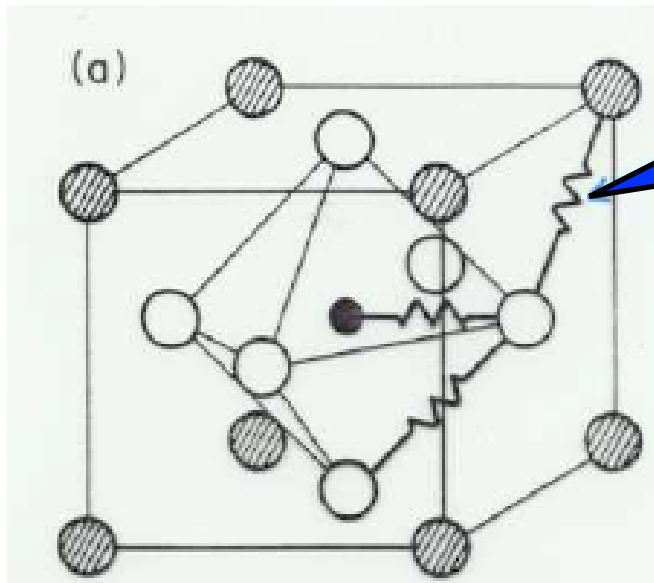


First-principles calculations: Exploration and understanding

Alberto García

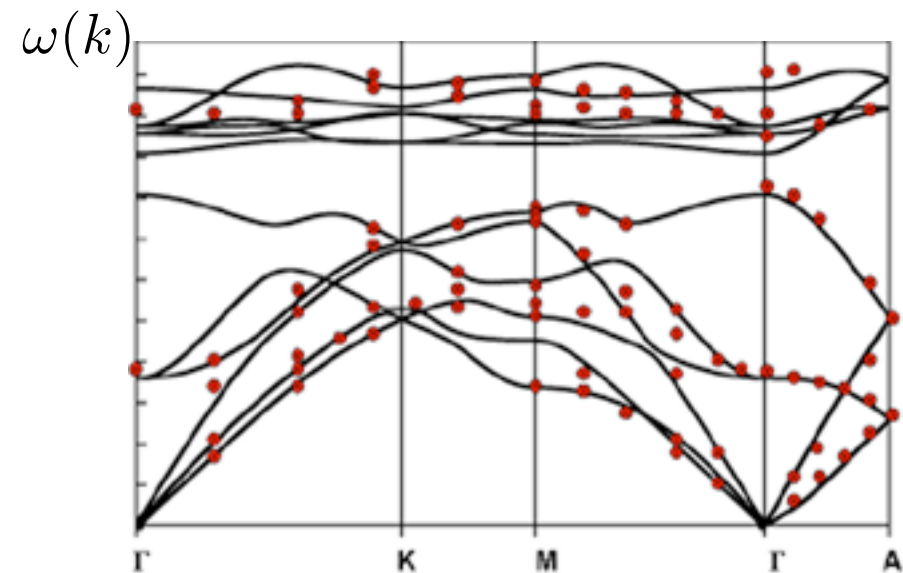
ICMAB

- 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?



