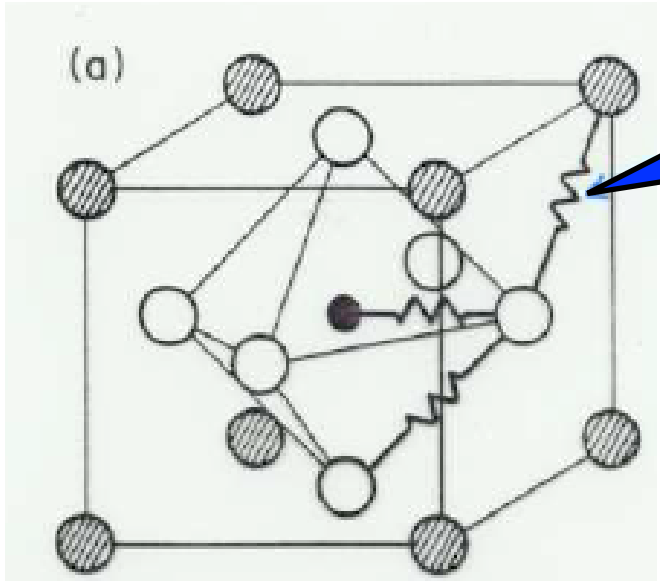
First-principles calculations: Exploration and understanding

Alberto García
ICMAB

- Scientific method: experiment, modelization, prediction, experiment...

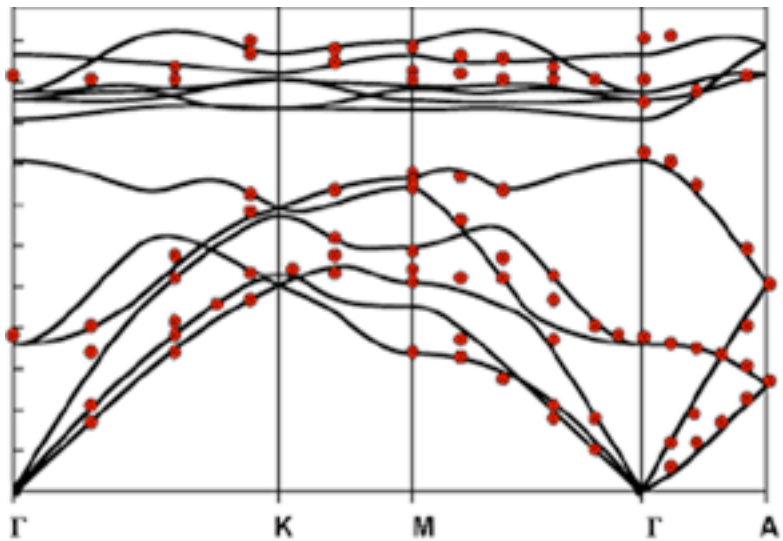
- We have the “ultimate model” for materials, and it involves the use of computers.

- What do the calculations teach us? How can we use them well?



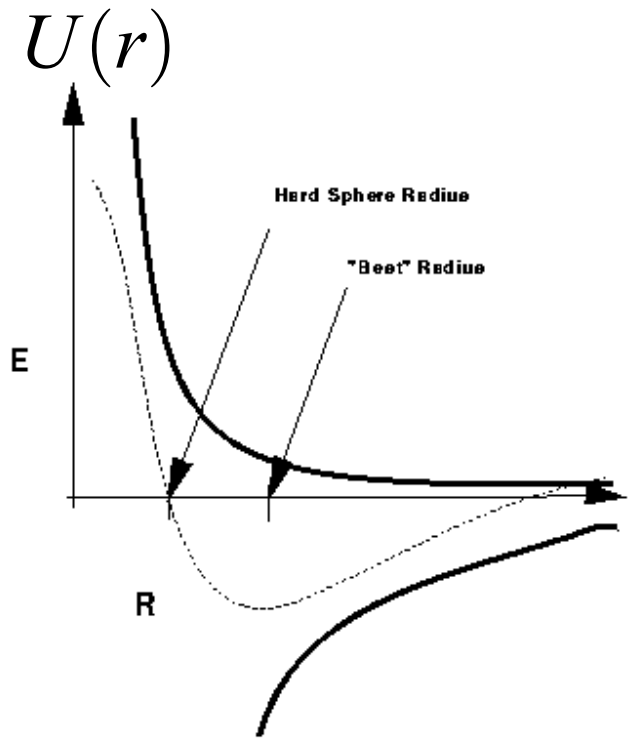
Spring constant

Basic idea: Vibrations around an equilibrium point



Parameters can be fitted to experiment

Interatomic potentials

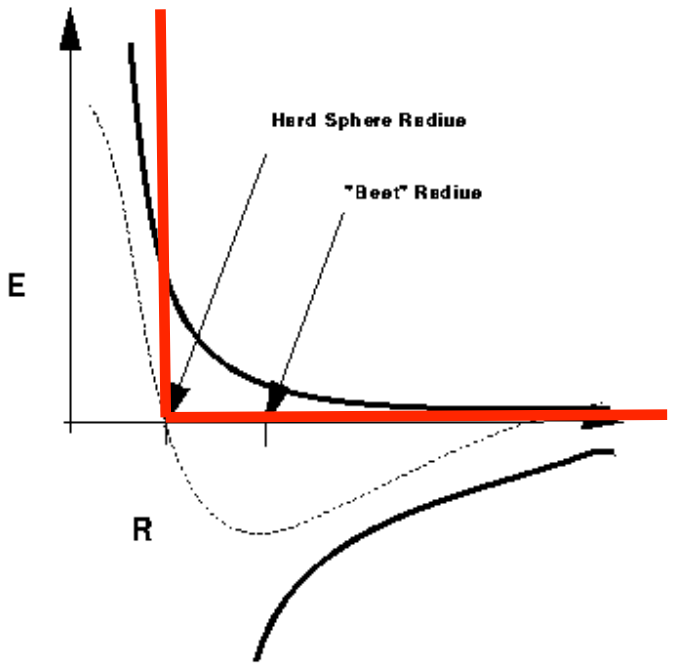


$$U(r) = Ae^{-r/\rho} - Cr^{-6}$$

$$U(r) = D\left\{\left[1 - e^{-A(r-r_0)^2}\right]^2 - 1\right\}$$

The model can get complicated for "pencil and paper" treatment

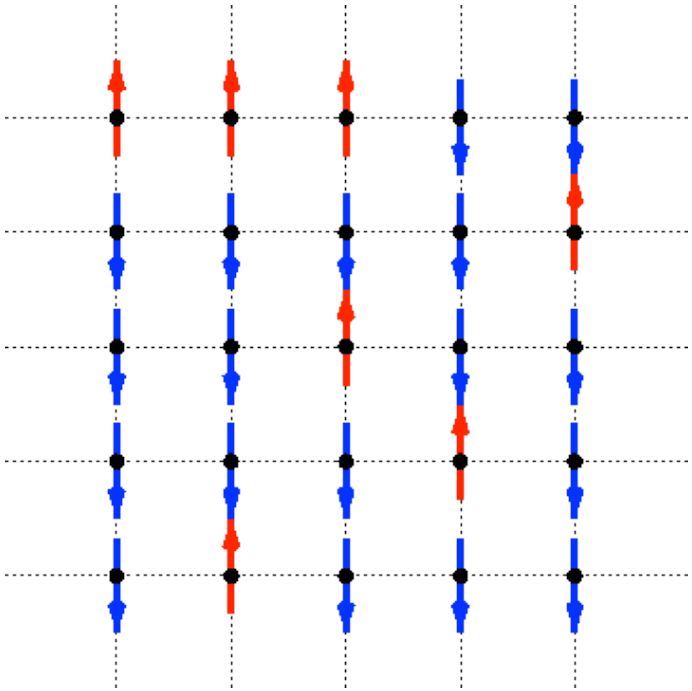
Molecular dynamics simulation



Alder+Wainwright (1956)
Hard-sphere liquid

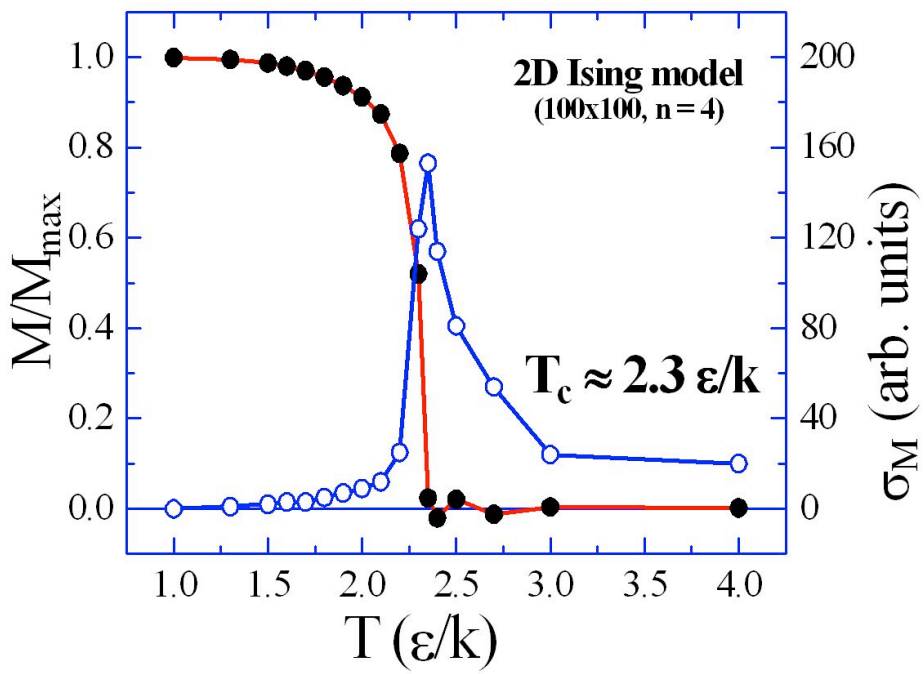
Tremendous growth

Exploration, validation of theories, and checks of interaction potentials



Ising Model

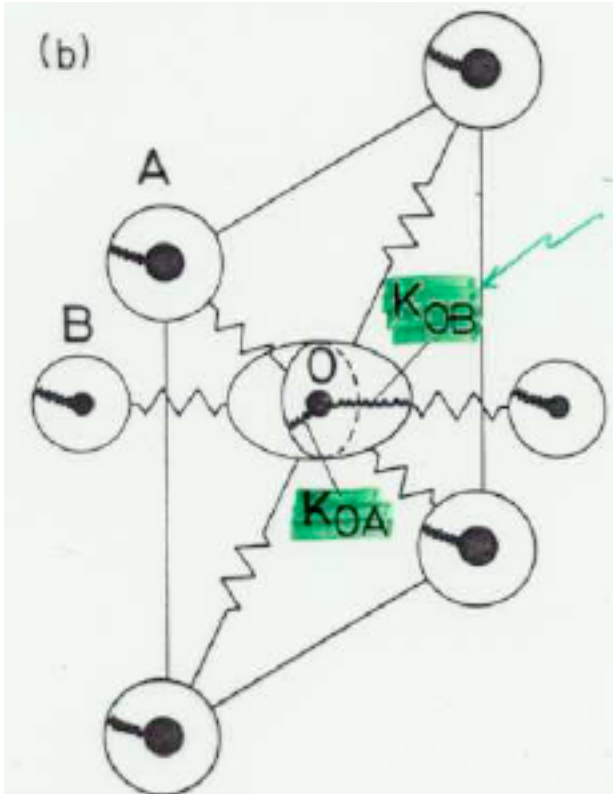
Monte Carlo Simulation

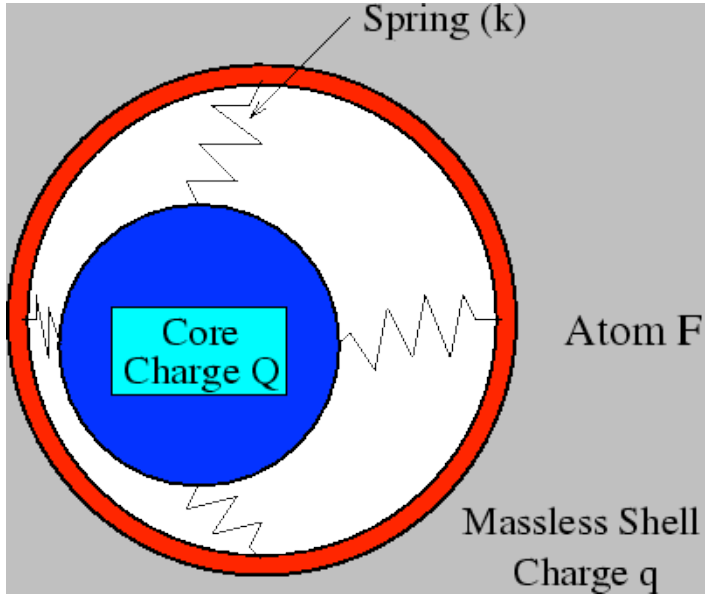


Emergent properties:
Not evident just by looking at the equations

The use of the computer is essential
for exploration of models

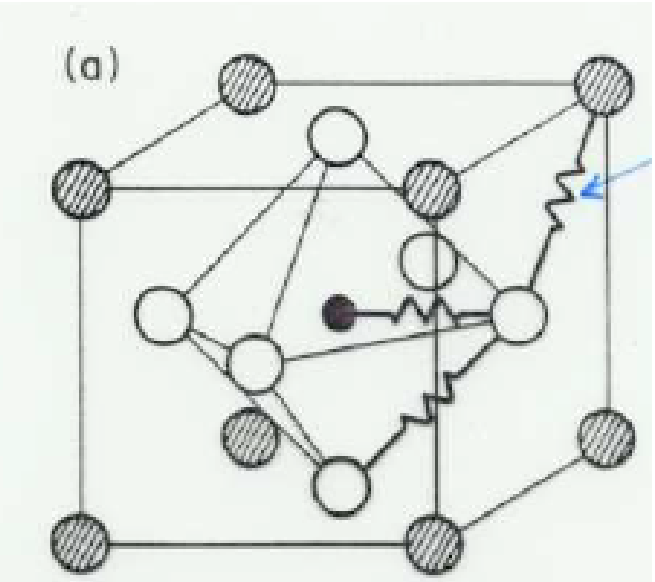
Refinement of the model: polarizable electrons (shell model)

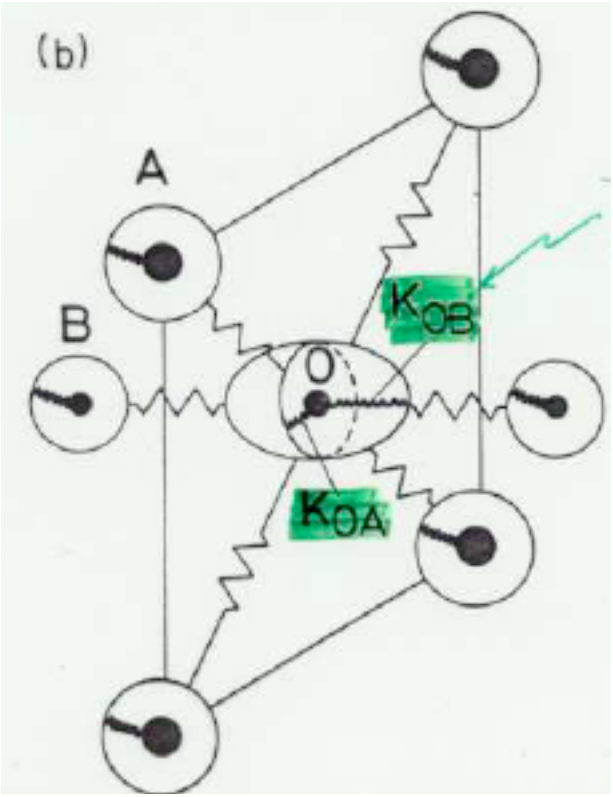




Internal structure of the atom acknowledged

Better fit to experiment
New phenomena





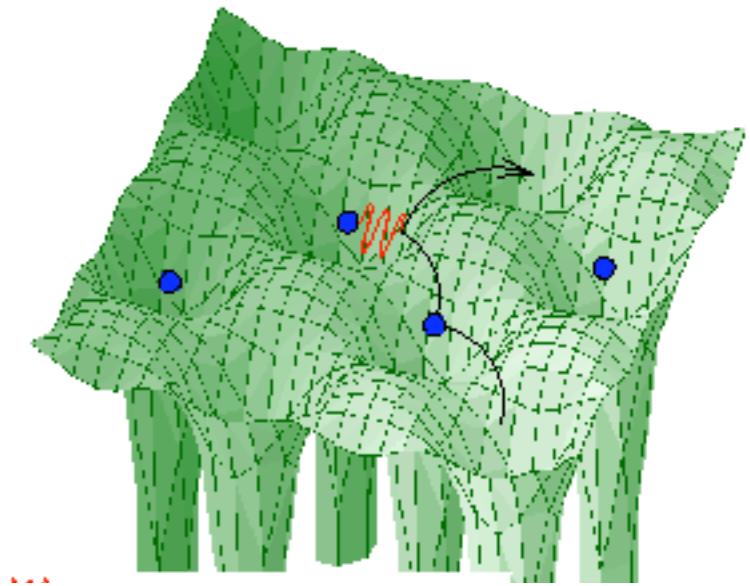
....

