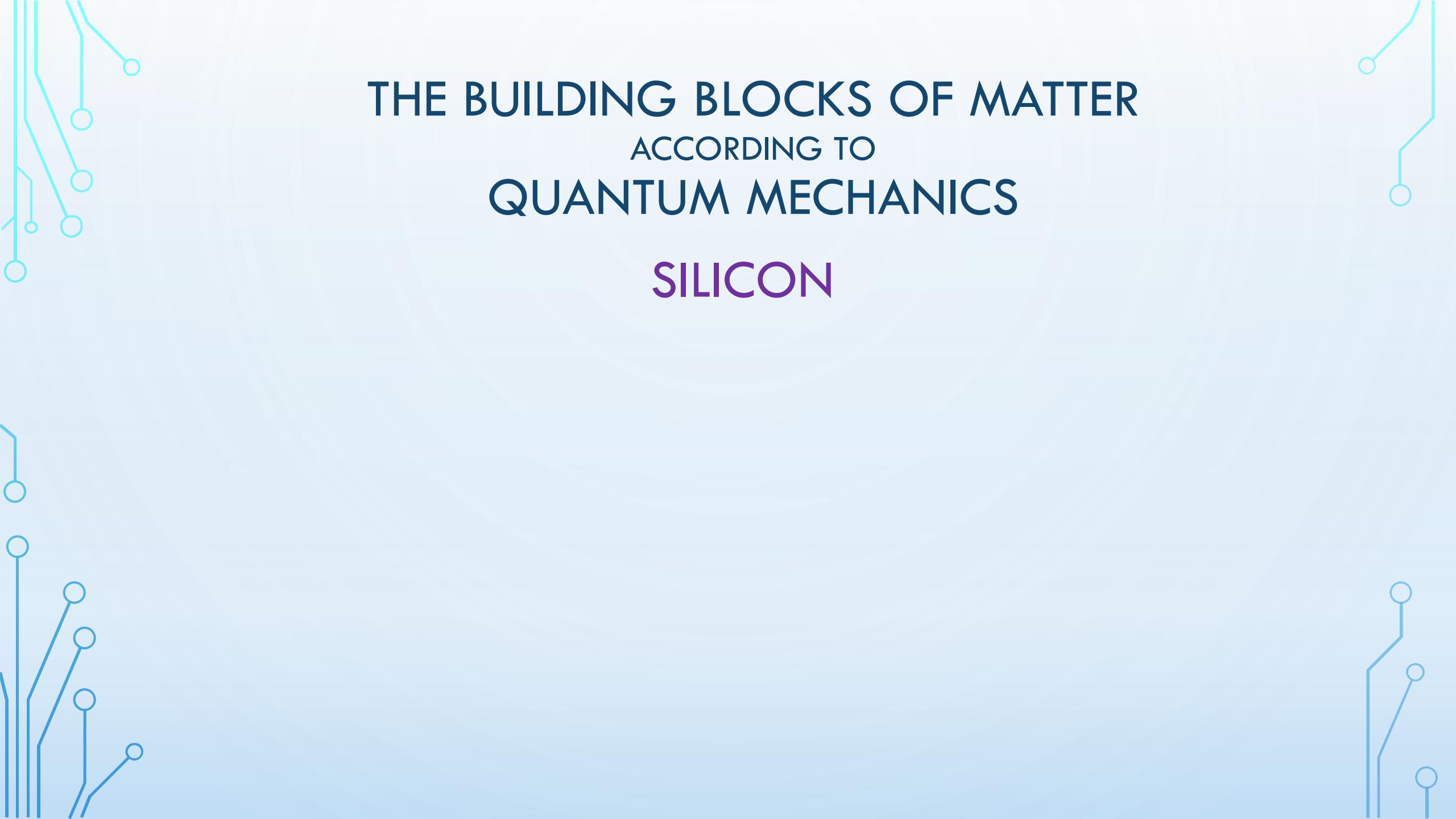
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THE BUILDING BLOCKS OF MATTER ACCORDING TO QUANTUM MECHANICS

SILICON

THE BUILDING BLOCKS OF MATTER ACCORDING TO QUANTUM MECHANICS

Si



SILICON

What an average person thinks...

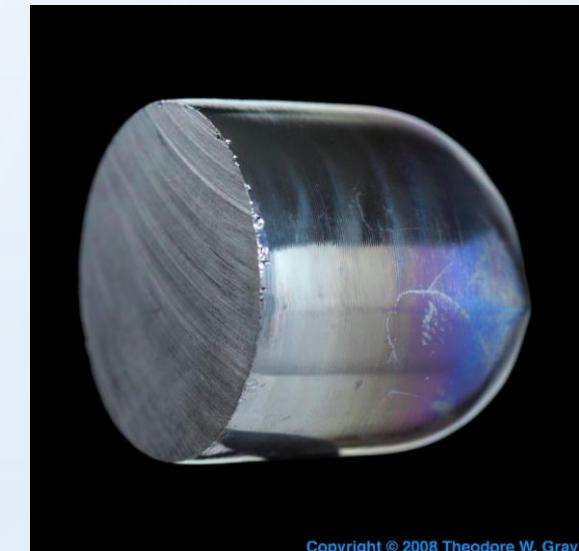
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Si



SILICON

What a Chemist thinks...



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What an average person thinks...