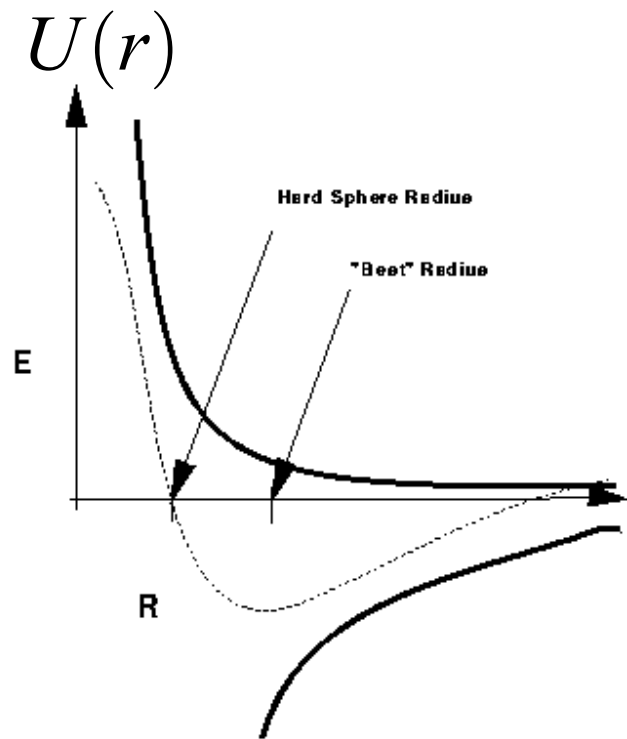
Spring constant

Basic idea: Vibrations
around an equilibrium point



Parameters can be fitted
to experiment

Interatomic potentials

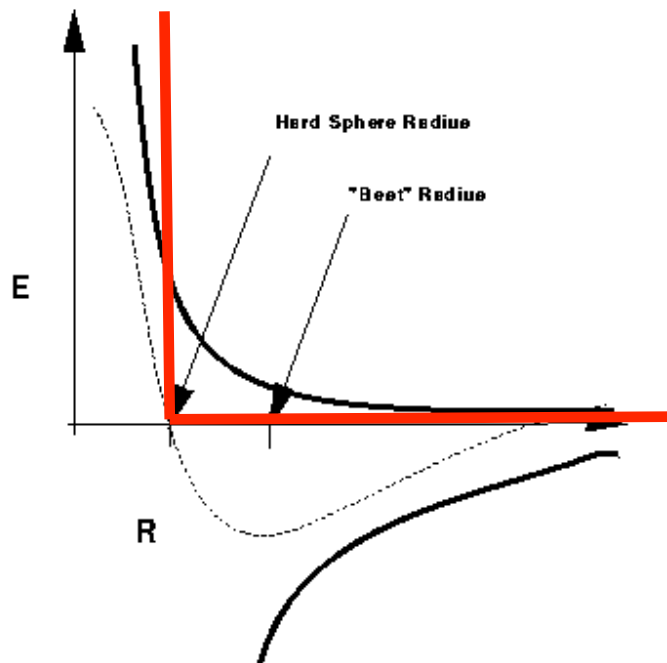


$$U(r) = Ae^{-r/\rho} - Cr^{-6}$$

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

The model can get complicated for
“pencil and paper” treatment

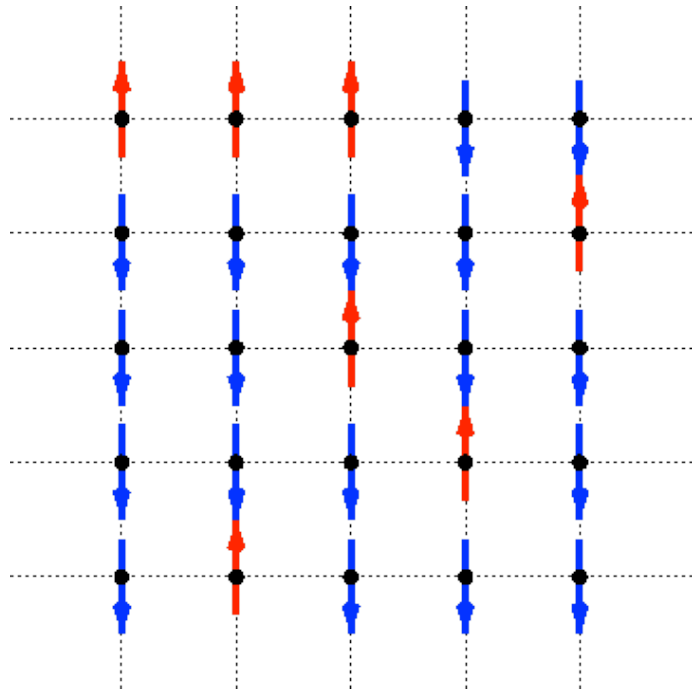