Electrons are the glue
holding solids together

We know the basic equations:
Quantum Mechanics and Electromagnetism

The "ultimate model" for electrons in a material

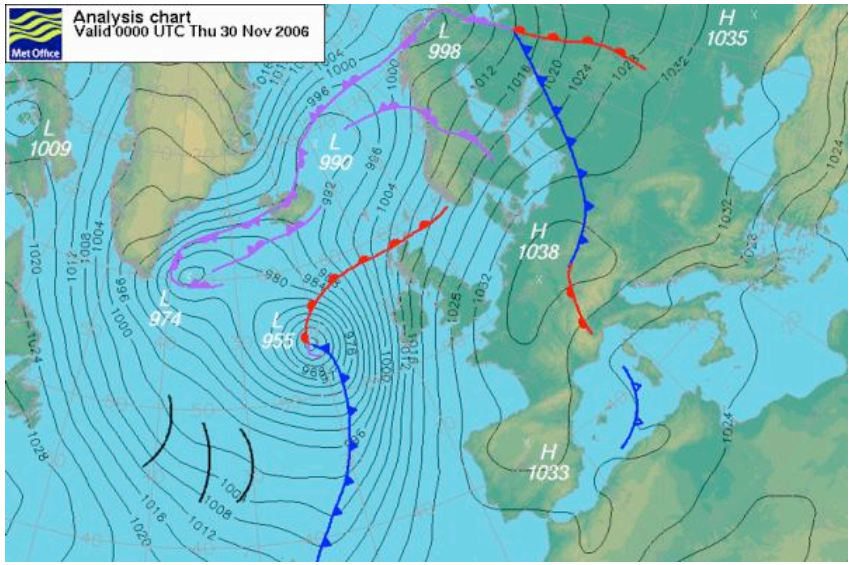
$$H = \sum_i \left[-\frac{\hbar^2 \Delta_i}{2m_e} + \sum_l \frac{-e^2}{4\pi\epsilon_0} \frac{Z_l}{|\mathbf{r}_i - \mathbf{R}_l|} ; \right] + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$



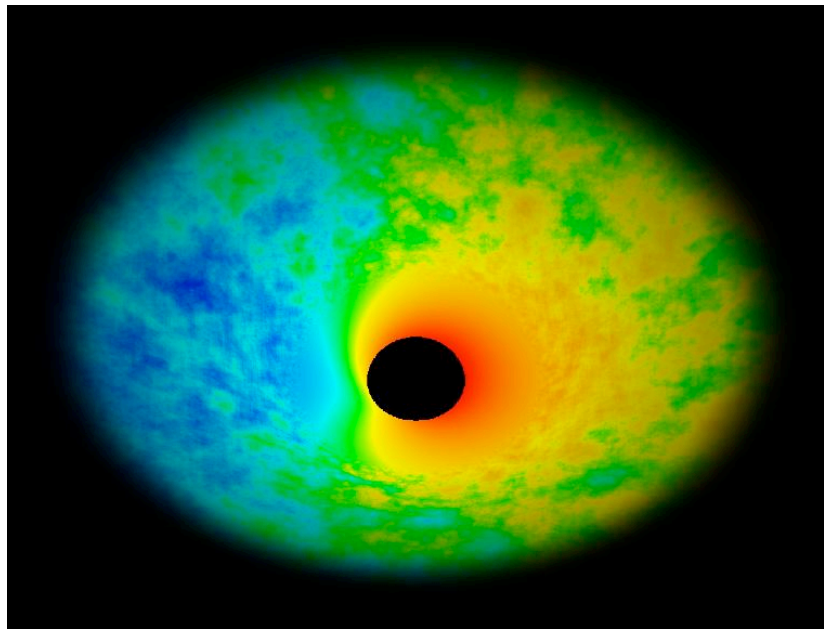
$$\hat{H}\Psi = E\Psi \qquad \Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n)$$

We could compute "everything"

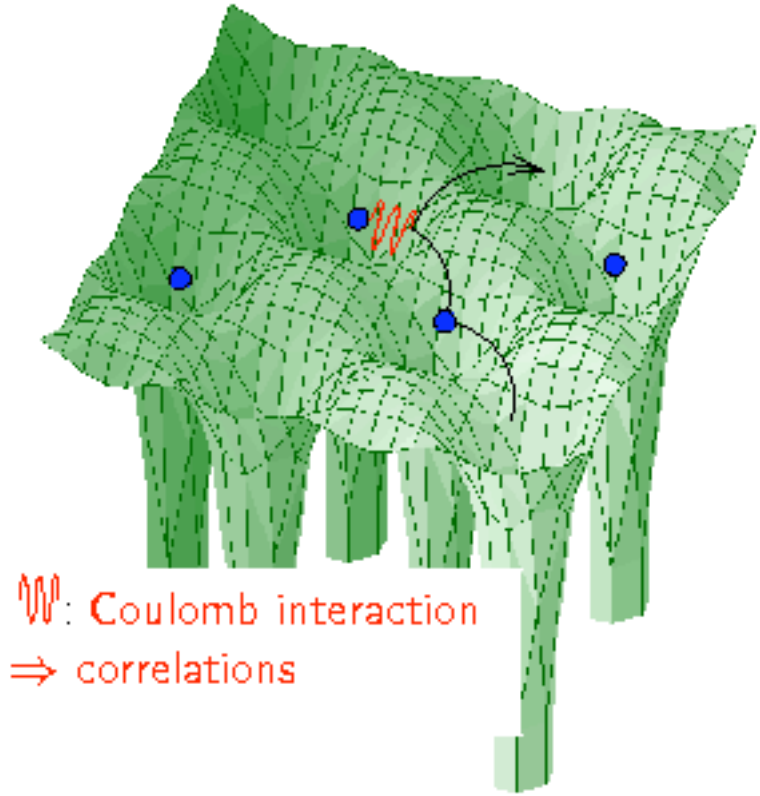
Simulation of reality

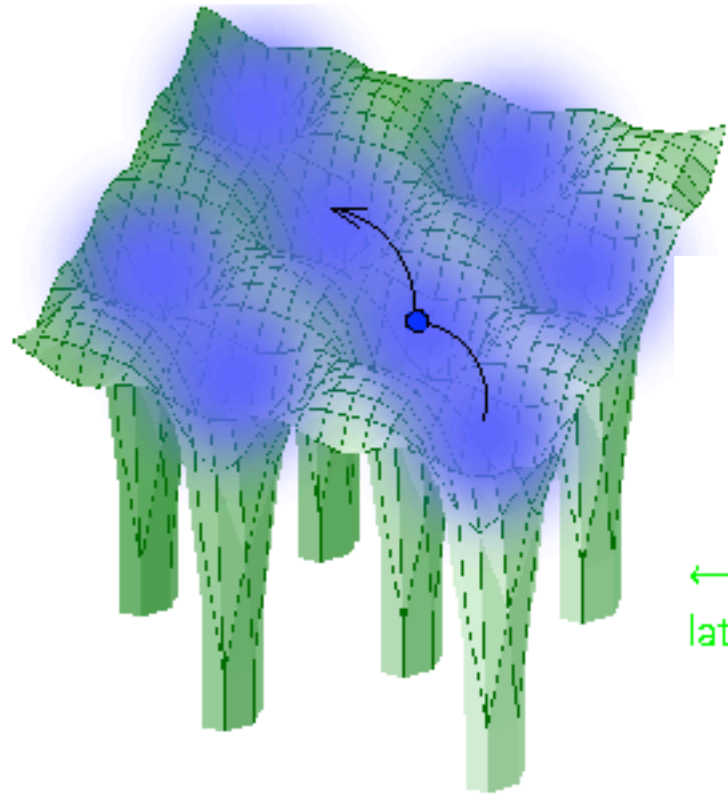


Meteorology:
We know the
basic equations



Astrophysics:
We know the
basic equations.
Little data



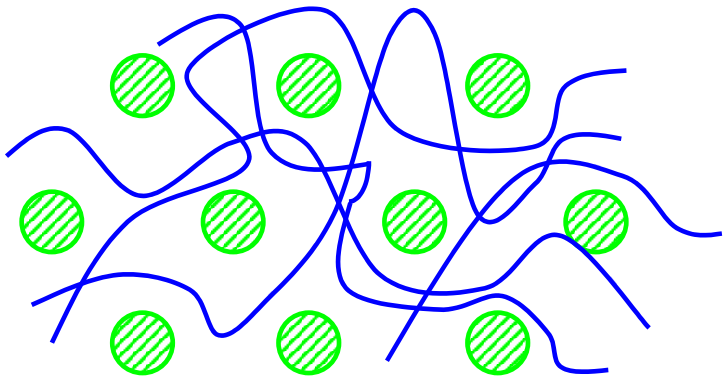


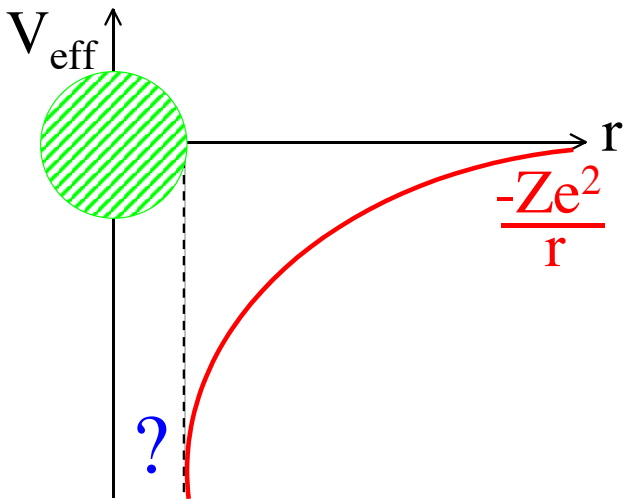
Density-functional theory $E = E[n] \quad n(\mathbf{r})$

$$\{-\nabla^2 + V_{\text{eff}}[n](\mathbf{r})\}\psi_i = \varepsilon_i \psi_i$$ One electron

$$V_{\text{eff}}[n](\mathbf{r}) = V_{\text{ext}}(\mathbf{r}) + V_{\text{H}}[n](\mathbf{r}) + V_{\text{xc}}[n](\mathbf{r})$$

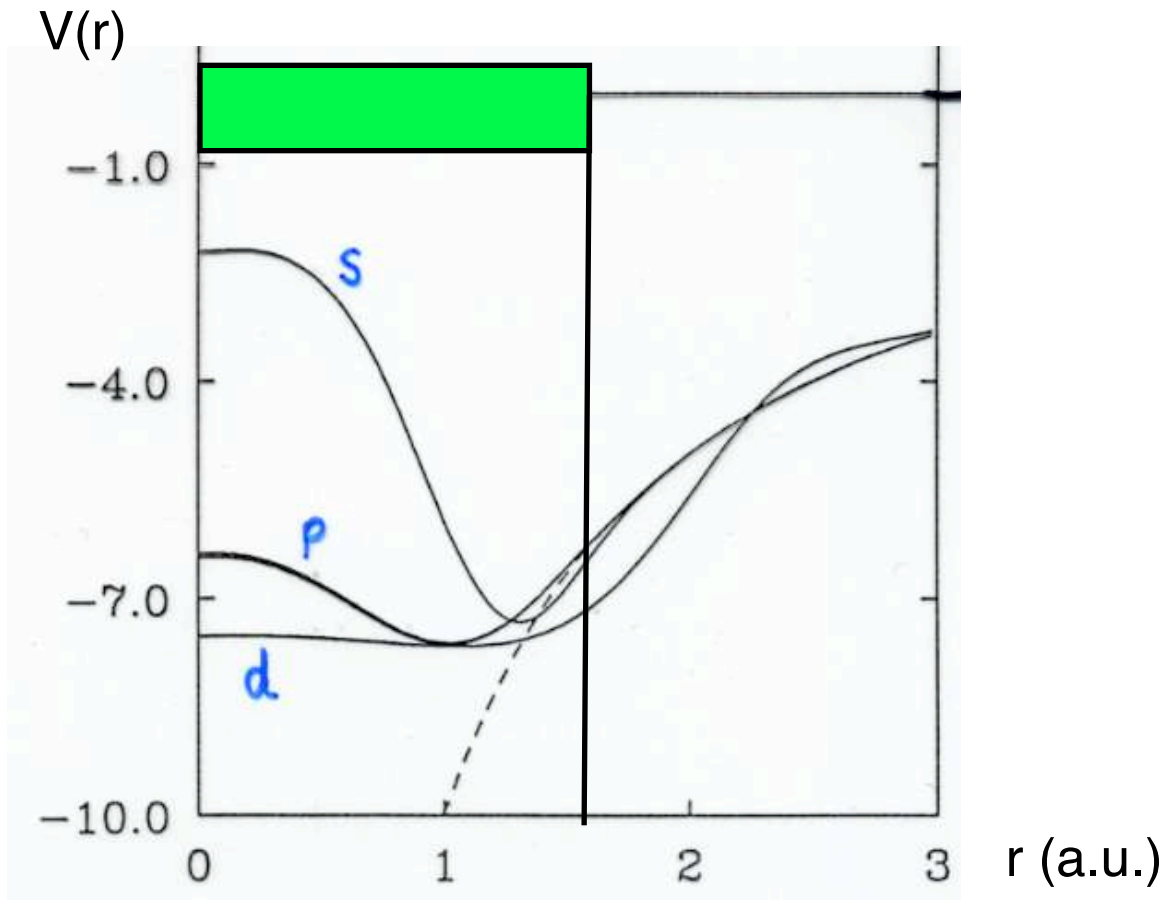
Internal electrons do not participate in the chemical bond





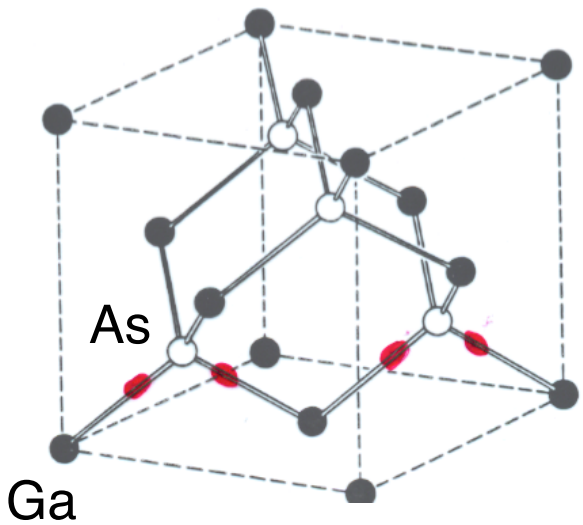
Effective potential for valence electrons