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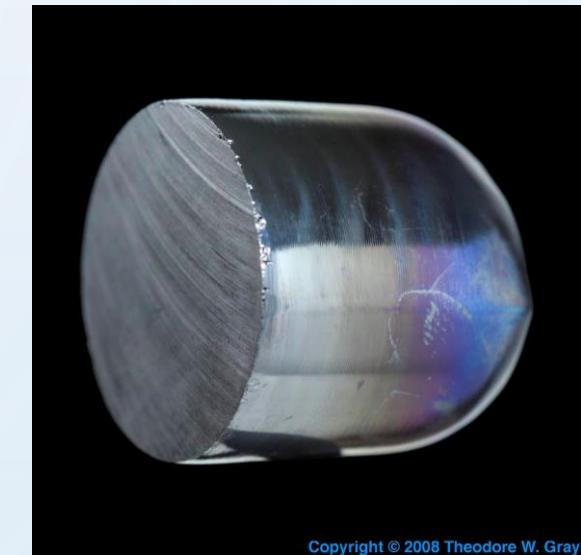
Si



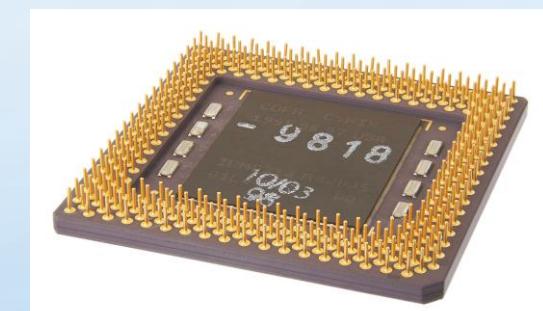
What an average person thinks...

SILICON

What a Chemist thinks...



What a Engineer thinks...



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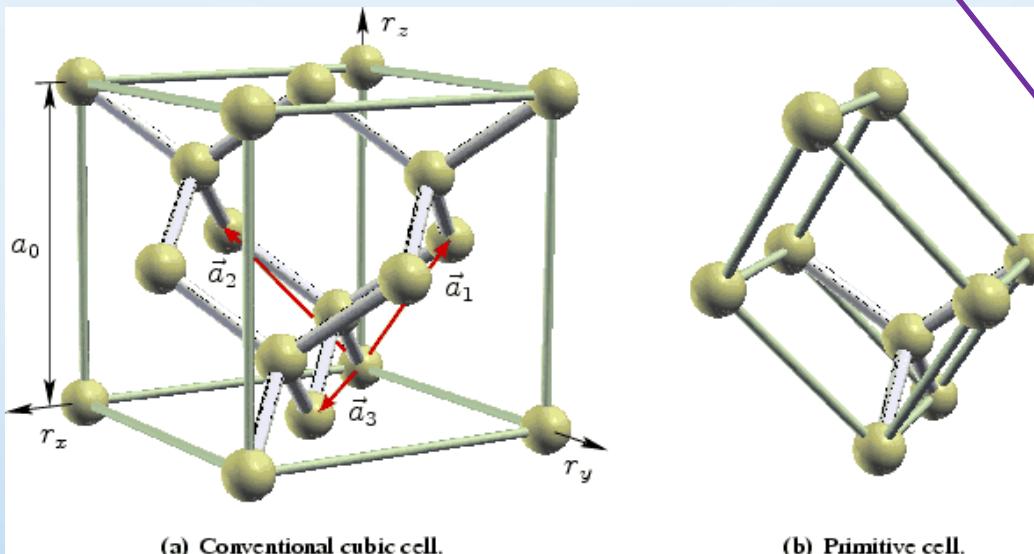


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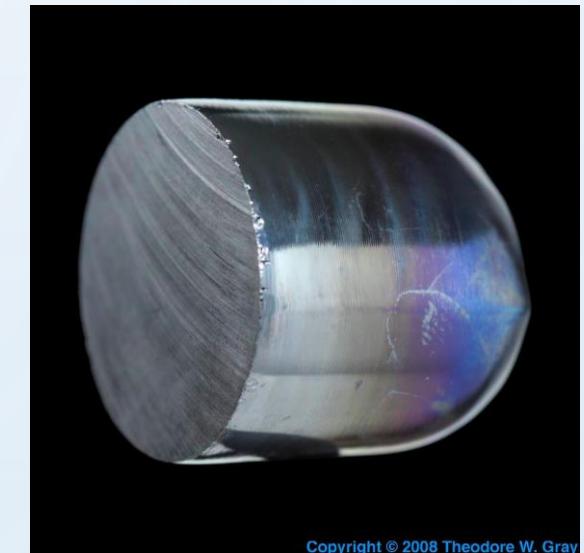
SILICON

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What a Physicist thinks...



What a Chemist thinks...



What a Engineer thinks...