Molecular dynamics simulation



Alder+Wainwright (1956)
Hard-sphere liquid

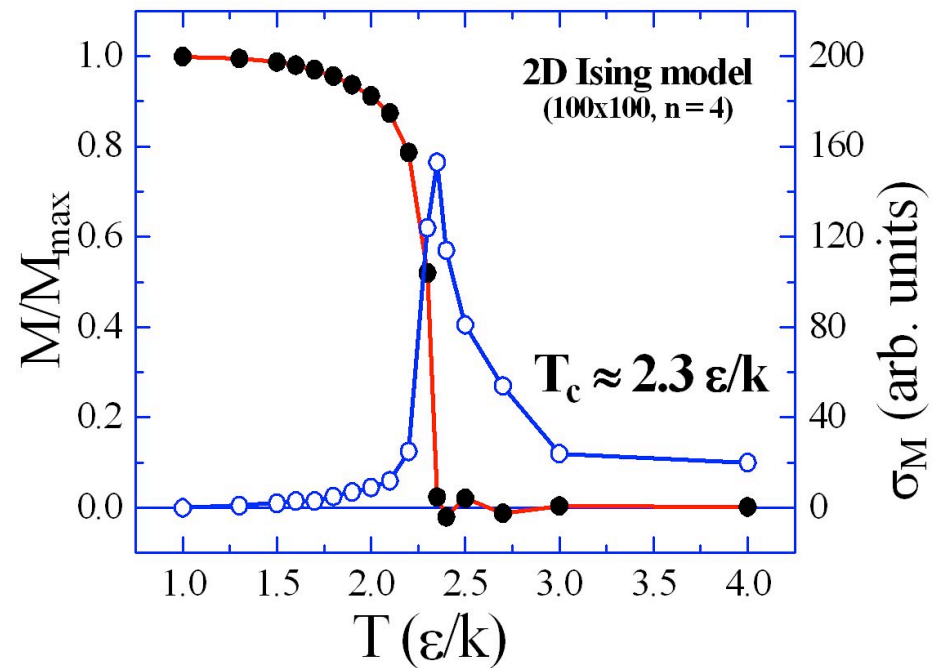
Tremendous growth

Exploration, validation of theories, and checks of
interaction potentials



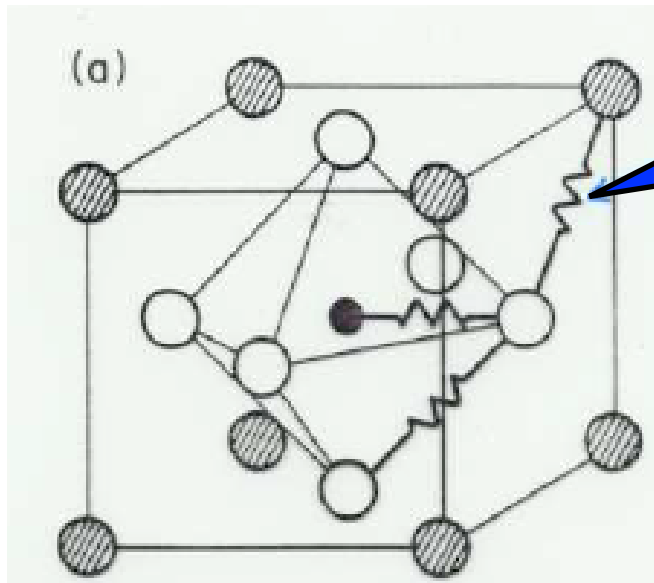
Monte Carlo Simulation

Ising Model



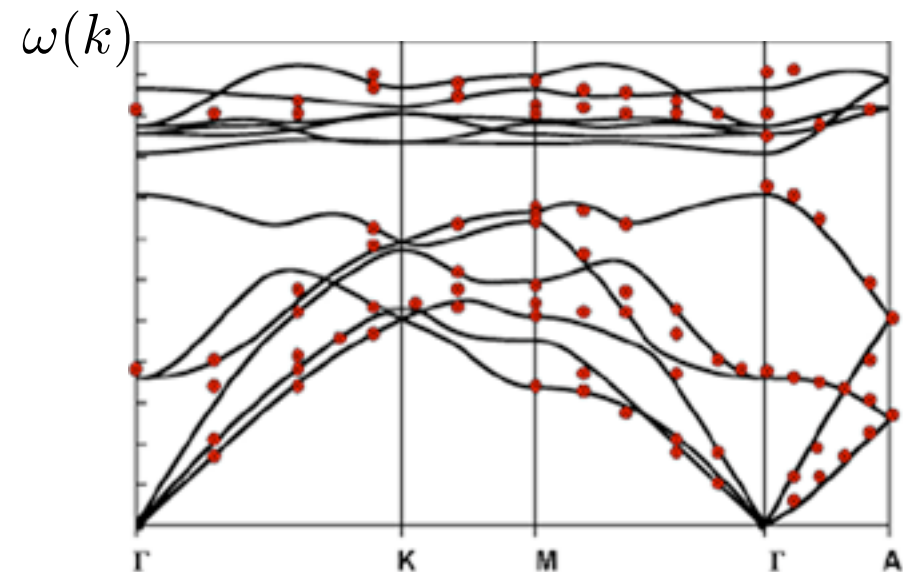
Emergent properties:
Not evident just by looking at the equations