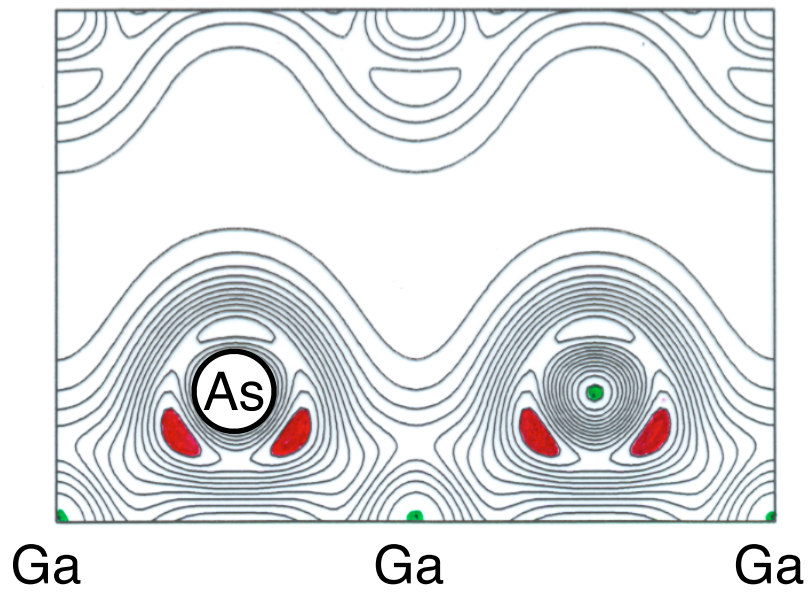
Pseudopotential

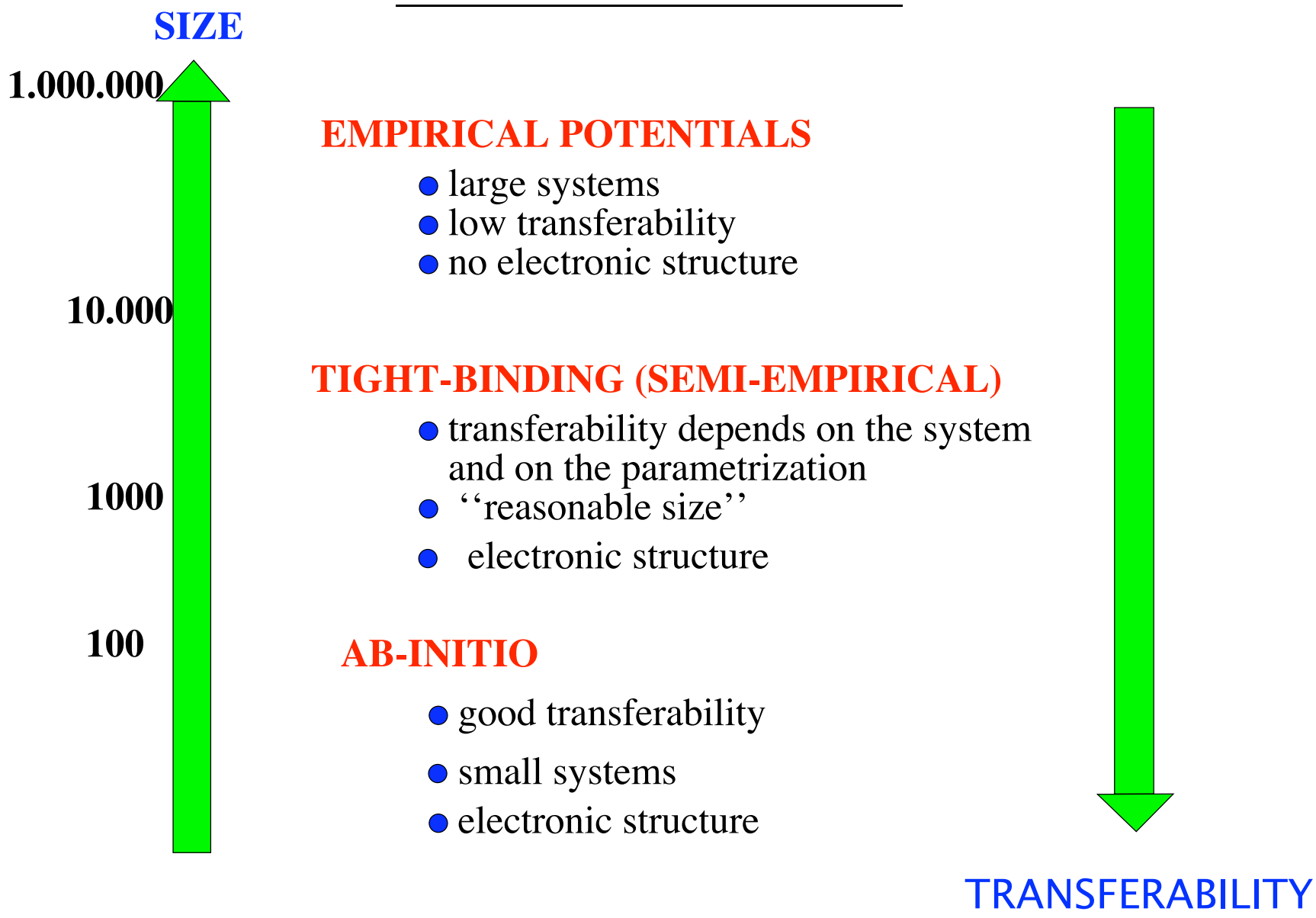


Output of the program

- Energy, forces, and stress for a given geometry
- Charge density, wave functions, band energies, and other low-level technical information






SIZE
1.000.000
10.000
1000
100
EMPIRICAL POTENTIALS
large systems
low transferability
no electronic structure
TIGHT-BINDING (SEMI-EMPIRICAL)
transferability depends on the system and on the parametrization
‘‘reasonable size’’
electronic structure
AB-INITIO
good transferability
small systems
electronic structure
TRANSFERABILITY

* *Calculation without Classic Standards is Dangerous.*
  A Computer is Incapable of Setting its own Standards.

* *By its Emphasis on Application of the Already Known, Computing can Delay Basic Discovery and thus Reduce the Field of Applications in the Future.*

* *Classic Theories used Inductive and Deductive Models.*
  Computing Encourages Floating Models.

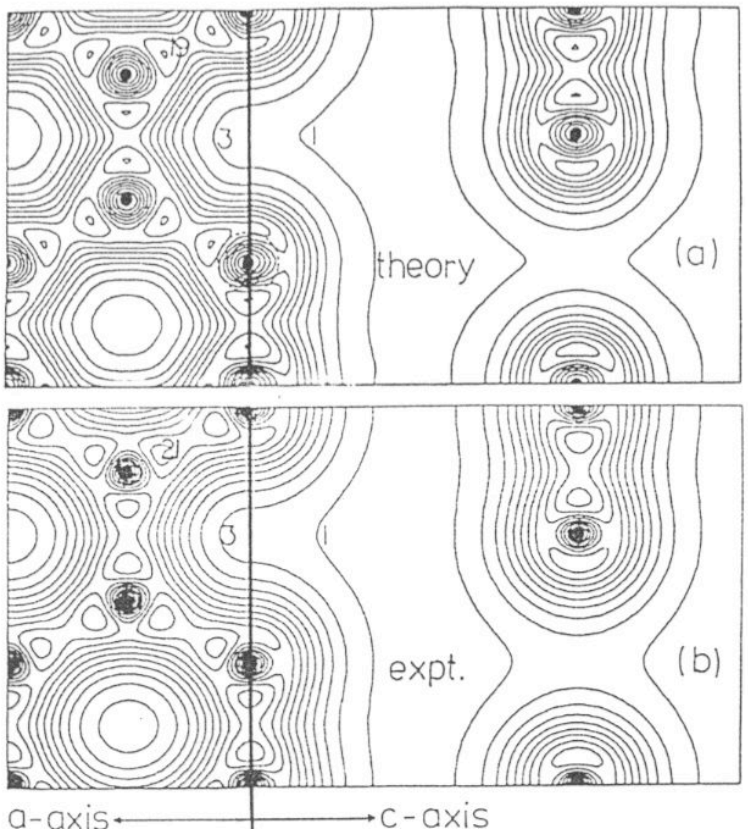
(Headings from the essay: "The Computer: Ruin of Science and Threat to Mankind", by Clifford Truesdell, in "An Idiot's Fugitive Guide to Science", Springer, 1984)

A simple model can shed more light on Nature's workings than a series of "ab-initio" calculations of individual cases, which, even if correct, are so detailed that they hide reality instead of revealing it. ...A perfect computation simply reproduces Nature, it does not explain it.

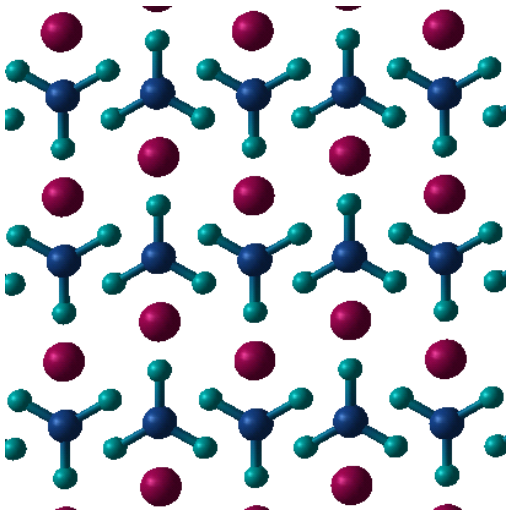
(P.W. Anderson)

Uses in materials science

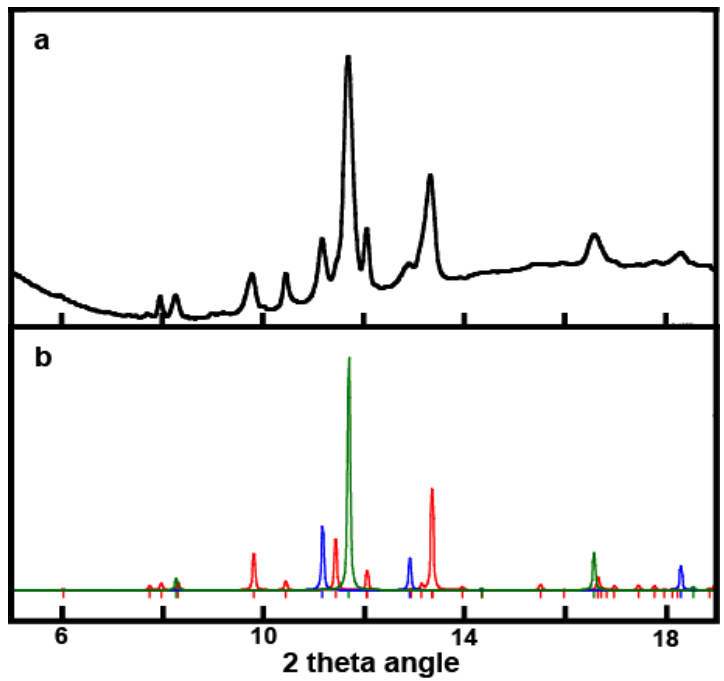
- Exploration and prediction, simulating experiments difficult or impossible in the laboratory.
- Clarification/complement to experimental information by means of the precise control of simulation conditions. (The computer is the ultimate control machine)
- Design of materials with desired properties. Reduction of the “trial and error” loop.
- Parametrization of simpler models



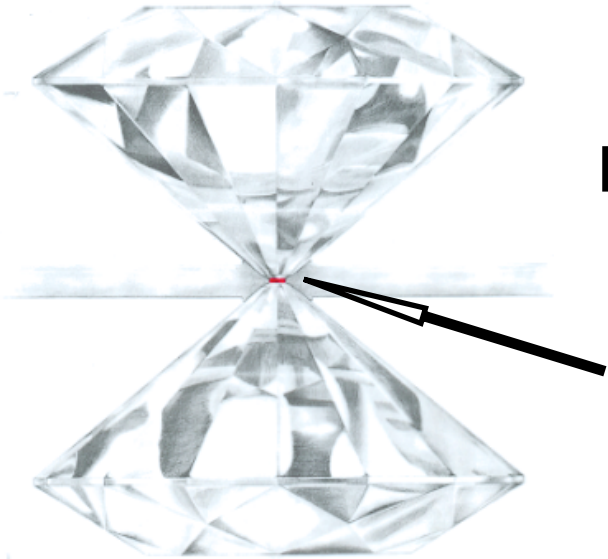
Calculation of electronic charge density
(Simulation of an X-ray experiment)



Synthetic diffraction diagram



High-pressure experiment

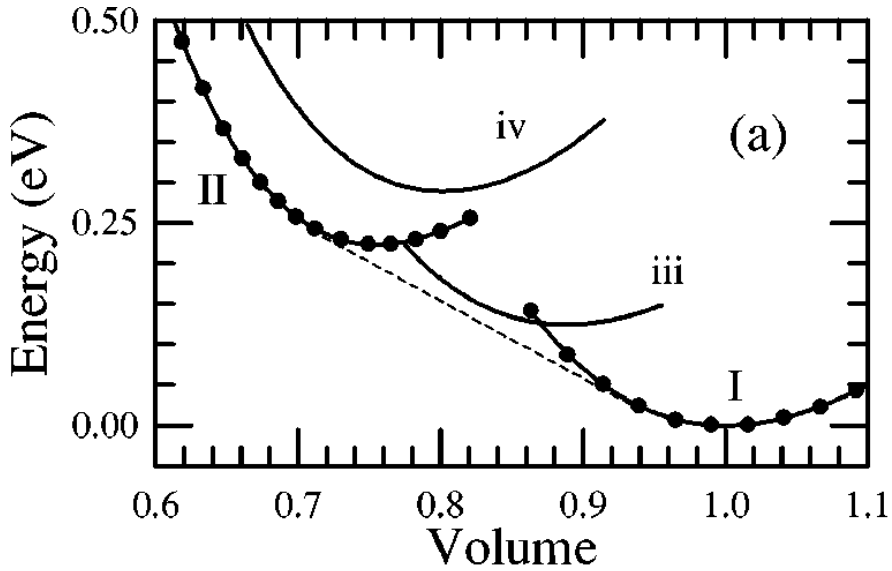


Diamond-anvil cell

Theoretical treatment

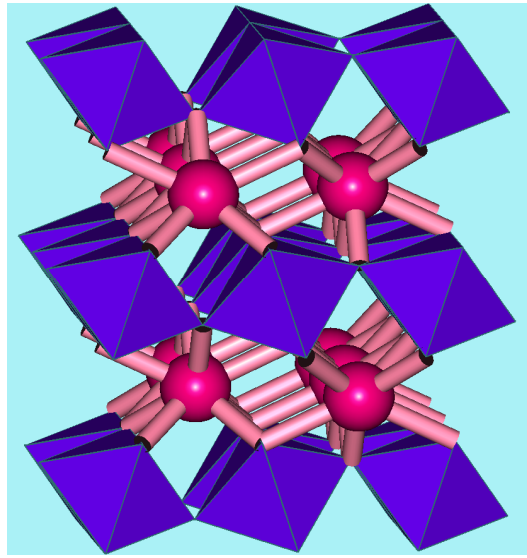
$$E = E(V), \quad p = -\frac{dE}{dV}, \quad p = p(V)$$

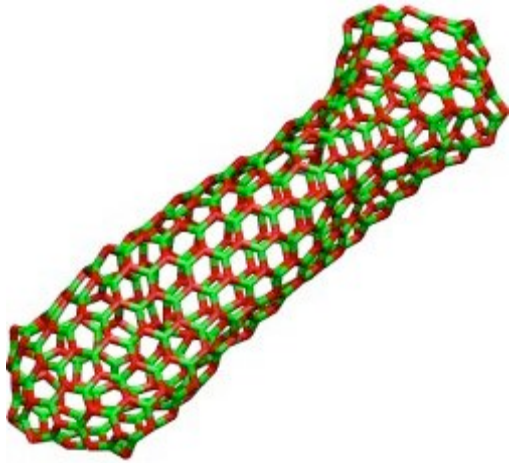
Equations of State
Phase transitions



Post-perovskite phase of MgSiO3

Oganov et al, Nature (2004)





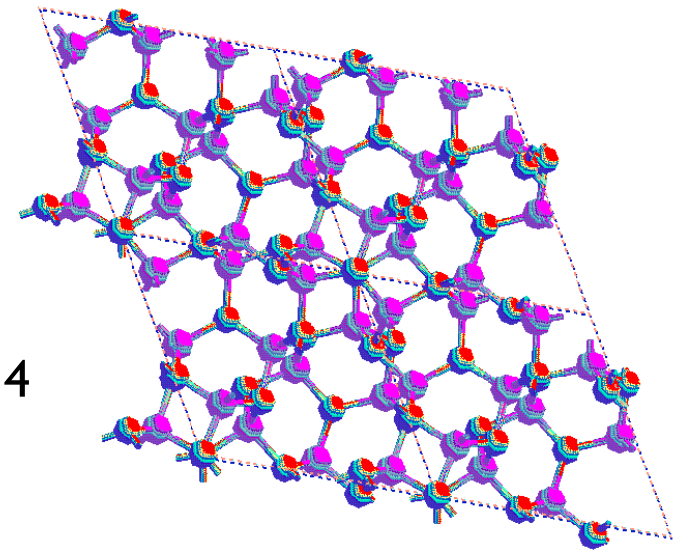
Prediction of BN nanotubes

Rubio, Corkill, Cohen, PRB (1994)

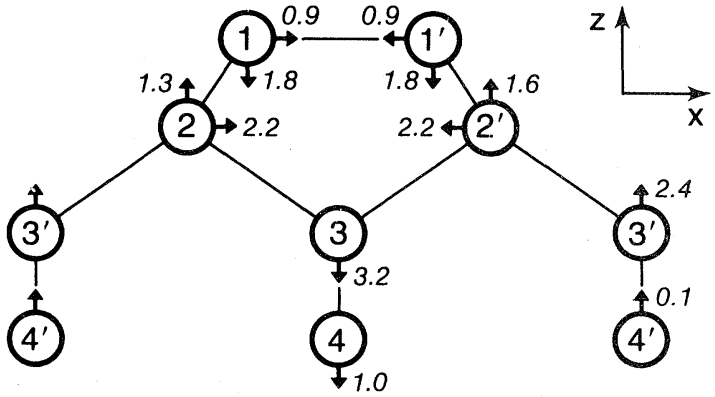
Proposal for a super-hard material

Liu, Cohen, Science (1989)