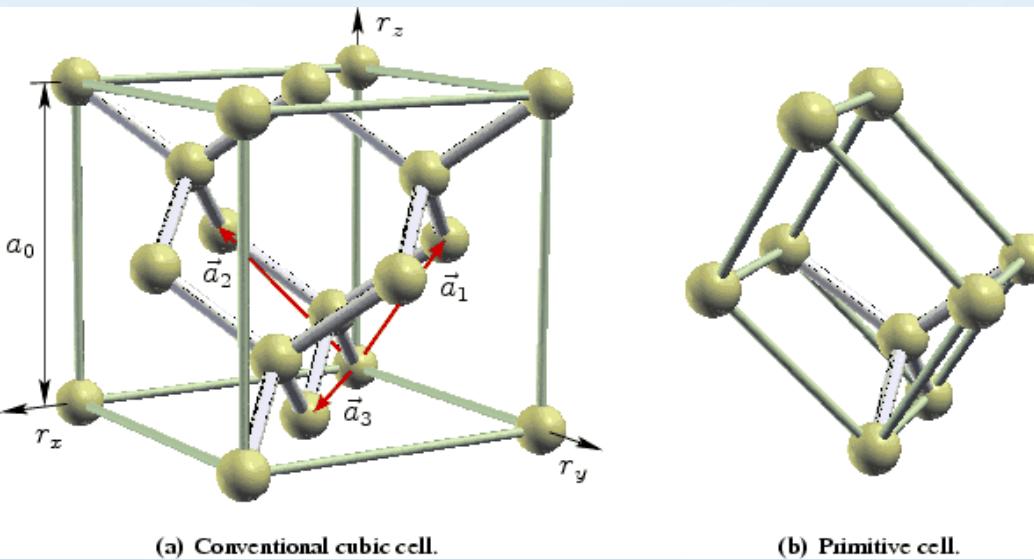


THE BUILDING BLOCKS OF MATTER ACCORDING TO QUANTUM MECHANICS

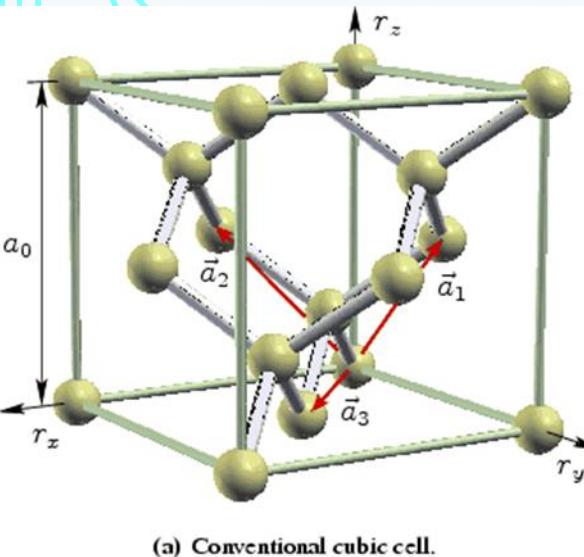
SILICON



What a Physicist thinks...



THE BUILDING BLOCKS OF MATTER ACCORDING TO QUANTUM MECHANICS



(a) Conventional cubic cell.

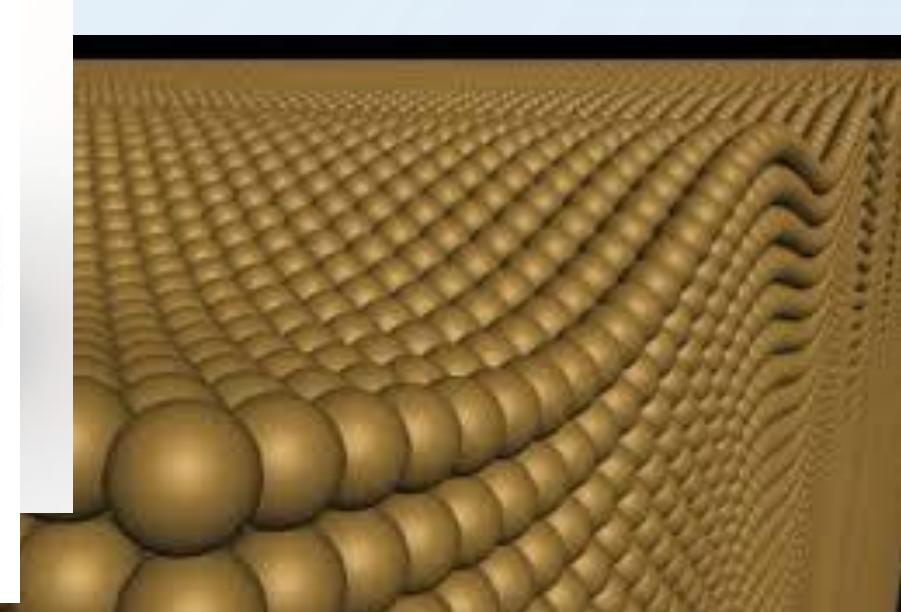
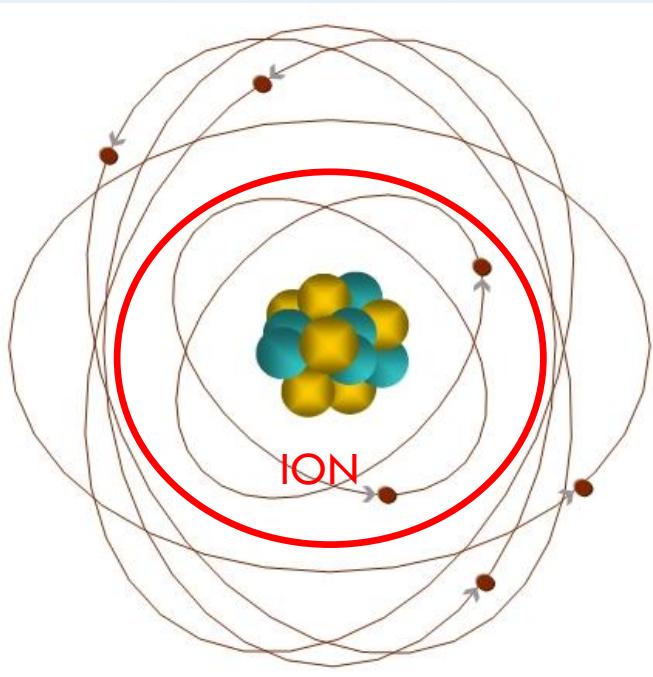
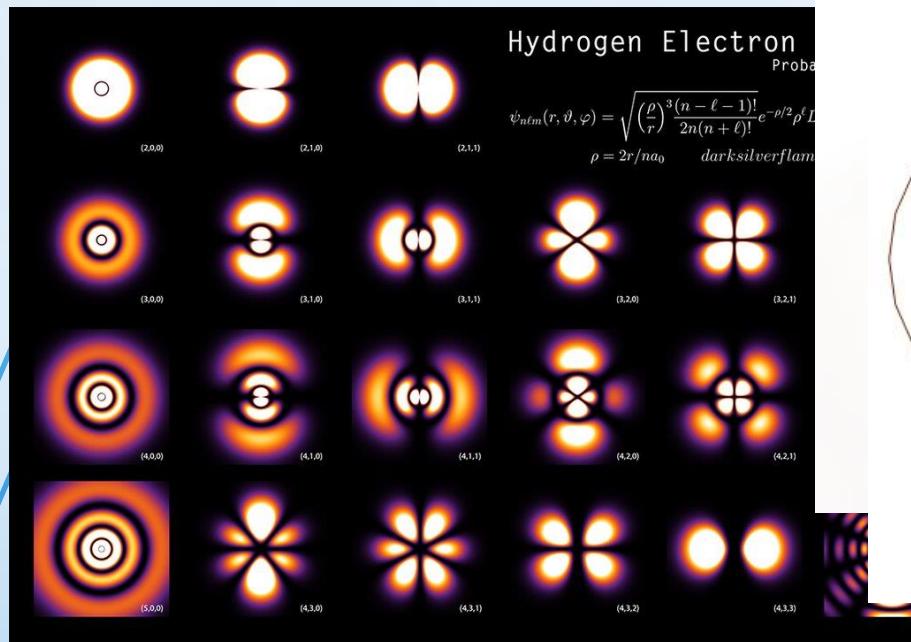
Solid