The use of the computer is essential
for exploration of models



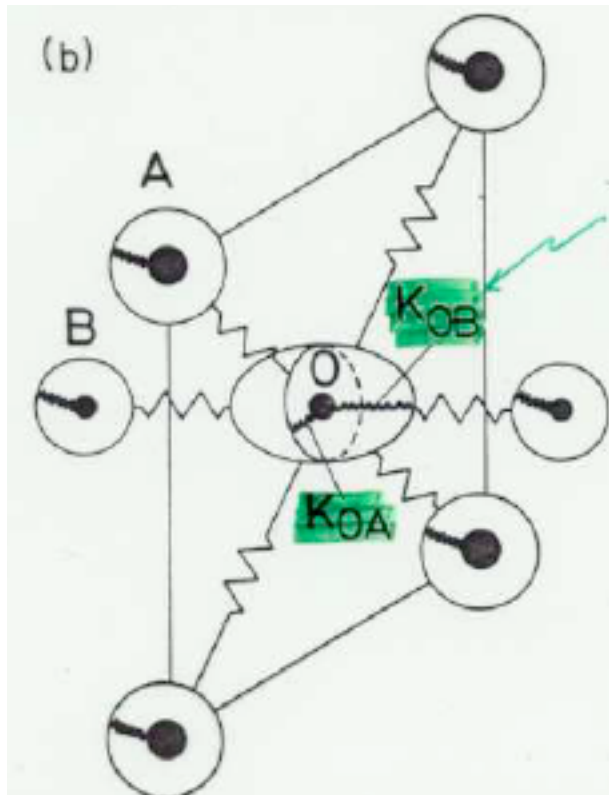
Spring constant

Basic idea: Vibrations
around an equilibrium point

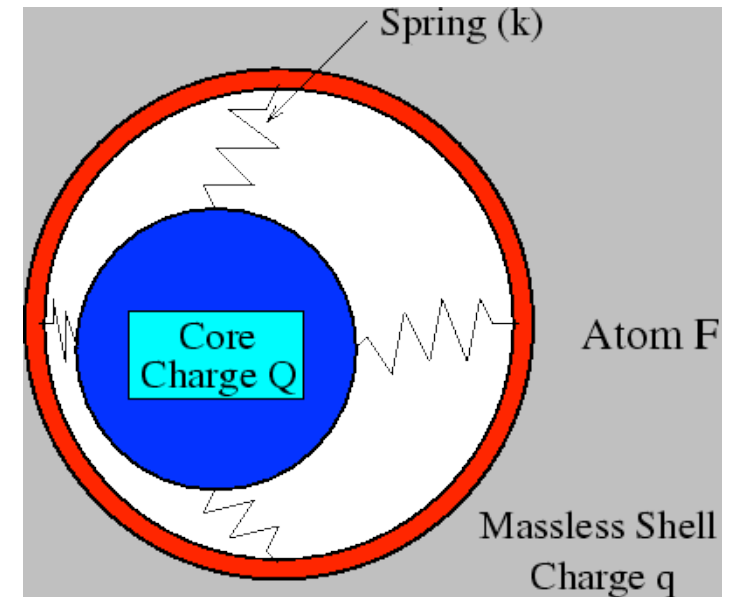


Parameters can be fitted
to experiment

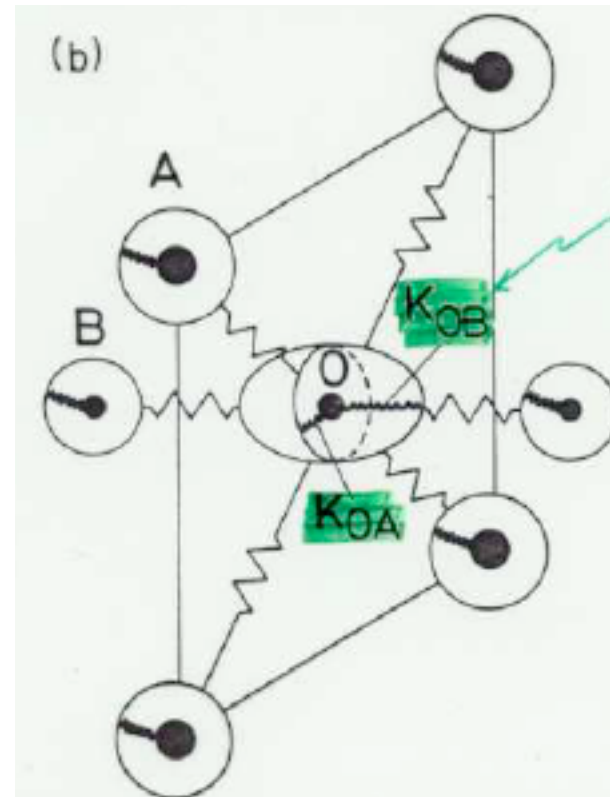
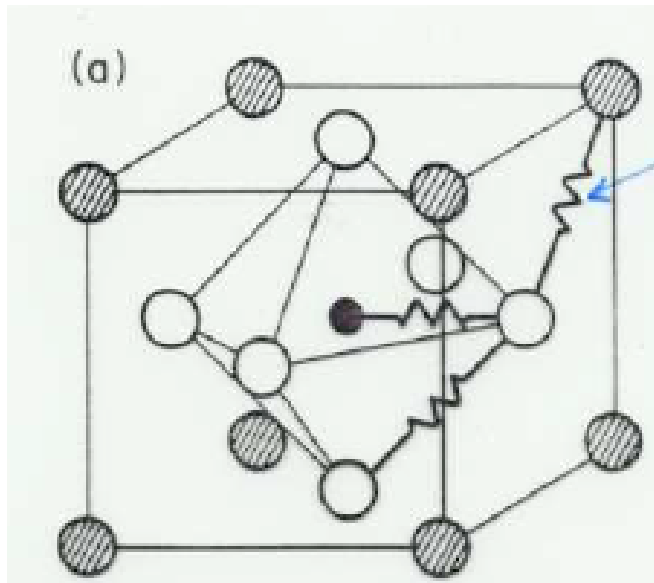
Refinement of the model: polarizable electrons (shell model)