C_3N_4

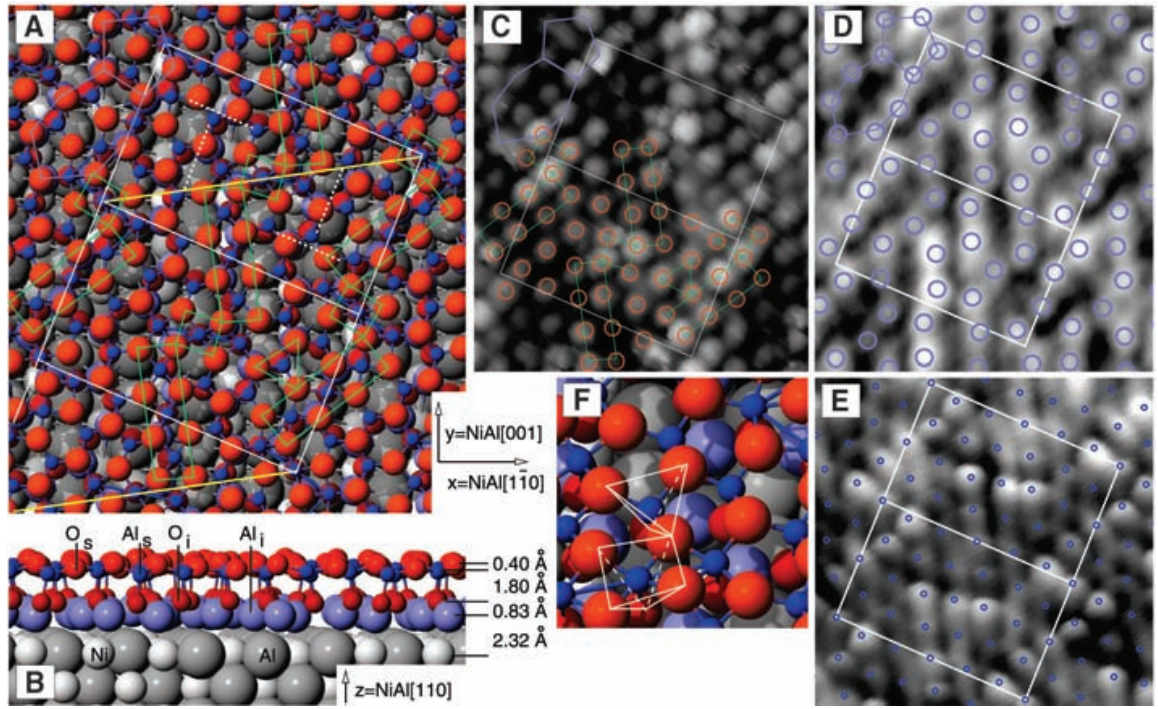


Surfaces



First work on Si(100)

Yin, Cohen, PRB (1981)

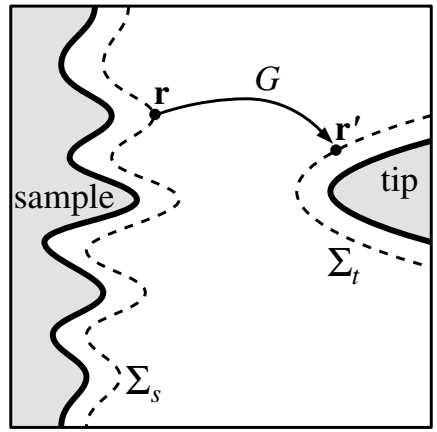


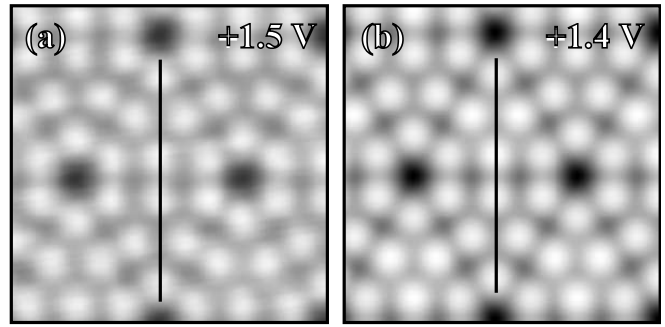
Oxidation of NiAl

Kresse et al, Science (2005)

New method for the simulation of STM images

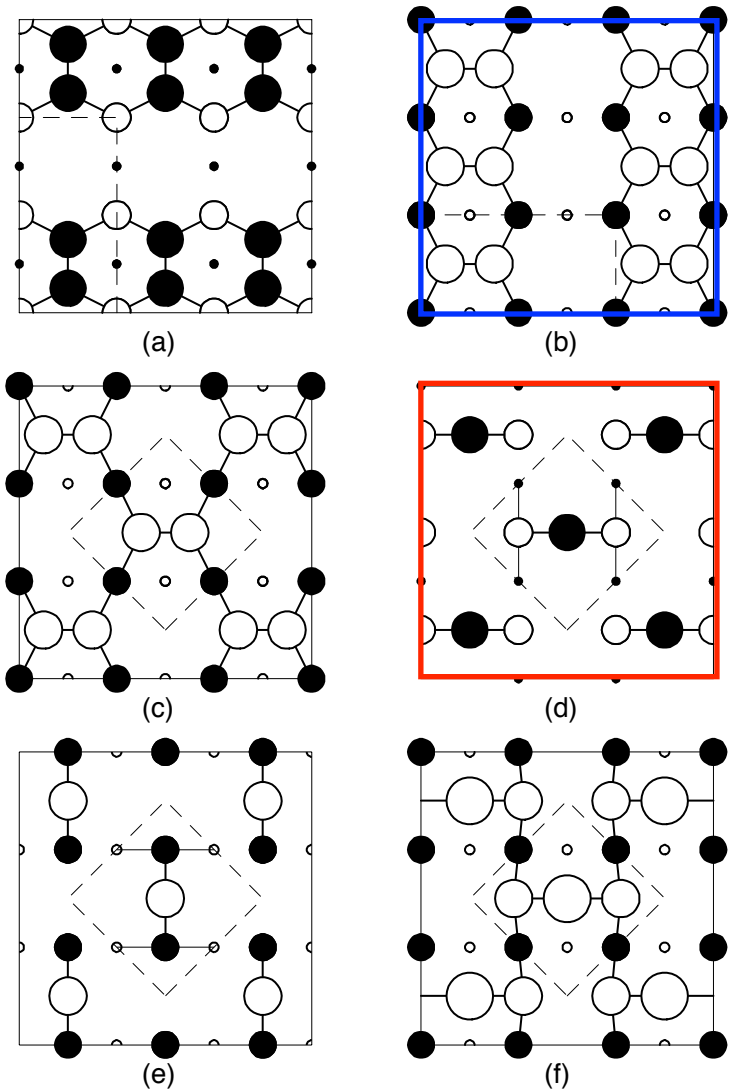
Paz et al, PRL (2005)

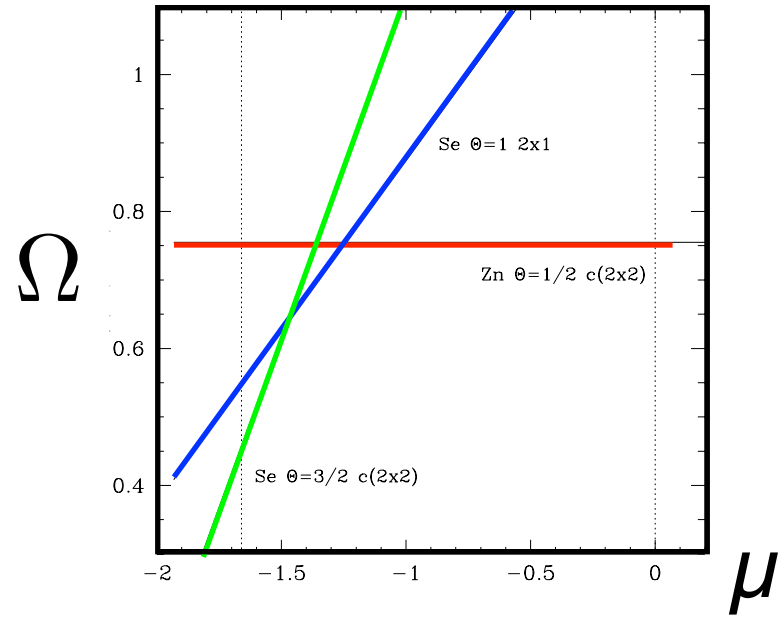




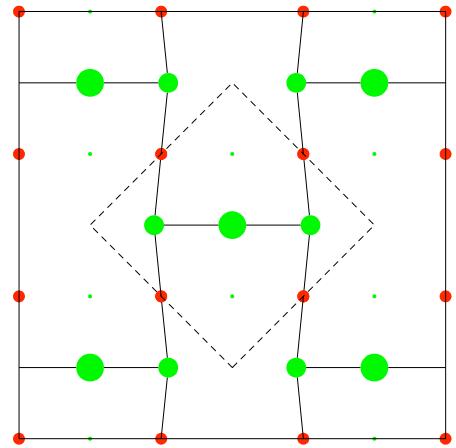
Exp Theory

Clarification of the structure and prediction of a new surface phase of ZnSe



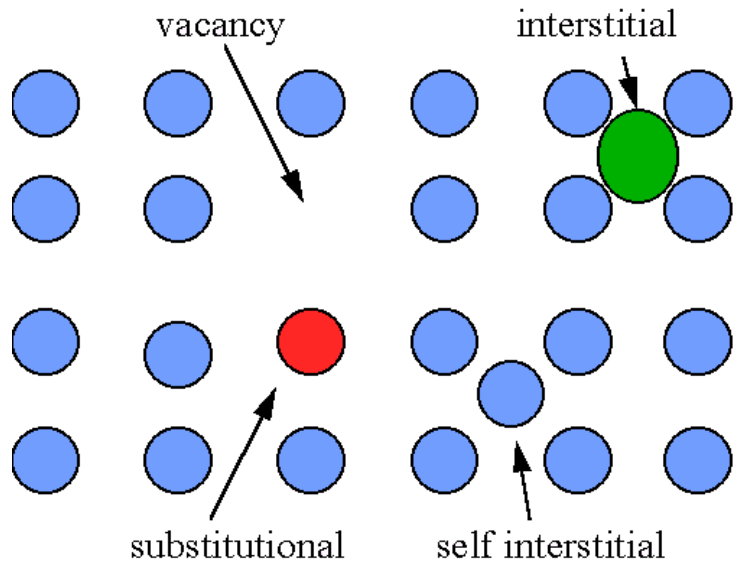


Garcia, Northrup, APL (1994)



Precise control of simulation conditions

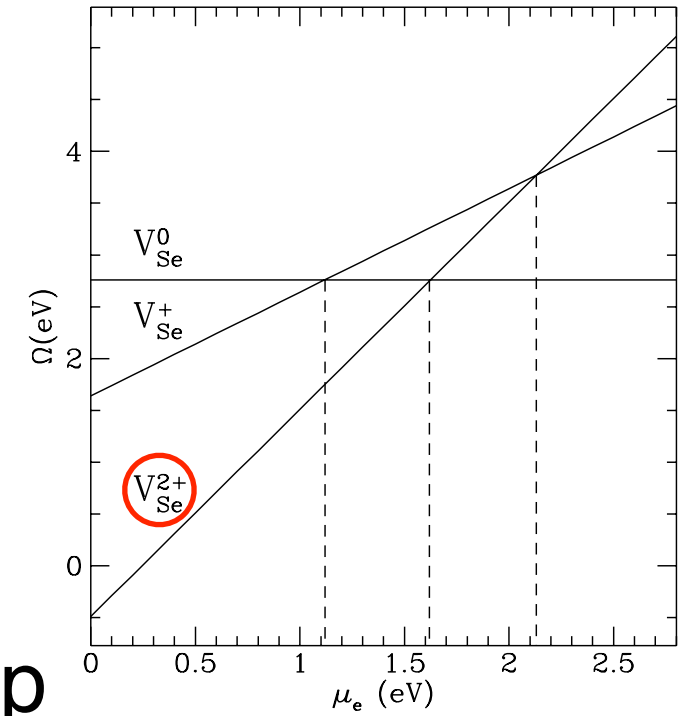
Point defects:
Great experimental complexity



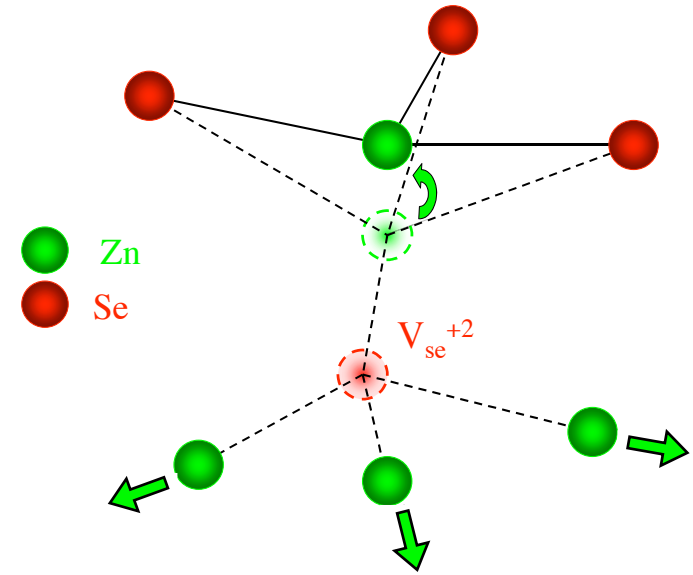
In a calculation they can be “prepared” (isolated or in complexes) and their energies of formation and bonding computed

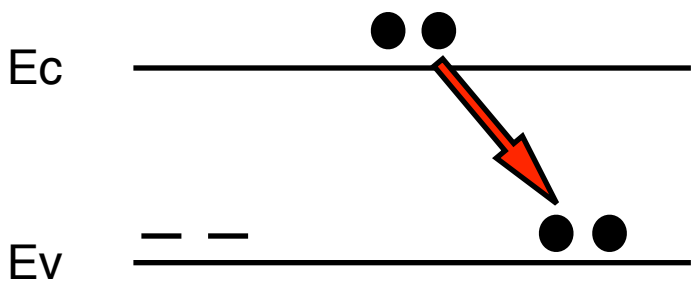
⇨ Help in the analysis of experiments, and direct testing of hypothesis