=

Crystal lattice

Electrons

Ions (nucleus+core)



THE BUILDING BLOCKS OF MATTER ACCORDING TO QUANTUM MECHANICS

The diagram illustrates the Schrödinger equation. At the top, two curved arrows point downwards from the text "Electrons (r, t)" and "Ions (R, t)" respectively. Below these arrows, the equation $i\hbar \frac{\partial}{\partial t} \Psi(r, R, t) = \mathcal{H}(r, R, t) \Psi(r, R, t)$ is centered. A purple bracket labeled "Wave function" points to the wave function $\Psi(r, R, t)$. Another purple bracket labeled "Energy operator 'Hamiltonian': [• Dynamics, • Energies, • Phys. observables]" points to the Hamiltonian $\mathcal{H}(r, R, t)$.

$$i\hbar \frac{\partial}{\partial t} \Psi(r, R, t) = \mathcal{H}(r, R, t) \Psi(r, R, t)$$

All that is needed to predict material properties is in the Schrödinger equation

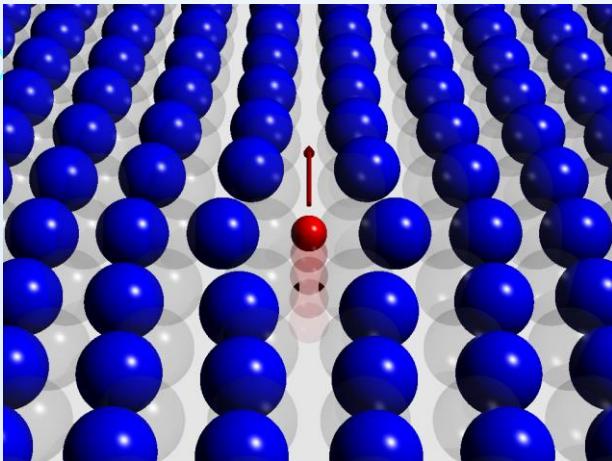
$$\mathcal{H}(r, R, t) = K_e + U_{e-e} + K_{Ion} + U_{Ion-Ion} + U_{e-ion}$$

-
- Exponential increase in the computational cost due to interactions ($\sim 10^{23}$ Atoms in 1 cm^3 of Silicon)
 - Analytical solution just in high-symmetry cases (Hydrogen atom)

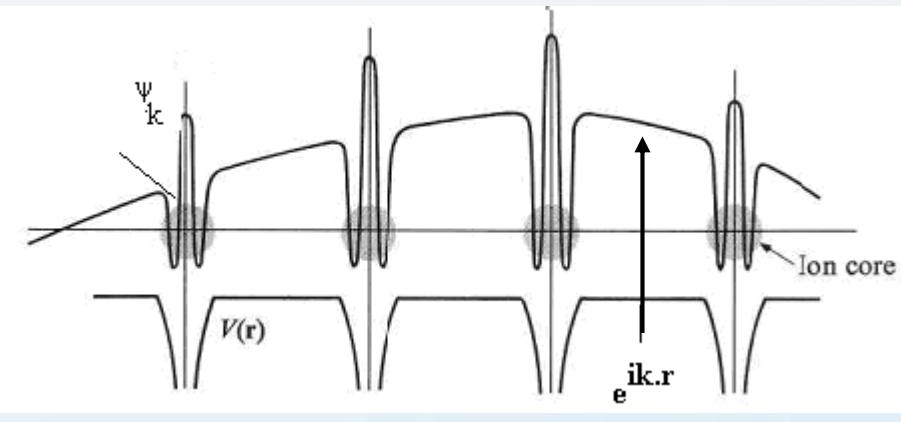
1- CRACKING THE SCHRÖDINGER EQUATION

ELECTRON'S BEHAVIOUR IN MATTER

Electron moving in Ions' lattice

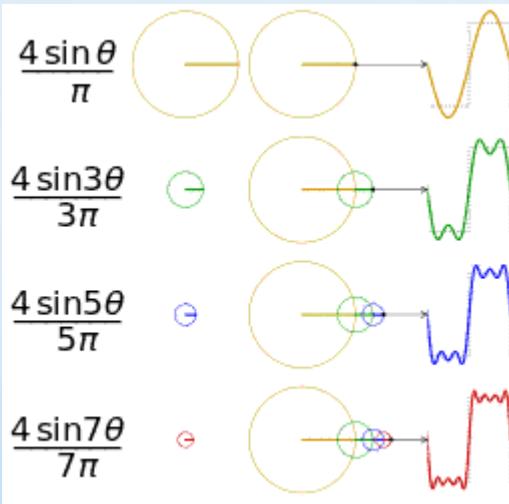


"Spatial domain"
Pos. - Wave Vec.
(r, k)



Fourier decomposition of the WF on the G lattice

Decomposition of a square wave in plane waves



"Time domain"
Time - freq.
(t, ω)
 $c_n e^{in\omega t}$

$$\Psi_k(r) = e^{ik \cdot r} f(r) \xrightarrow{\text{Periodic } f} \Psi_k(r) = \sum_{G \text{ lattice}} c_G e^{ir \cdot (k+G)}$$

Plane
wave

The Hamiltonian becomes a matrix, $\mathcal{H}_{GG'}(k)$

Solve the Schrödinger equation in the plane waves' wave-vector space \mathbf{G} .