Internal structure
of the atom acknowledged



Better fit
to experiment
New phenomena



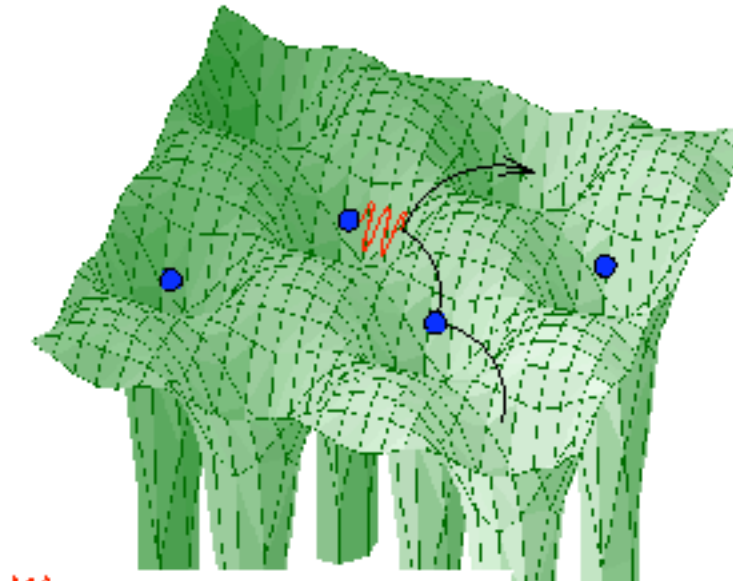
...

Electrons are the glue
holding solids together

We know the basic equations:
Quantum Mechanics and Electromagnetism

The “ultimate model” for electrons in a material

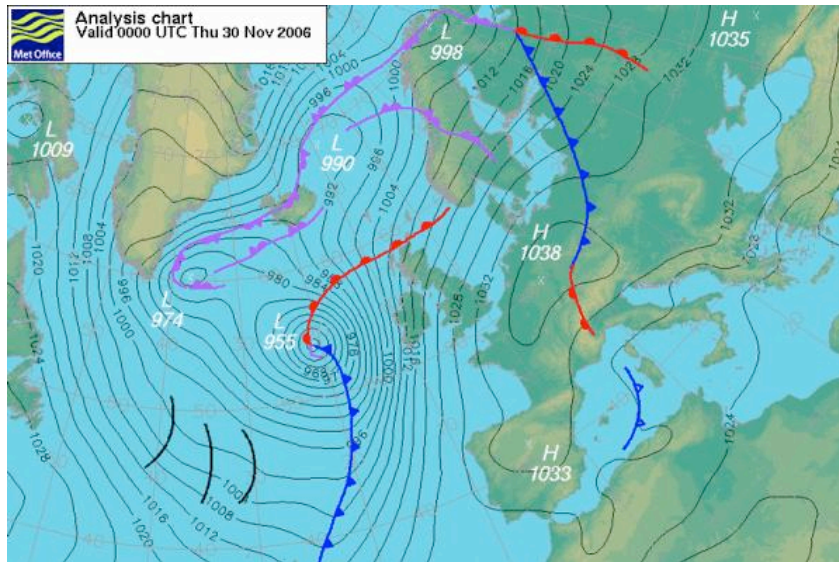
$$H = \sum_i \left[-\frac{\hbar^2 \Delta_i}{2m_e} + \sum_l \frac{-e^2}{4\pi\epsilon_0} \frac{Z_l}{|\mathbf{r}_i - \mathbf{R}_l|} \right] + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$