Mechanism for p-doping saturation in ZnSe



p n

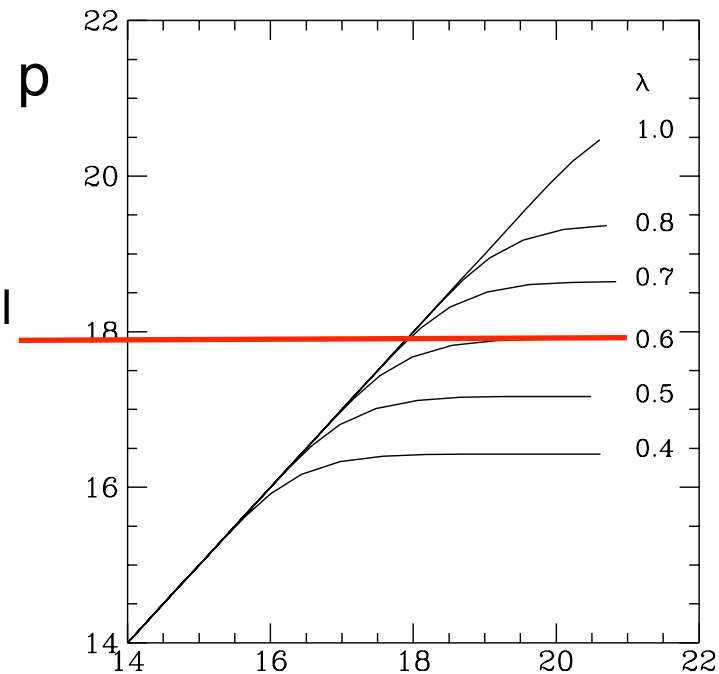




Compensation of two holes by V_{Se}^{+2}

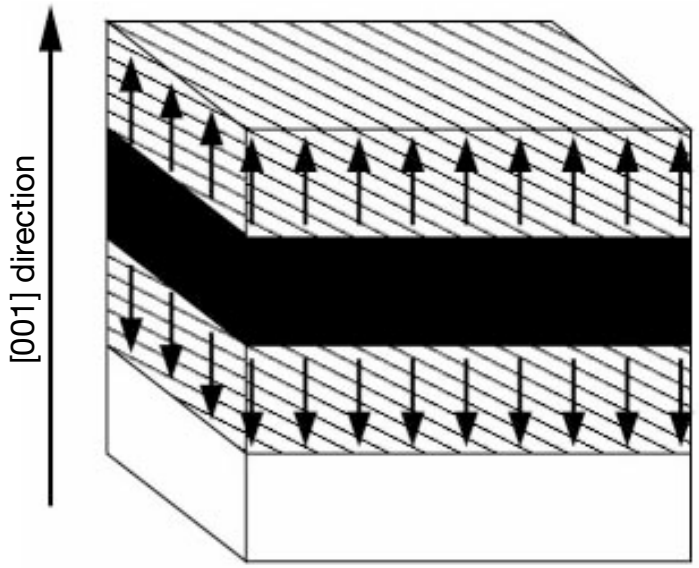
Experimental saturation level

log p



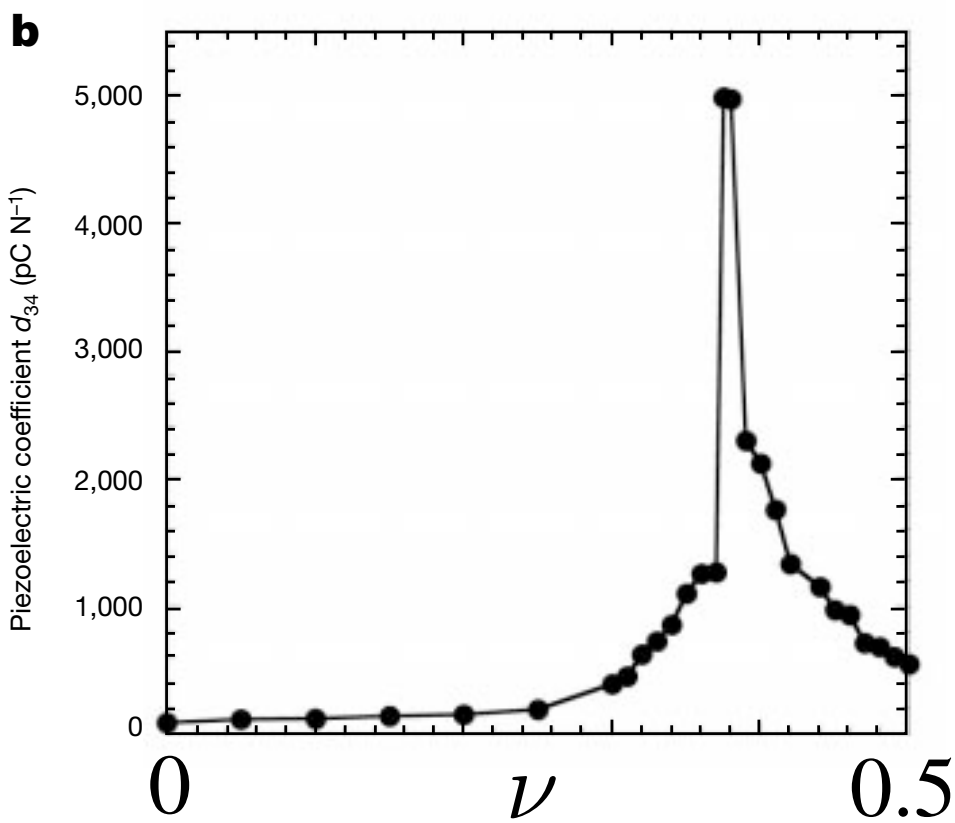
Garcia, Northrup, PRL (1995)

$$Pb(Sc_xNb_{1-x})O_3$$



$$x = 0.5 - \nu$$

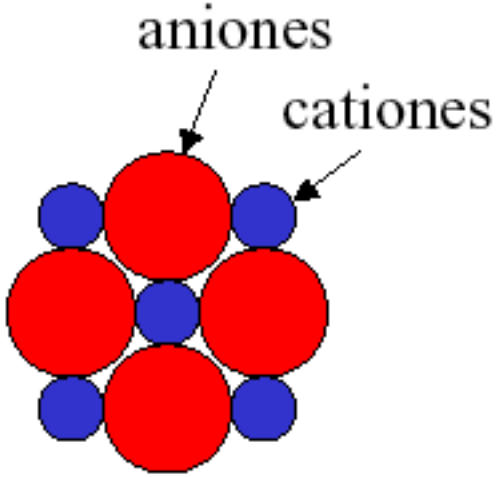
$$x = 0.5 + \nu$$



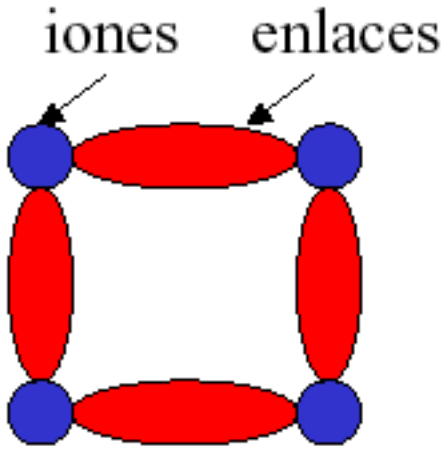
Design of materials with optimized piezoelectric response

George, Iñiguez, Bellaiche
Nature 413, 54 (2001)

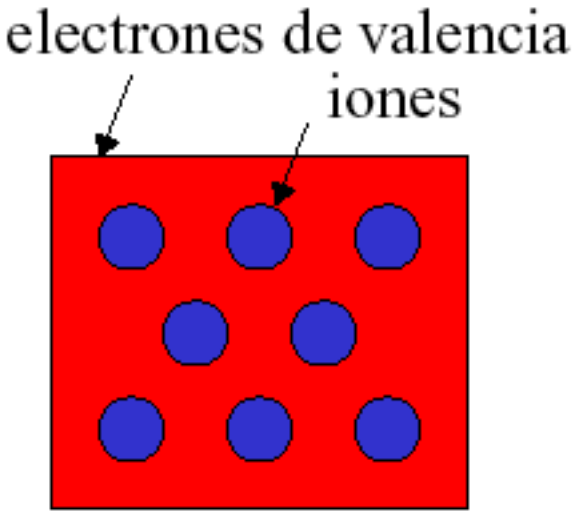
What of Anderson’s claim?
Do we understand more?



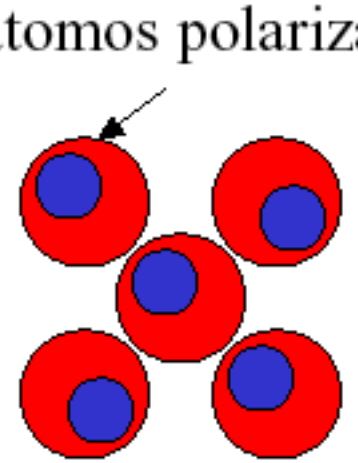
Iónico



Covalente

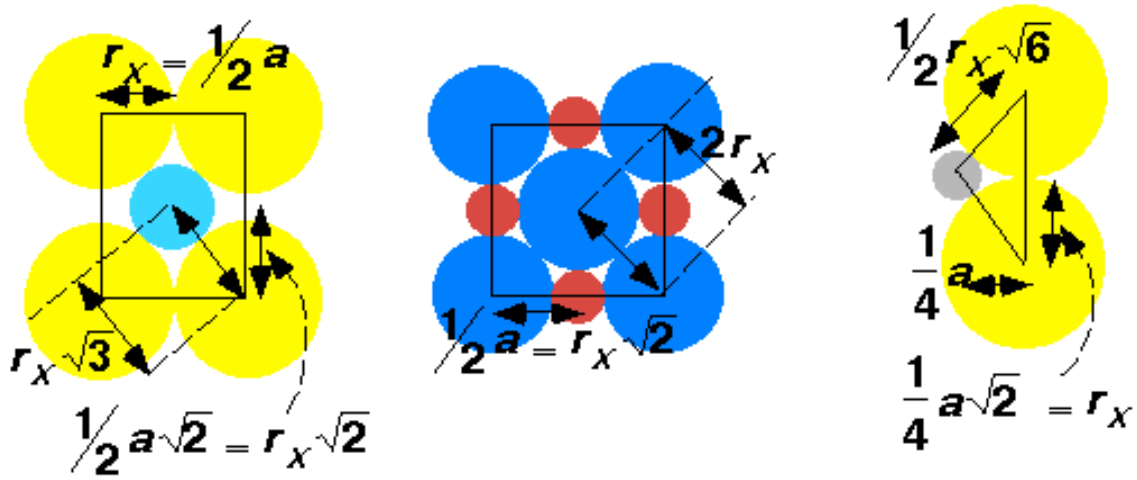


Metálico

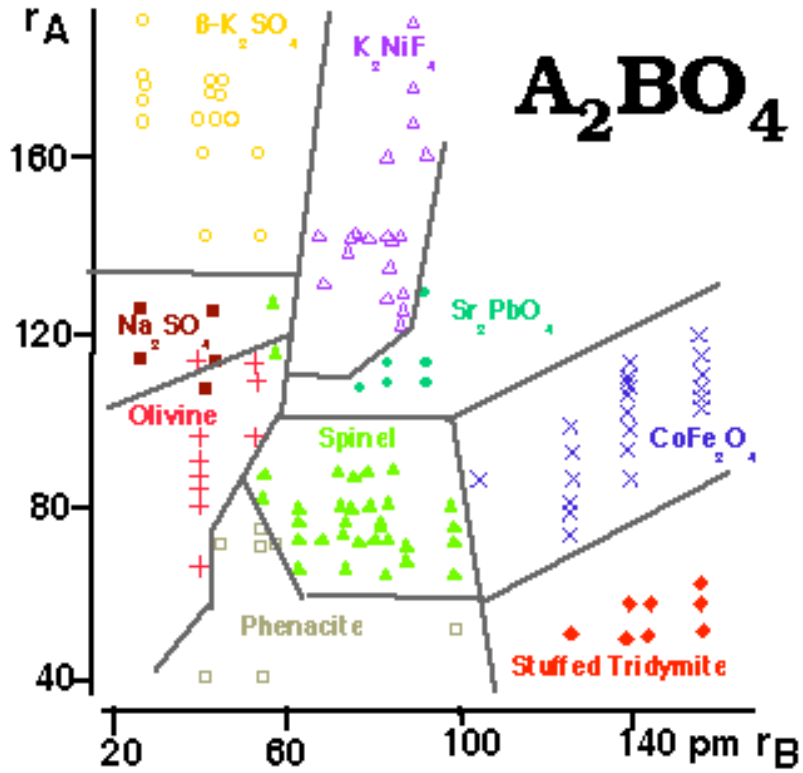


Molecular

Electronegativity difference is enough!



Classification involving ionic radii



Simulation as a route for comprehension (1)

It provides more "experimental data" to construct theoretical models Exploration

Can serve to test hypotheses in optimal conditions.

Simulation as a route for comprehension (II)

Low-level
theoretical ingredients

Charge density
Wave functions
Energy

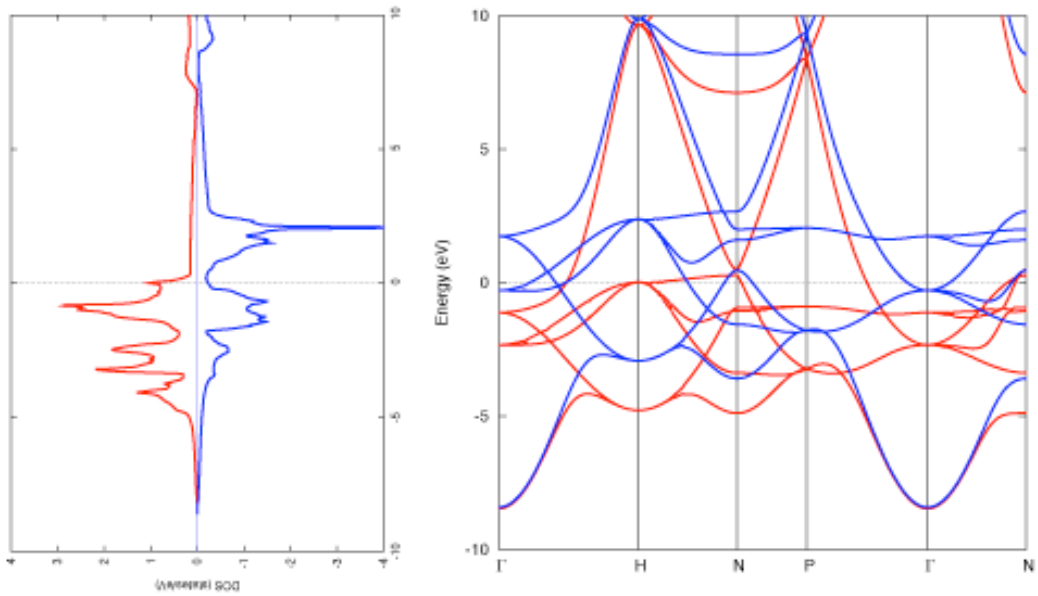
High-level
physical concepts

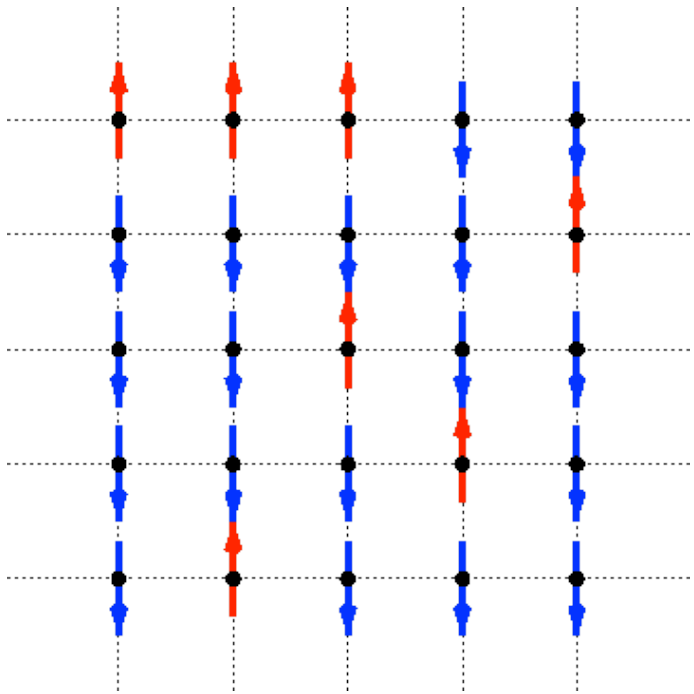
Electronegativity
Bonding
Parametrization of
simple models

One can use first-principles methods to compute **parameters** for simple but relevant and realistic models

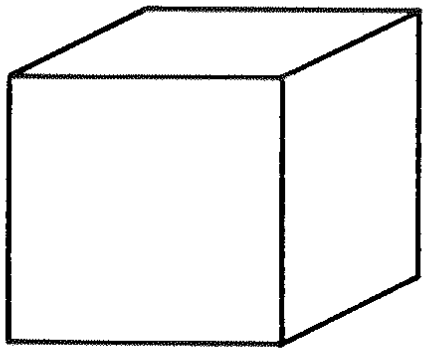
Parametrization of a Heisenberg model from the electronic structure.