- Weak, periodic potential: just "few" Fourier components needed!
- Electrons' energies are the eigenvalue of \mathcal{H} matrix

1 - CRACKING THE SCHRÖDINGER EQUATION

TWEAKING THE FOURIER DECOMPOSITION

Diagonalize the Hamiltonian $\mathcal{H}_{GG'}(k)$ (G space) \Rightarrow Obtain the energy level of the electrons $\varepsilon(k)$

- The matrix is densely populated: calculation more burdening.
- ✓ The matrix has as few off-diagonal elements as possible: easy-peasy!

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WF defined up to a (global) phase: $\Psi_k(r) \simeq \Psi_k(r) \cdot e^{i\phi(k)}$ equivalent from the point of view of the physics

$$| \mathbf{R}n \rangle = \frac{V}{(2\pi)^3} \int_{BZ} | \psi_{n\mathbf{k}} \rangle e^{i\varphi_n(\mathbf{k}) - i\mathbf{k} \cdot \mathbf{R}} d\mathbf{k}$$

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We can tweak the new basis sets to be MAXIMALLY LOCALIZED:

Basis function have small spatial R overlap $\Leftrightarrow \mathcal{H}_{RR'}(k)$ (R space) is “almost” diagonal

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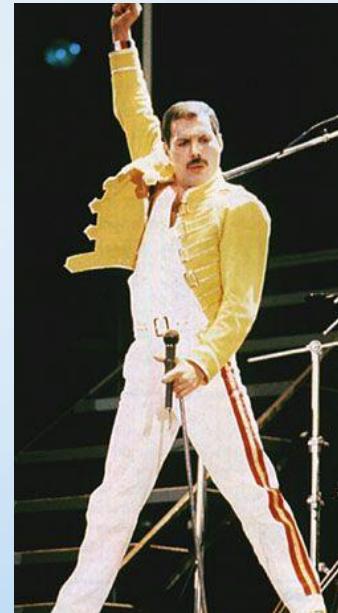


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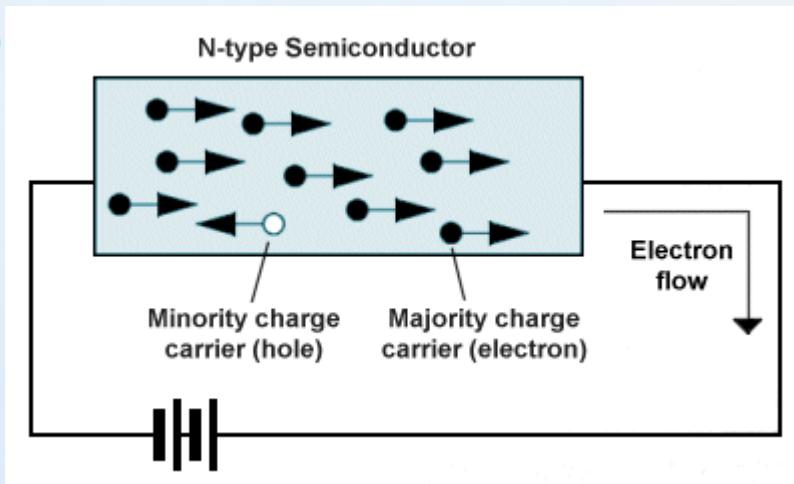
**ORDERS OF MAGNITUDE SPEED-UP & IMPRESSIVE SCALING
of the electron energies calculations!!!**

E.G. Si electronic energy bands PW: 5 mins (~ 10 cores)
WF: < 1 sec (1 core)

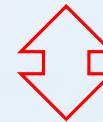


2 - ELECTRONS FLOWING IN MATTER

THE BOLTZMANN EQUATION



Electric field accelerates the electron (coherent momentum gain)



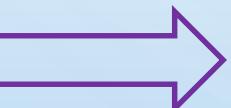
Lattice vibrations and defects slow electrons down (momentum loss, disorder)

Steady current when a balance is achieved: formally, the Boltzmann equation.

$$\frac{\partial f_0}{\partial \epsilon} \mathbf{v} \cdot \left\{ Ee + \frac{\nabla T}{T} [\epsilon - \mu] \right\} = \frac{V}{8\pi^3} \beta \int_{BZ} d_3 k' C_{kk'}^0 \phi_{k'}$$

Driving forces

Transistion mat.
(collision effects)



Theoretically predict the electronic flows properties of matter from the FIRST-PRINCIPLES
SOLVE THIS LINEAR SYSTEM in the k-space (Si : electronic states space $\sim 10^{3-4}$)

2 - ELECTRONS FLOWING IN MATTER CONJUGATE GRADIENTS

How can we solve a linear system with a minimization technique?