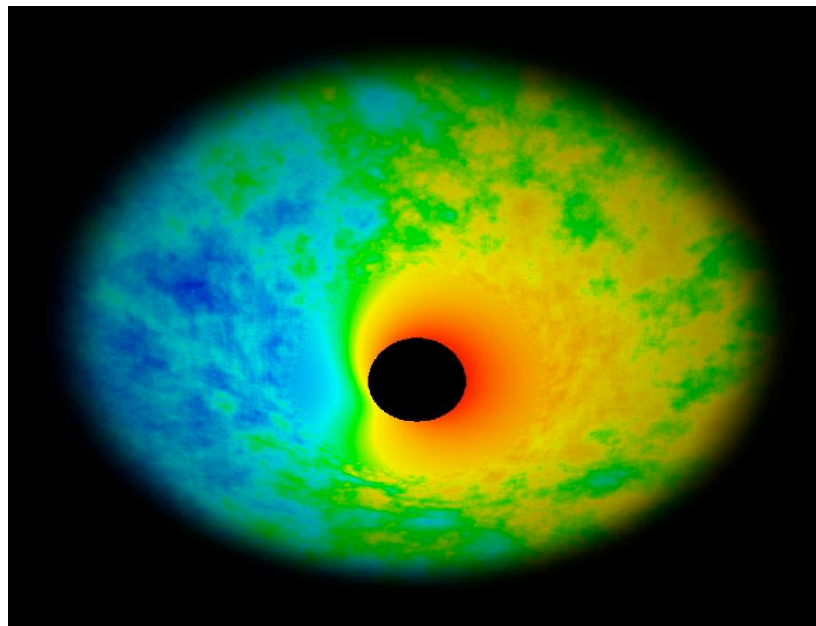
$$\hat{H}\Psi = E\Psi \quad \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n)$$