Relevant for magnetic properties

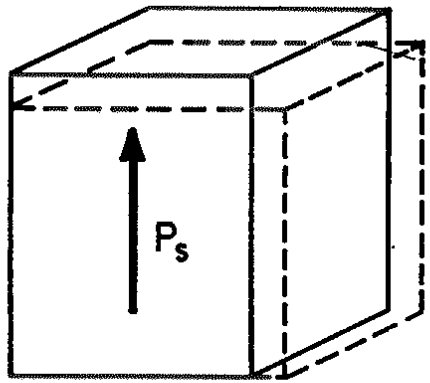




Ferroelectricity

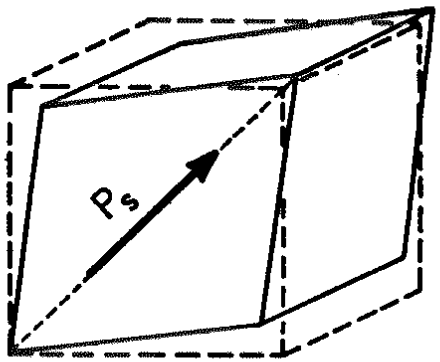


Cubic

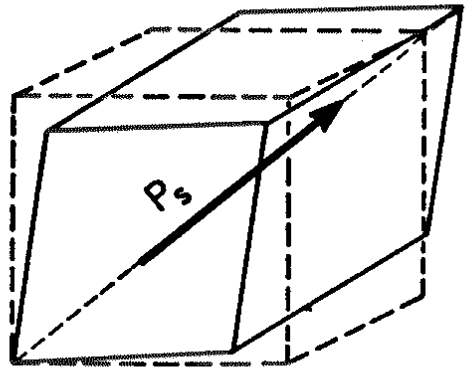


Tetragonal

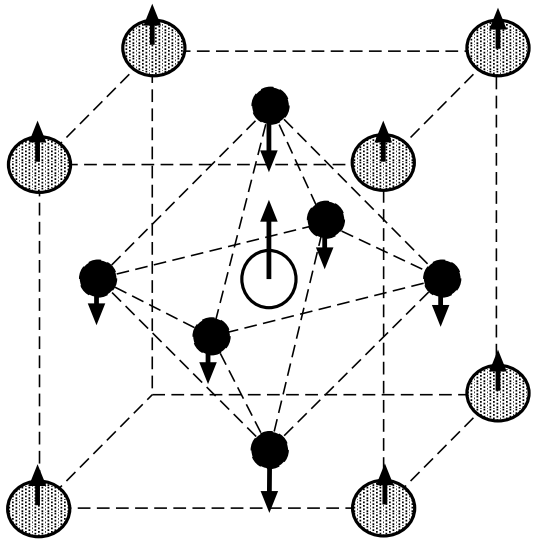
$BaTiO_3$

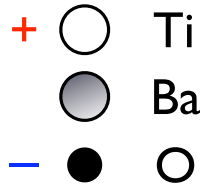


Orthorhombic

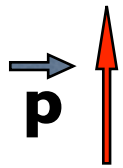


Rhombohedral

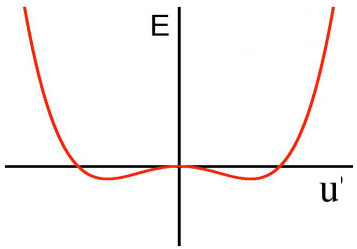




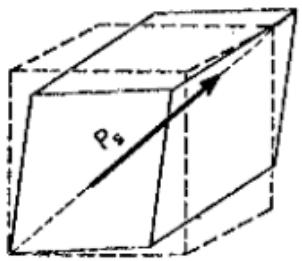
Basic distortion involved in ferroelectricity (soft mode)



Relevant degree of freedom

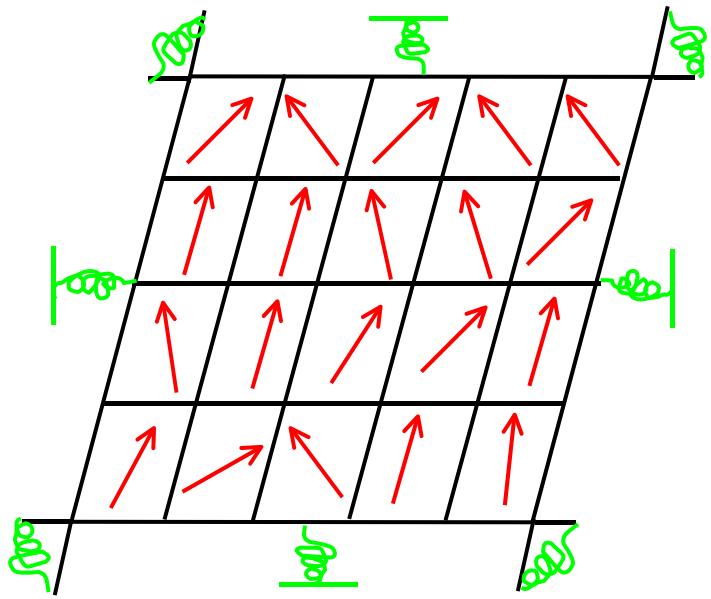


Local mode u

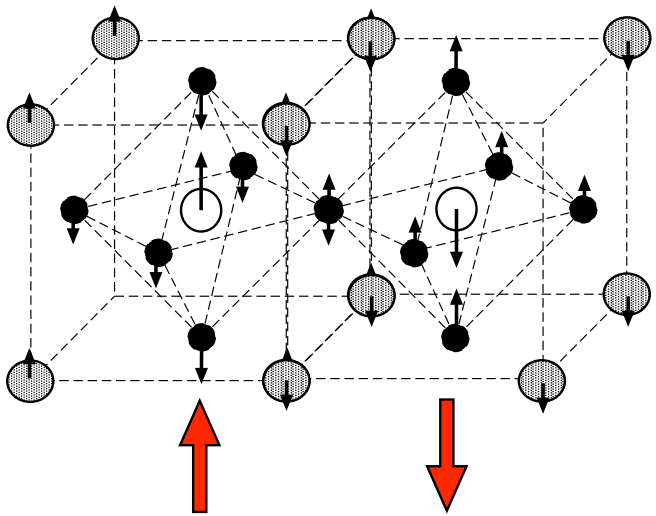


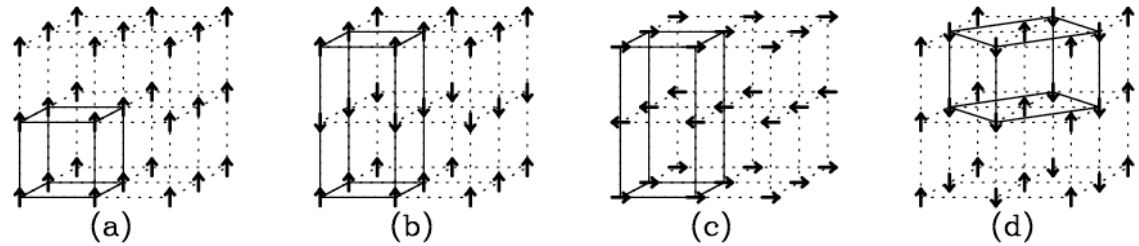
Lattice Strain

Model system



Zhong, Vanderbilt, Rabe, PRL 73, 1861 (1994)

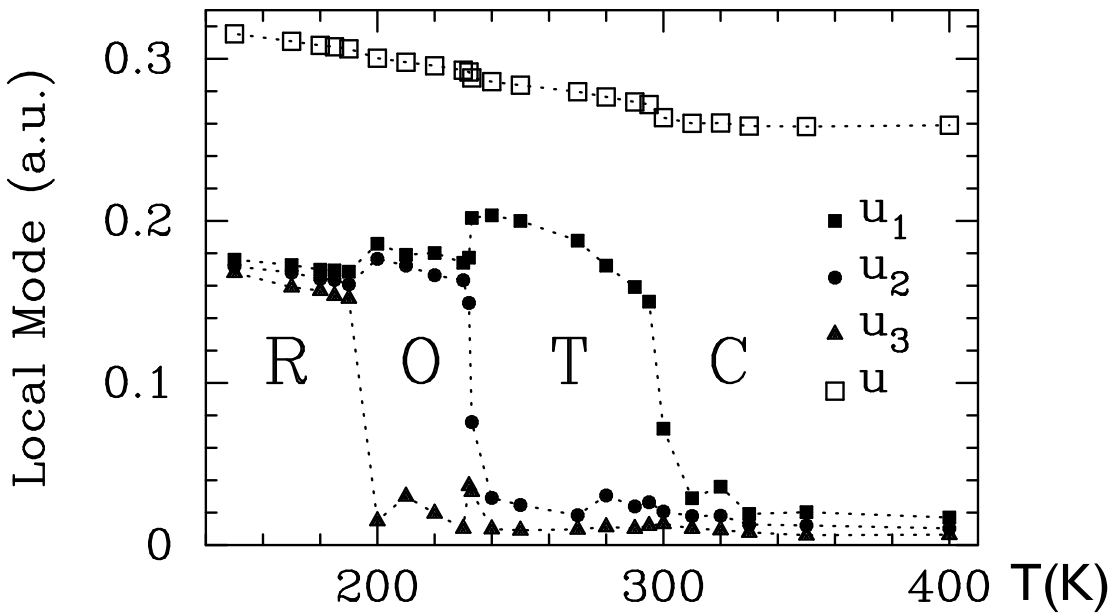


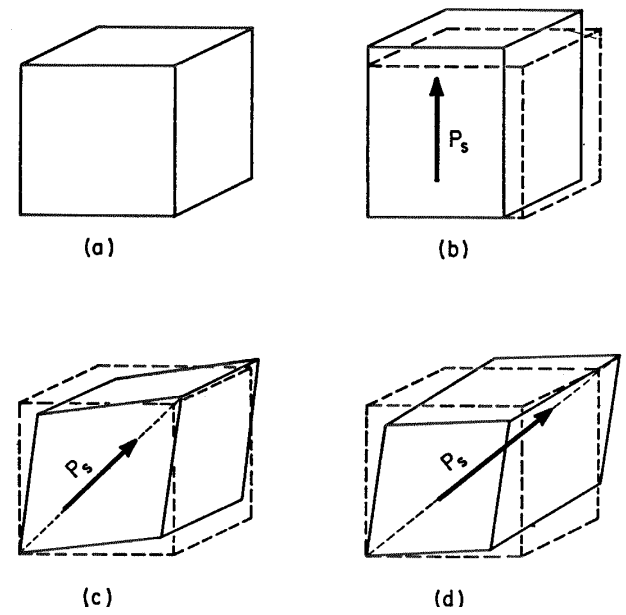


$$E_{\text{short}}(\{\mathbf{u}_i\}) = \frac{1}{2}\sum_{i\neq j}\sum_{\alpha\beta} J_{ij,\alpha\beta}u_{i\alpha}u_{j\beta}$$

Effective-Hamiltonian parametrized ab-initio

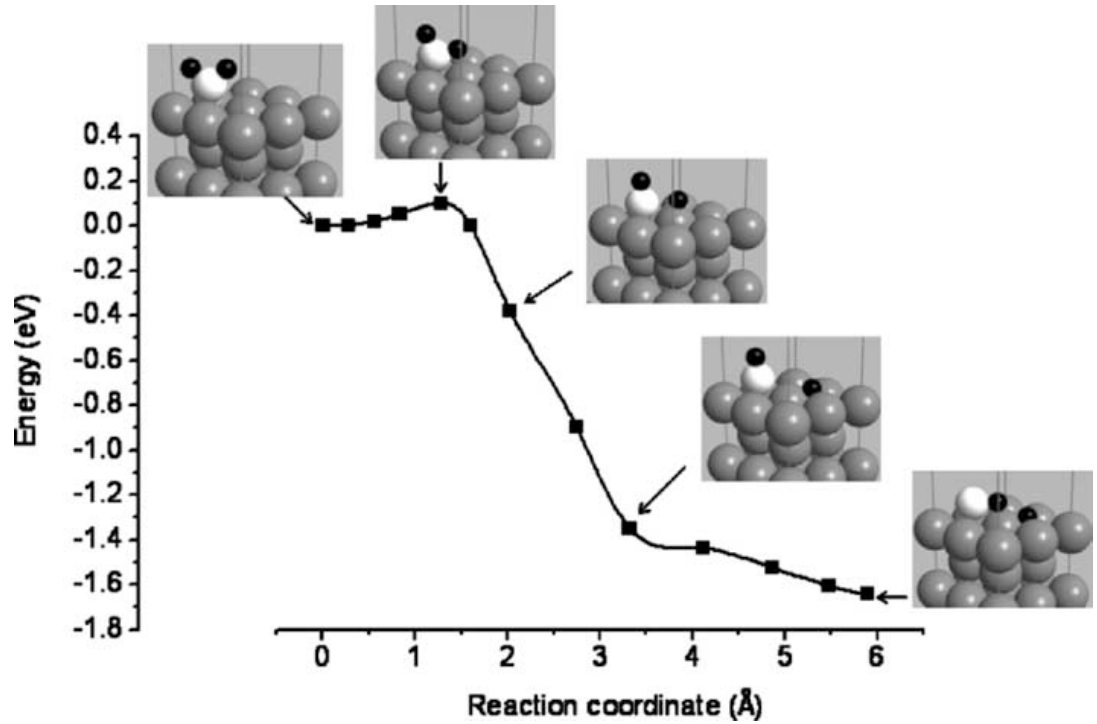
Phase transition sequence obtained from Monte Carlo simulations



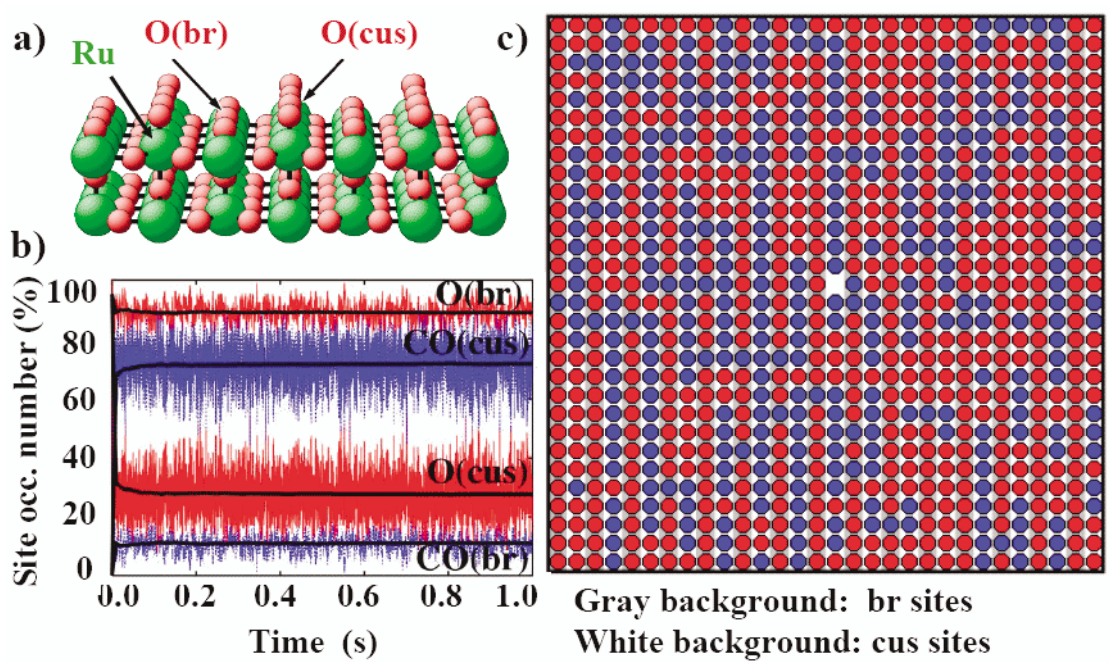


Disociation of H_2S in Fe(110)

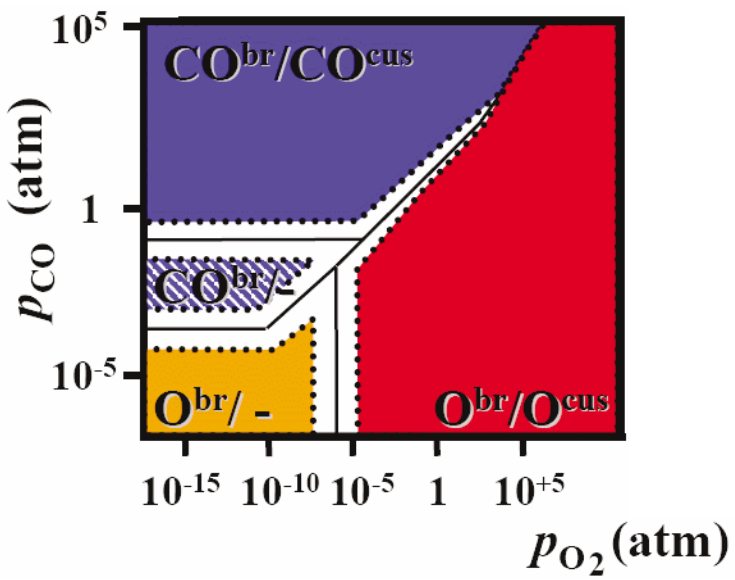
Jiang, Carter, Surf. Sci (2005)