$$\mathbf{b} = M\mathbf{x}$$

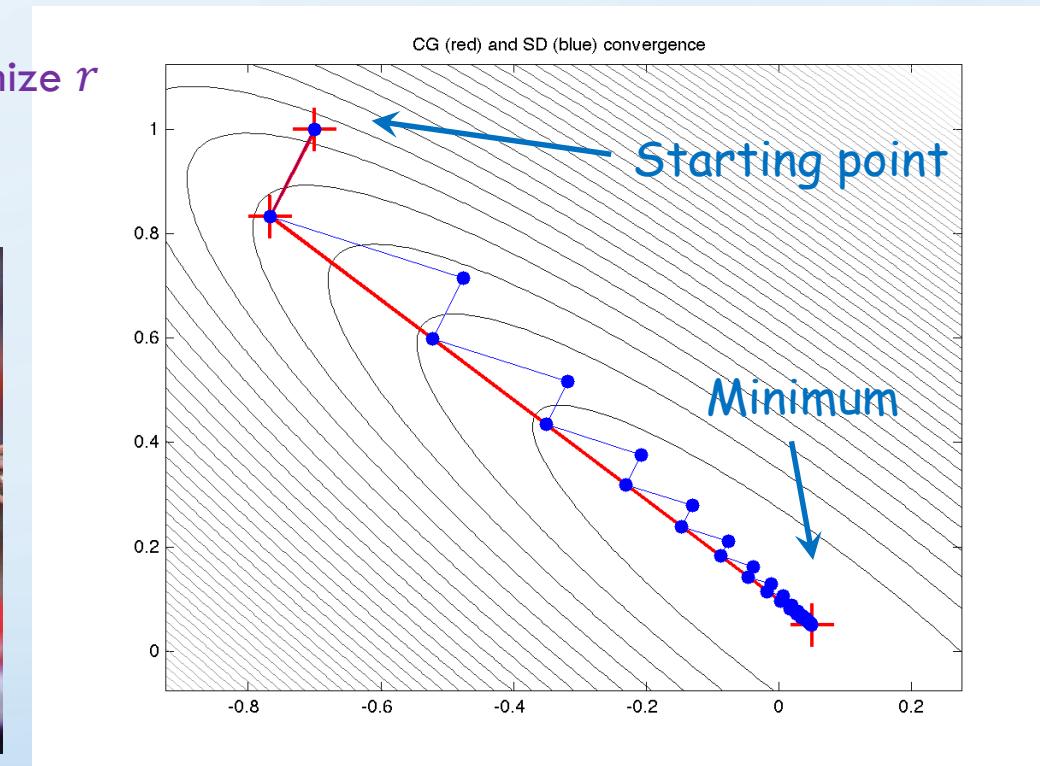
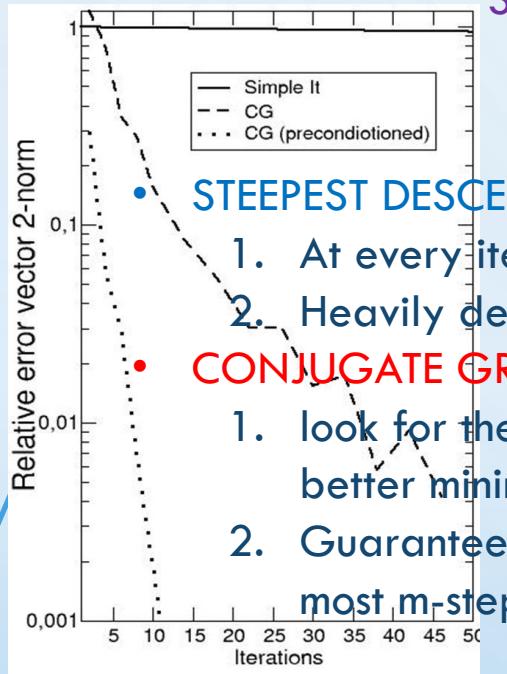
- Iterative techniques: start with a guess for \mathbf{x} and refine it minimizing the error, $r = \|\mathbf{b} - M\mathbf{x}_i\|$
- Gaussian elimination... (and many others)
- LU, Cholesky decomposition: The off-diagonal els. of M are much smaller than the one on diag:
 - Requires storing of additional matrices
 - 2. Refine: core part involves expensive calculations

$$\mathbf{x}_n = a_n M^n \mathbf{b} + a_{n-1} M^{n-1} \mathbf{b} + \dots$$

3. MINIMIZE: choose the coefficients a_n to minimize r

My usual (simple) case:

- dimensionality of the space $\sim 10^{3-4}$

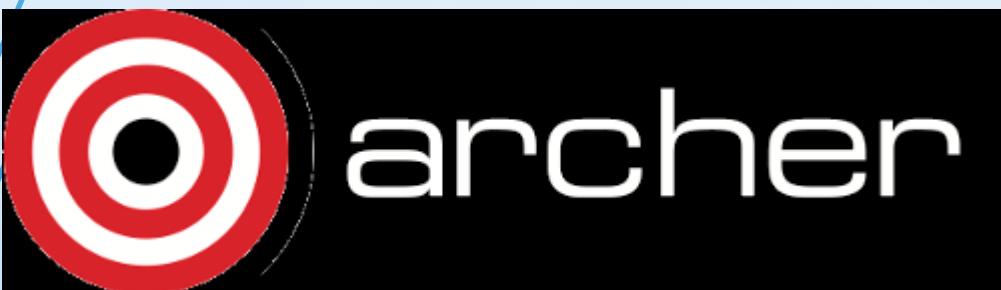


3 – EFFICIENT CODES & BIG COMPUTERS CALCULATING EVERYTHING FROM FIRST PRINCIPLES

(Why are you physicists so obsessed with small things????)

Solving the Schrödinger/Boltzmann equation is costly: why not use a simplified model?

- Models come from our impression of nature:
 1. it is very hard to build one for something that we have not seen yet! (Material discovery)
 2. they carry the cognitive biases of the scientists (we should not like “sexy” models too much)
- Building models from first-principles (electron, ions)...
 1. ... makes the model valid for a wider range of situations (temperature, pressure, length scales...)
 2. ... enhances the possibility of a “theoretical” discovery of new physics (theoreticians’ dreams to Nobel)
 3. ... all its building blocks have a connection with reality (at least in physicist’s minds)