We could compute “everything”

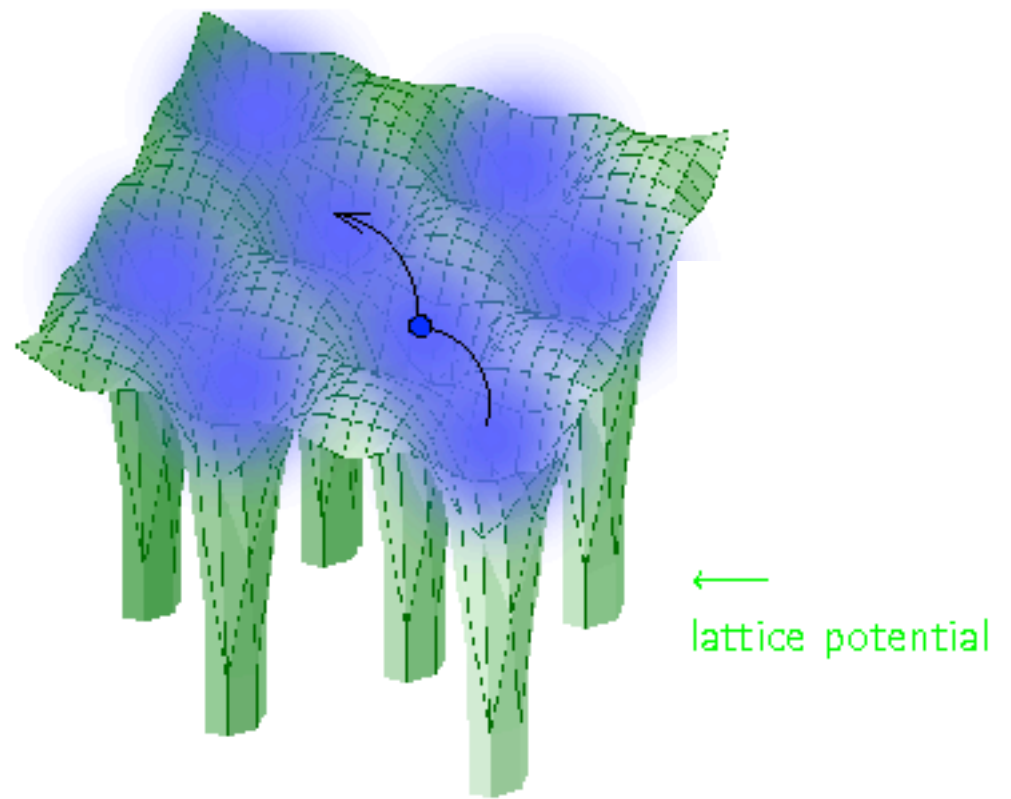
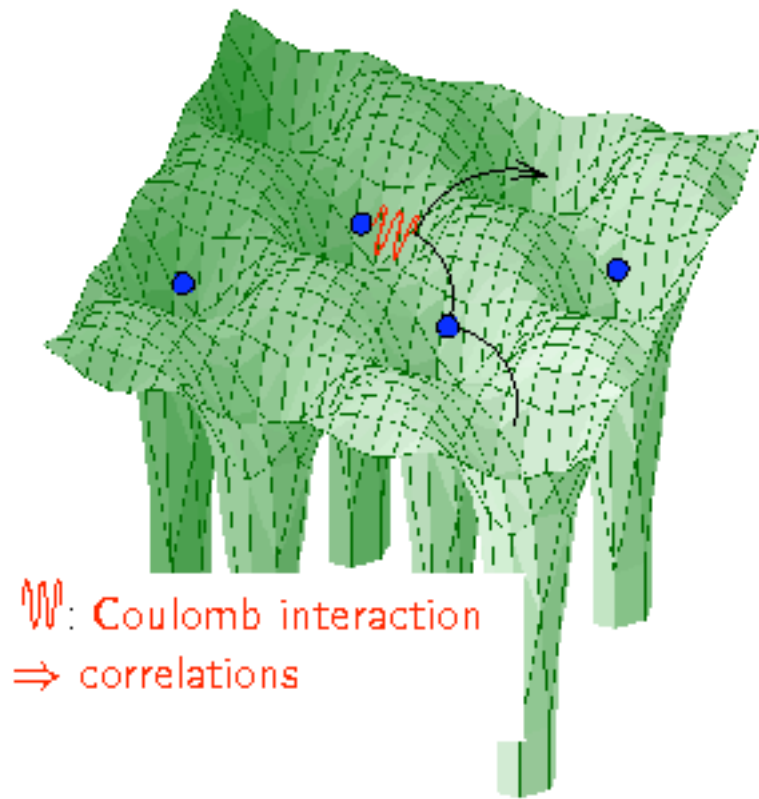
Simulation of reality