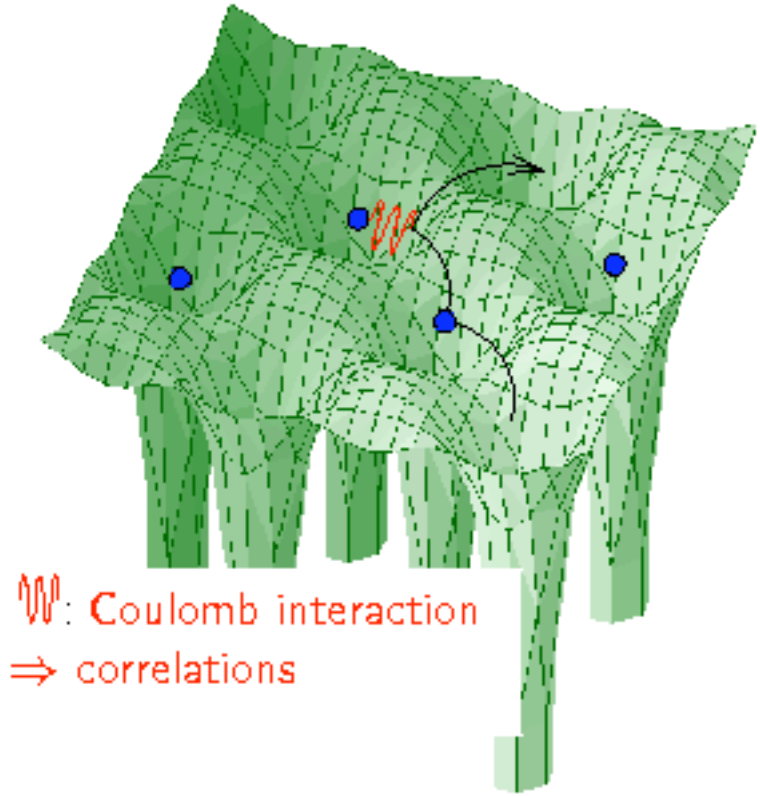
Kinetic-Monte Carlo method for catalysis -- parametrization

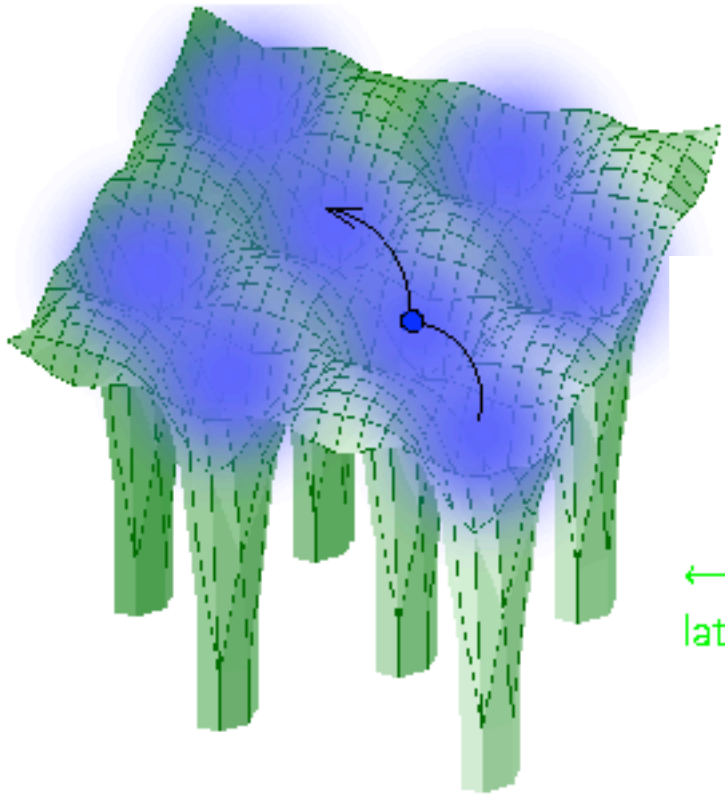


Reuter et al, PRL (2004)



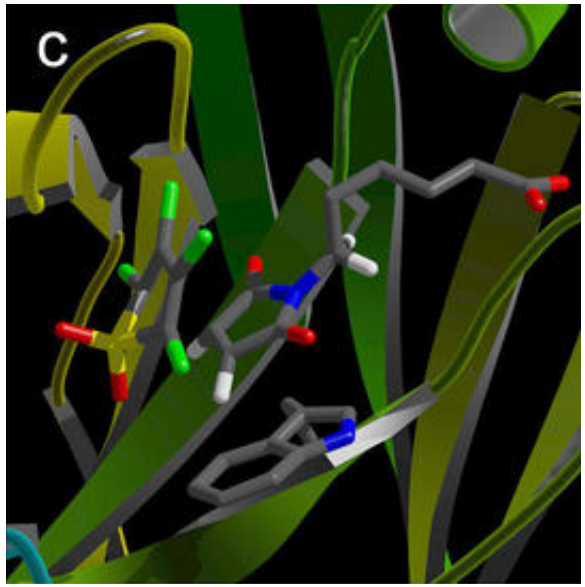
Challenges





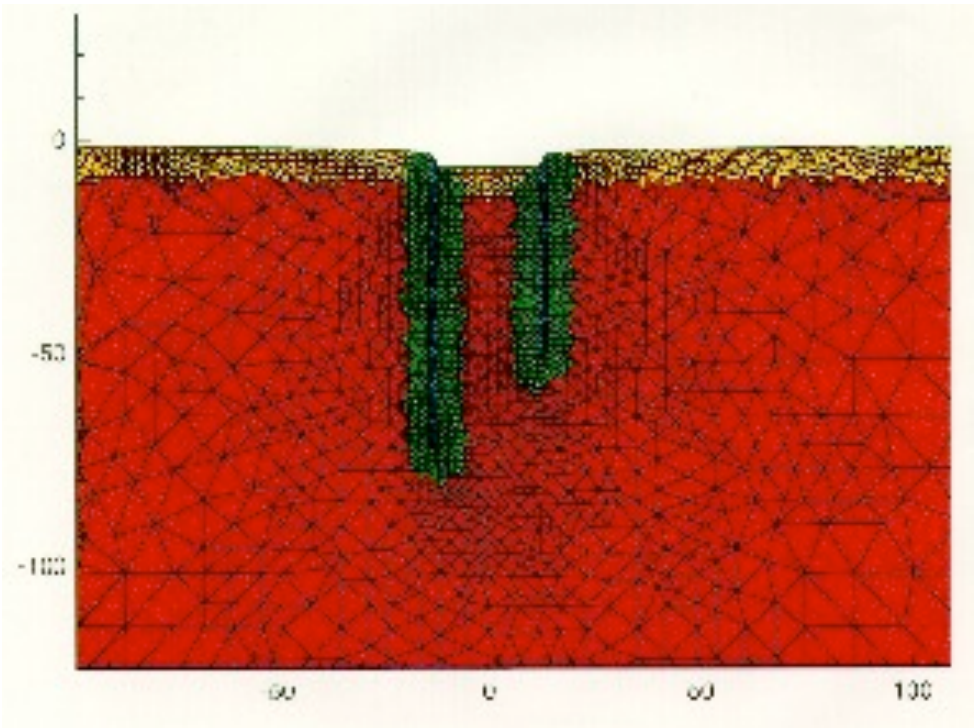
Better treatment of electronic correlation,
essential to describe localized states
in transition metals and rare earths

Hybrid methods to bridge length scales



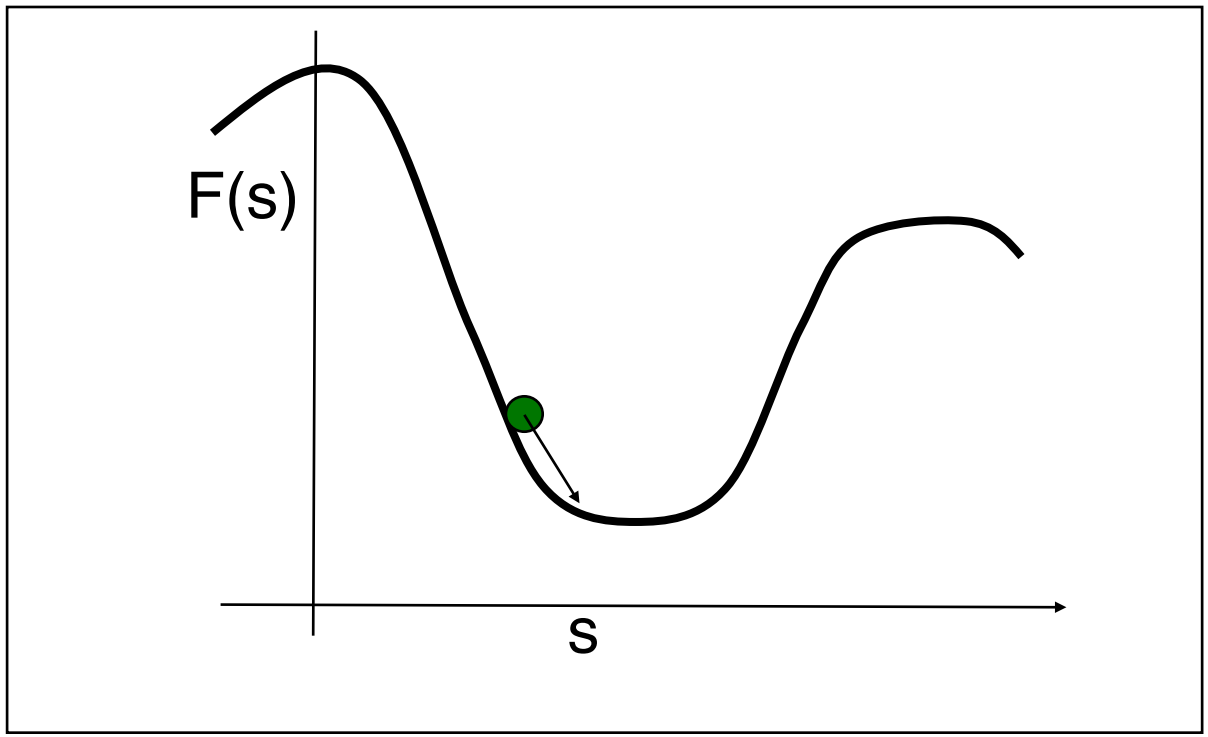
QM-MM: Precise treatment (QM) of a special part of the system. Rest treated at a lower level of quality.

Matching of atomistic methods with the continuum approximation



Escaping free-energy minima

Phase transition mechanisms, new crystal structures



Metadynamics

(Laio & Parrinello, 2002; Martonak et al., 2003)

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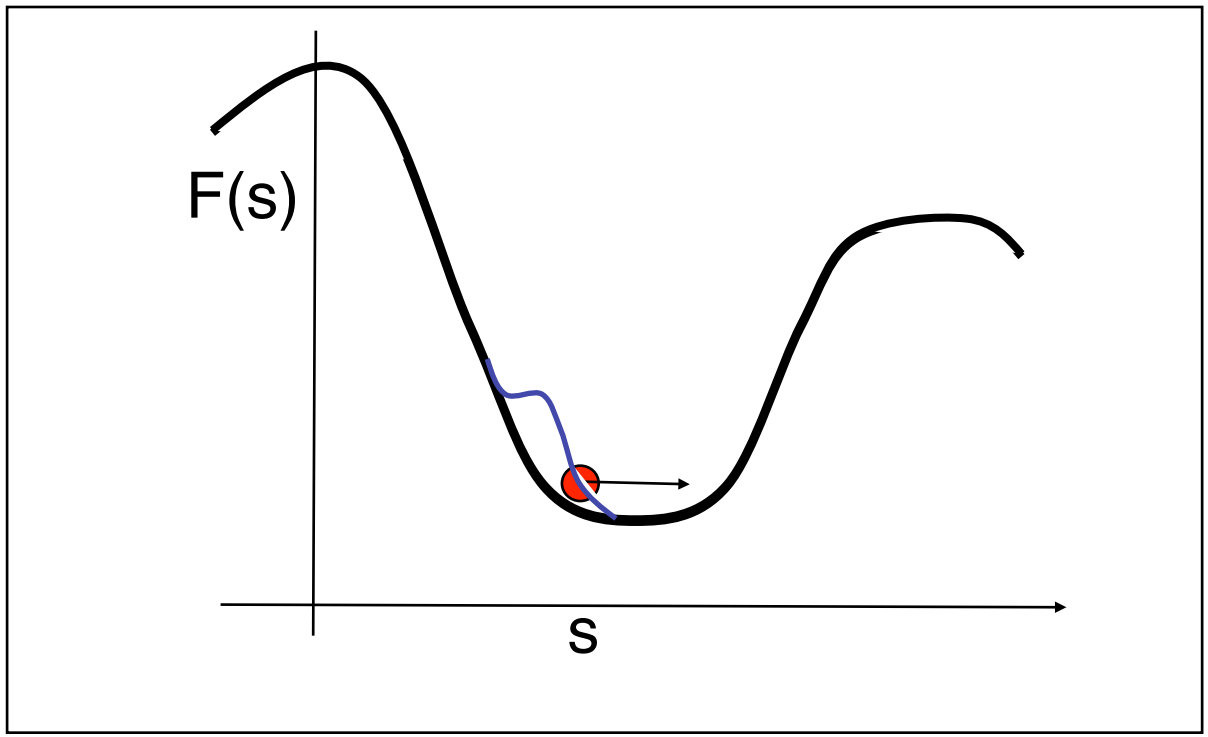

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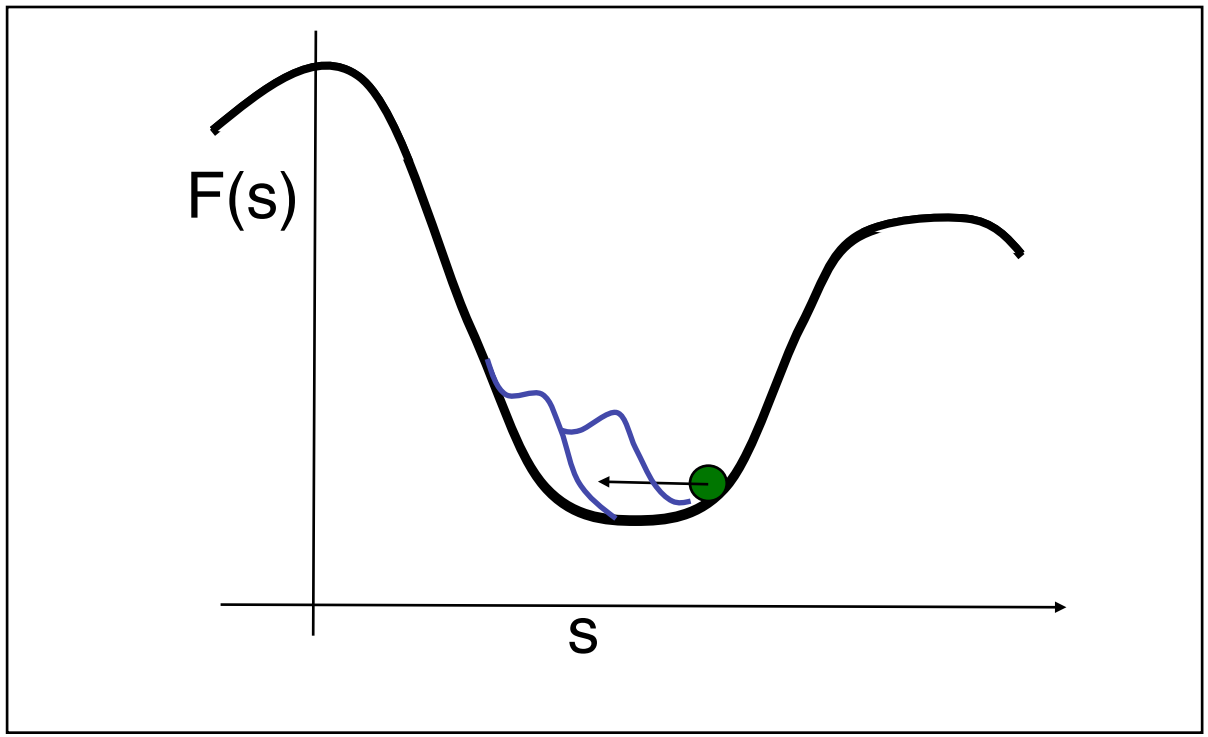