- 72,192 cores
- 216,576 GB RAM
- 400 – 1200 kW power



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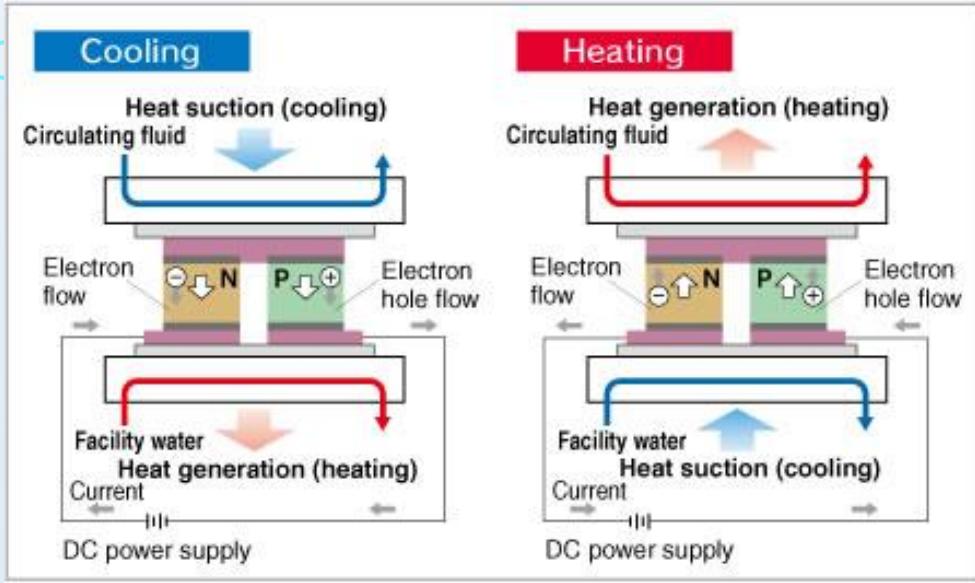
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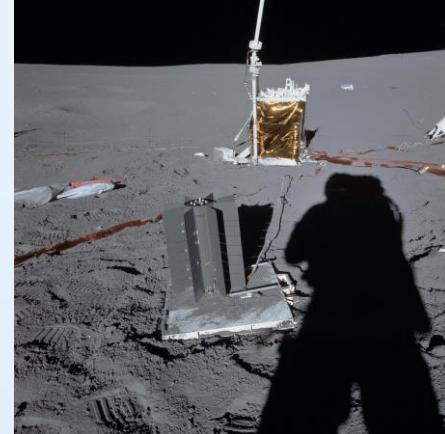
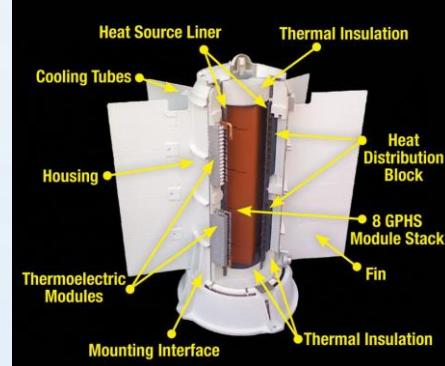
THERMOELECTRICITY

STATE-OF-THE-ART

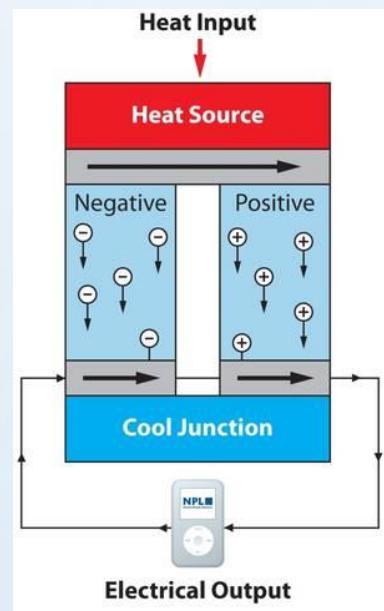
Reversible conversion between electricity and heat



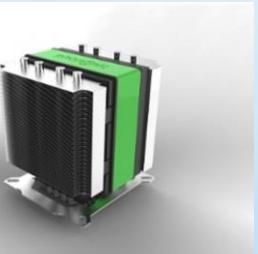
Lunar power gen. Apollo 12 to 17 missions



Energy harvesting



"Phononic" HEX CPU Cooler
(on sale now!)



0.013mA - $\Delta T \sim 30^\circ$



Wearable thermoelectric gen.

→ 10^5 hours running at 0° !