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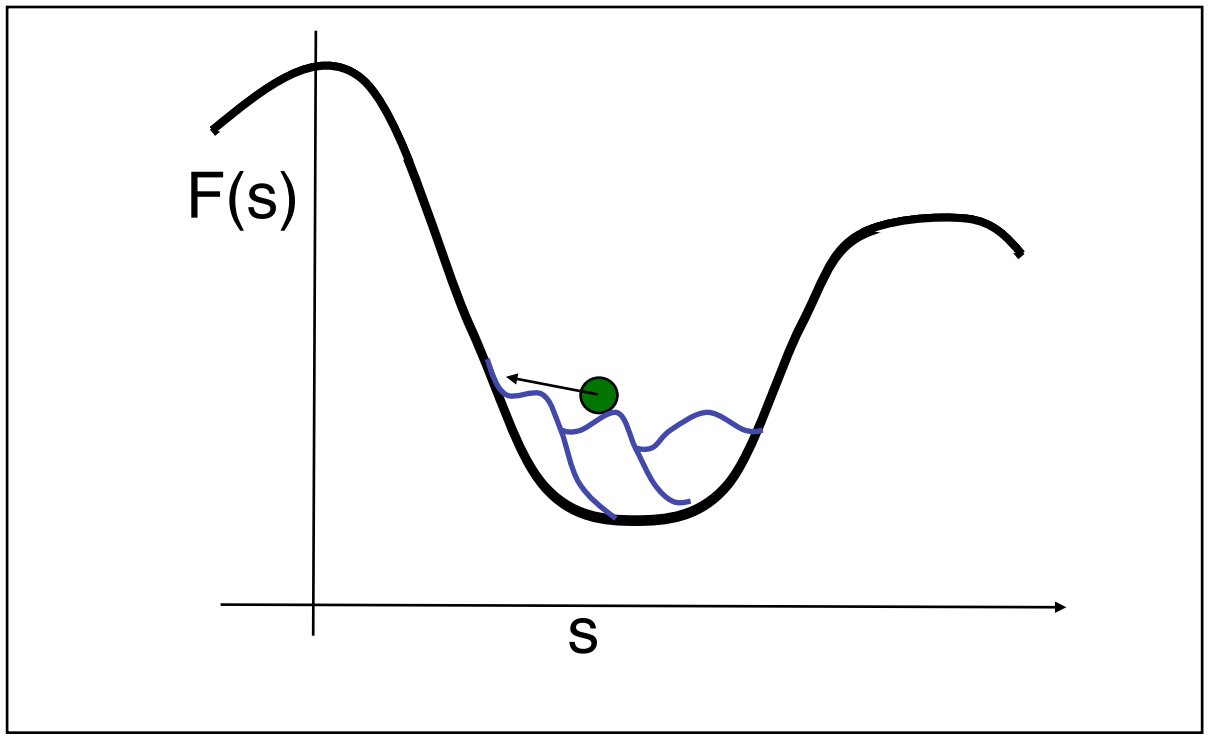

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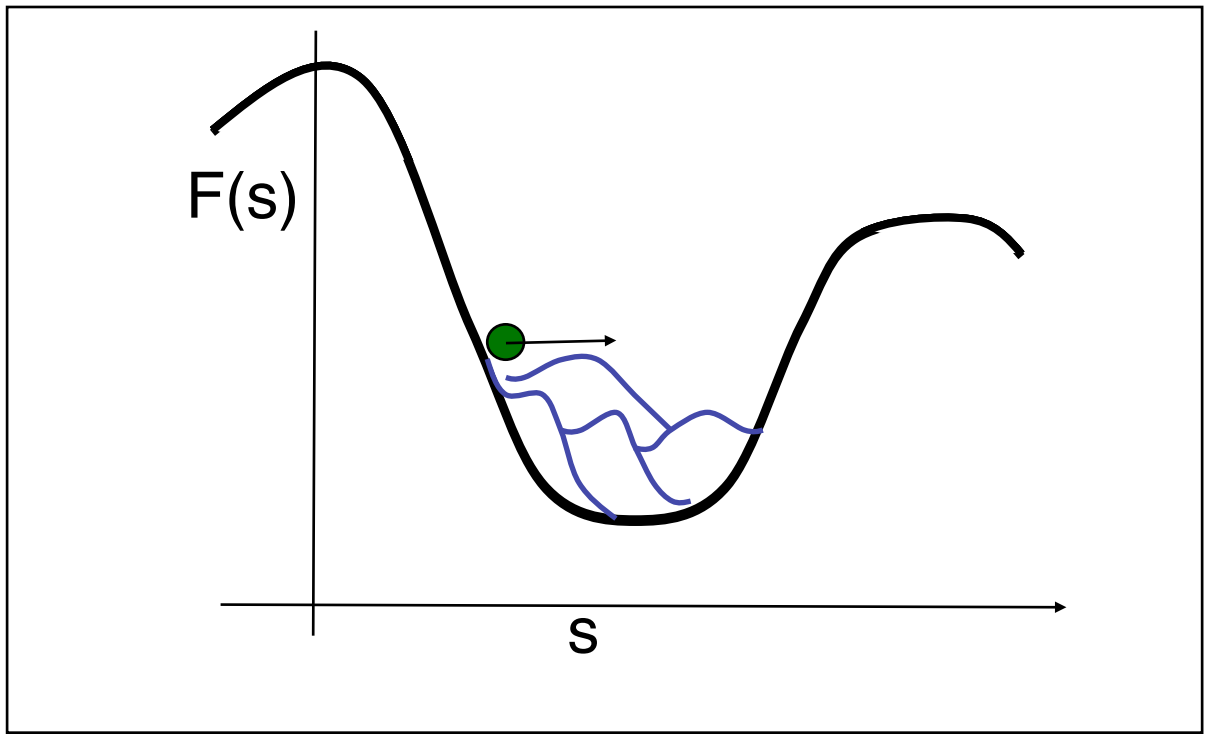

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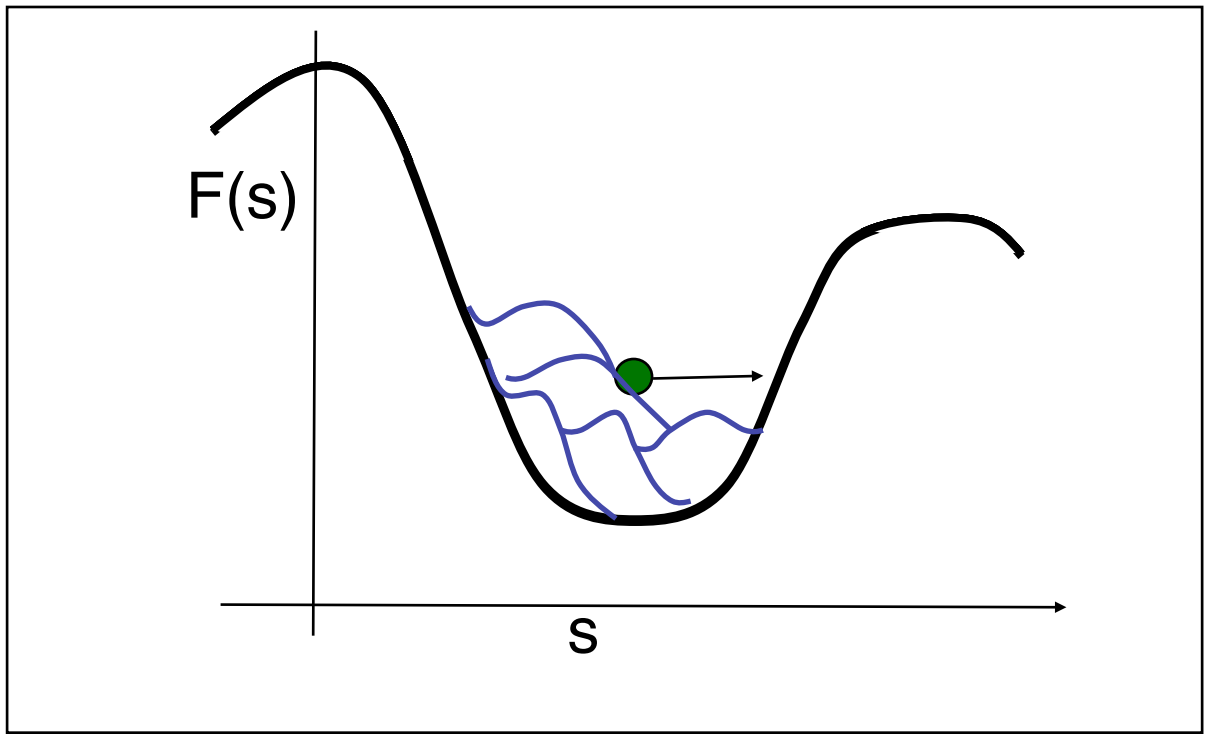

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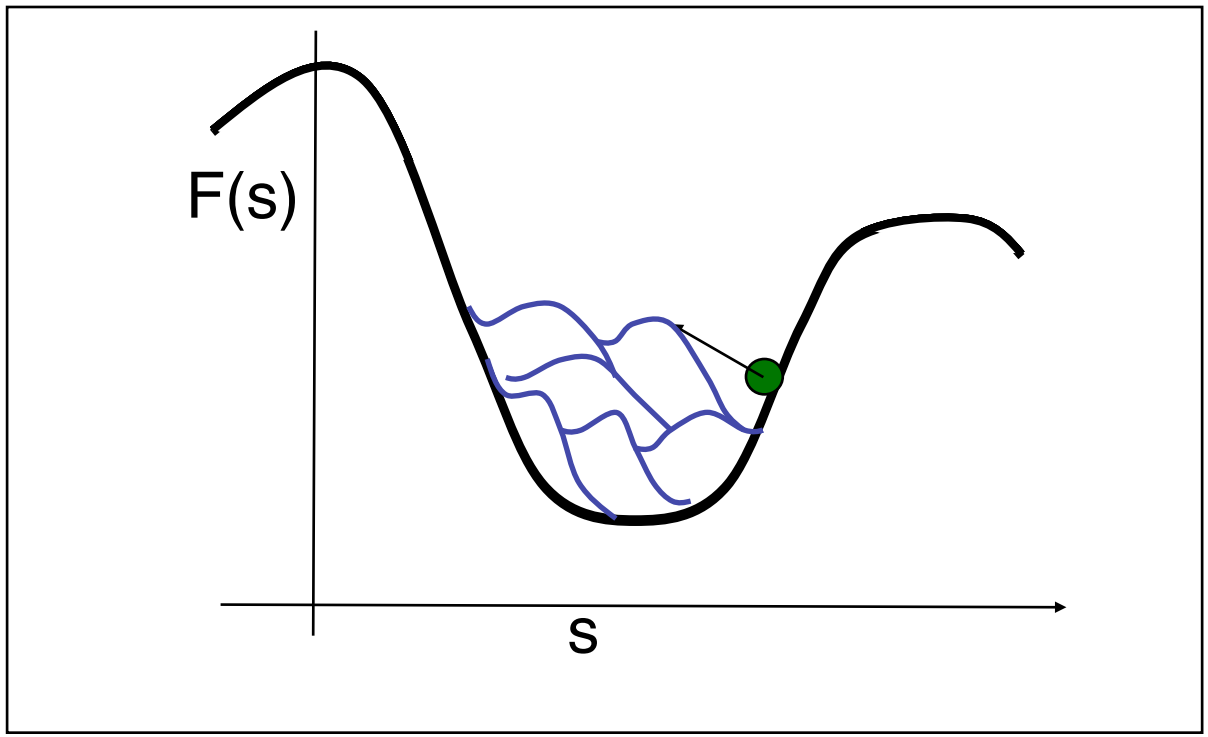

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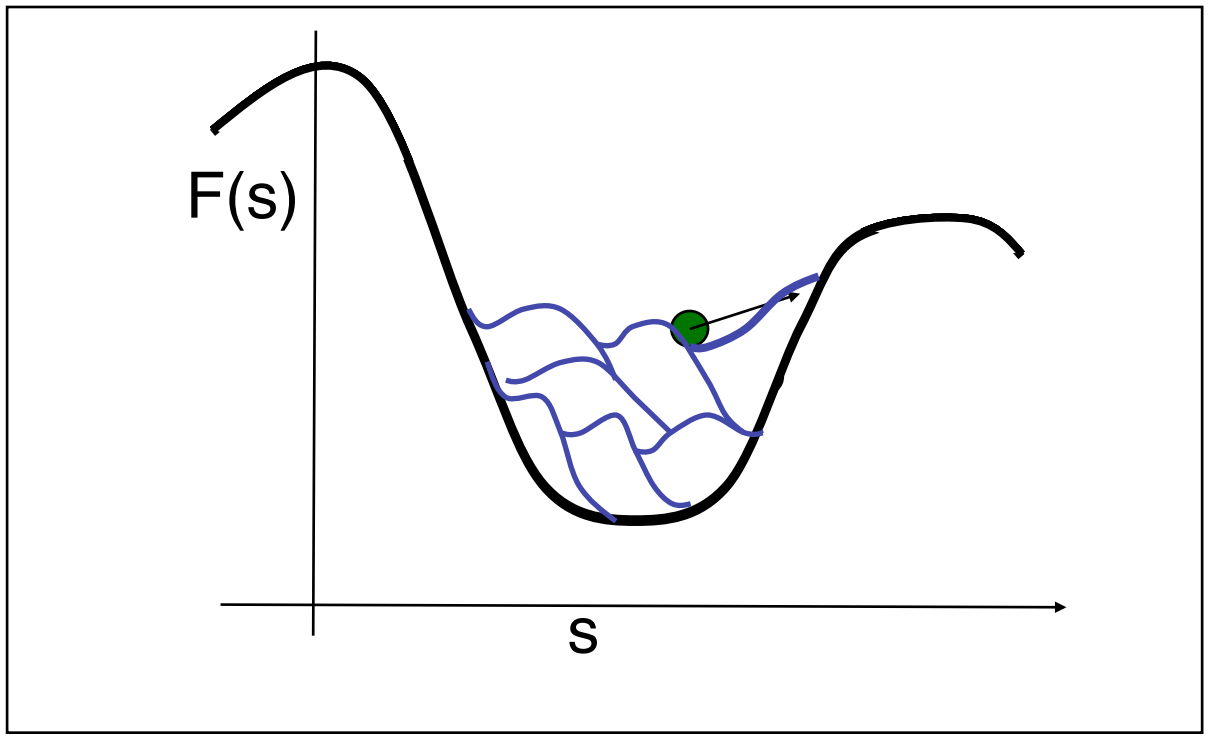

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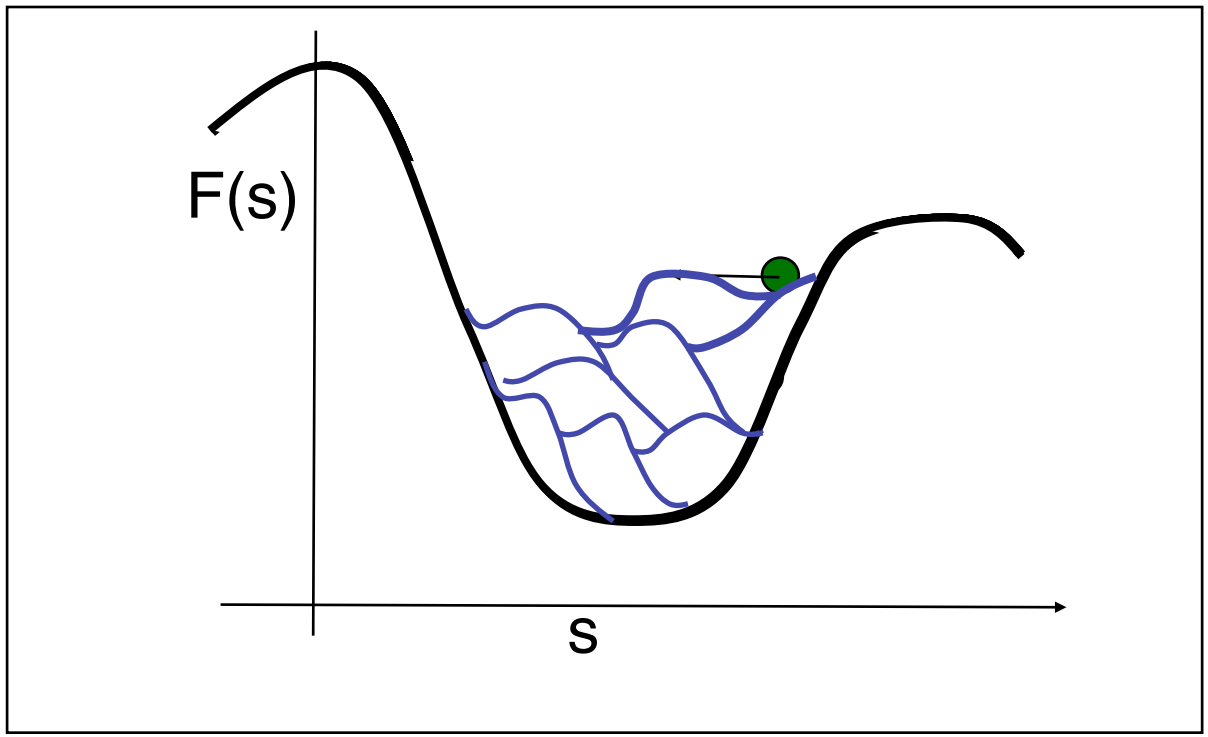

Metadynamics

(Laio & Parrinello, 2002; Martonak et al., 2003)

The Torii Analogy
(Prof. H. Nakamura)

First-principles calculations

Theory Experiment