"Powering Your Car with Waste Heat"
MIT Technology review 25-05-2011



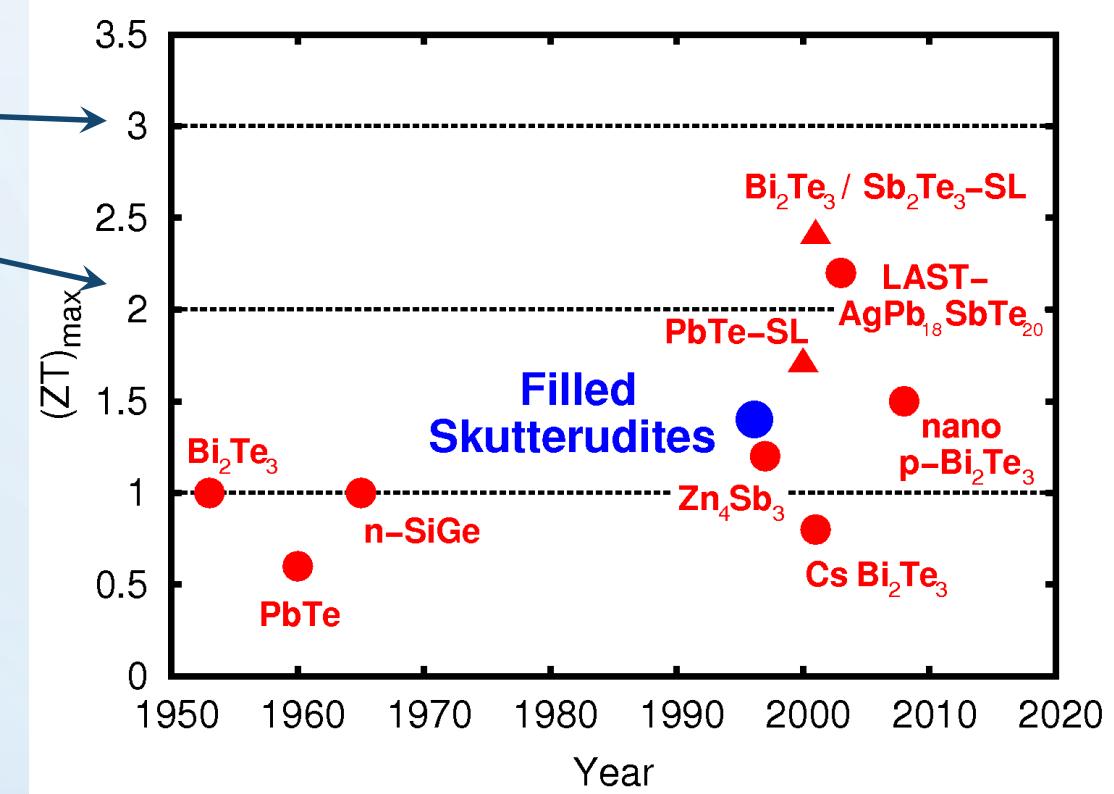
THERMOELECTRICITY

CURRENT LIMITS

Thermoelectric figure of merit

Conventional
generators / coolers

Commercial feasibility



ZT

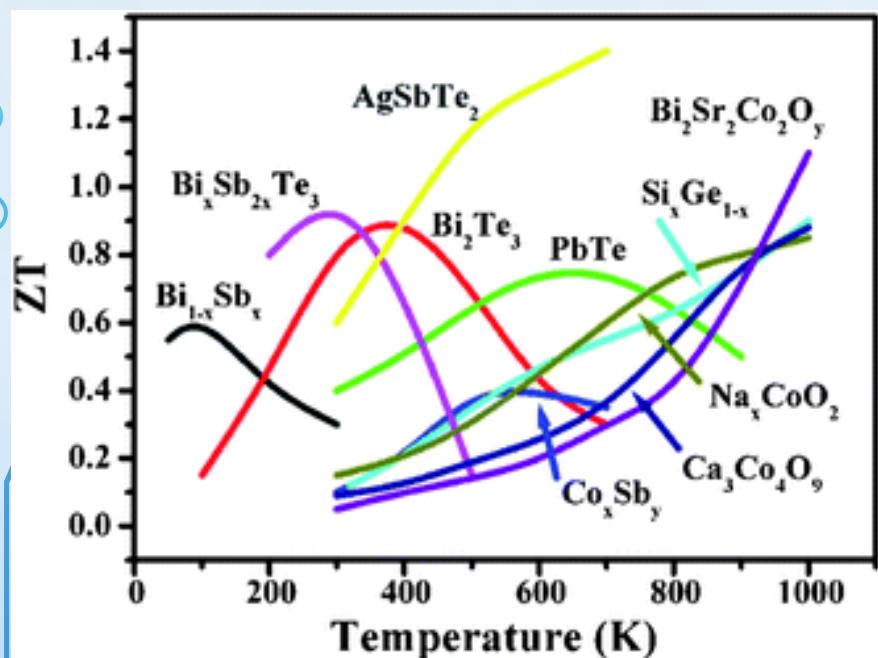
Figure of merit \sim efficiency

- Small/variable efficiency
- Dirty materials: lead, tellurium, caesium

THERMOELECTRICITY

ENHANCING THE PERFORMANCE

Thermoelectric figure of merit

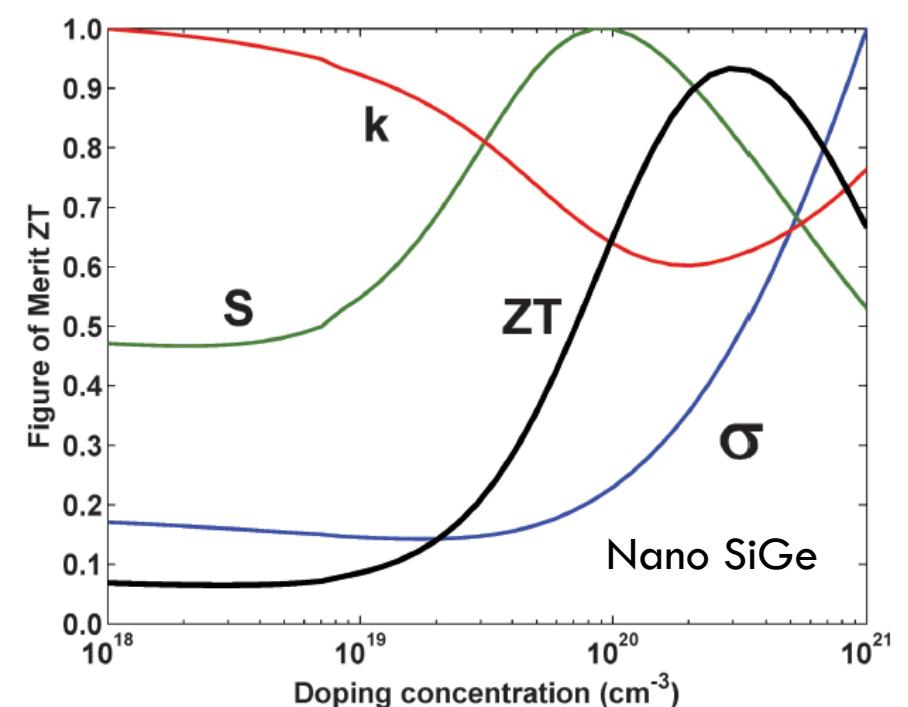
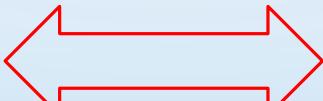


$$ZT = \frac{S^2 \sigma}{T} \cdot \left[\begin{array}{l} \text{"Heat-to-electricity conversion"} \\ \text{Electric conduction} \end{array} \right]$$

Heat conduction $\rightarrow K$

Lattice vibrations

Not a clear relation with
macroscopic variables
Temperature, doping, strain



THERMOELECTRICITY: BACK TO THE FIRST PRINCIPLES

Electronic energies
Vibrational frequencies
Interaction between electrons and vibrations

FIRST PRINCIPLES



Putting everything together: my research!

COMPUTATIONAL TECHNIQUES

From plane waves to wannier functions
Solve the Boltzmann equation – CG

- Fortran2003 (- C/C++)
- Python
- MPI (-openMP)
- Distr. mem. clusters: $\sim 10^{2-3}$

PHYSICS

Thermoelectric properties

- Change the temperature
- Add electrons
- Select lattice vibrations
- Tune the interaction el-lattice

➡ What happens to ZT?

HAPPY TO FURTHER DISCUSS WITH YOU



Contacts

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