Meteorology:
We know the
basic equations



Astrophysics:
We know the
basic equations.
Little data

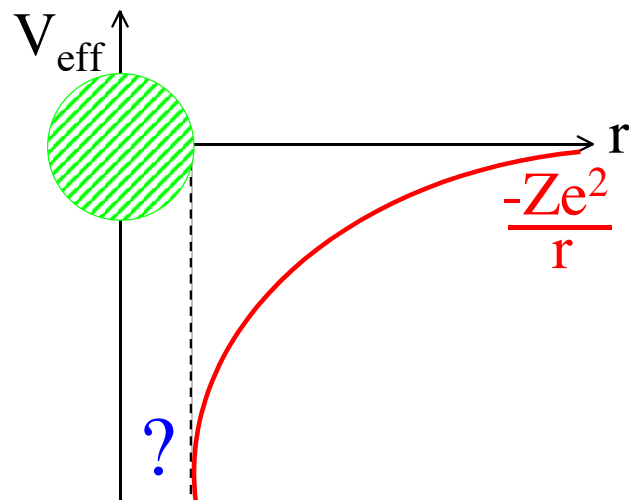
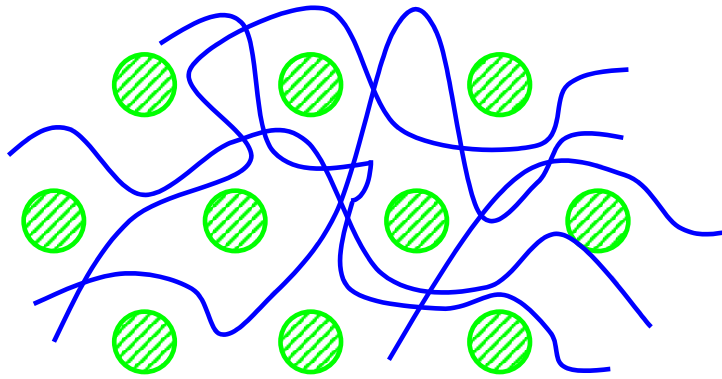


Density-functional theory $E = E[n] \quad n(\mathbf{r})$

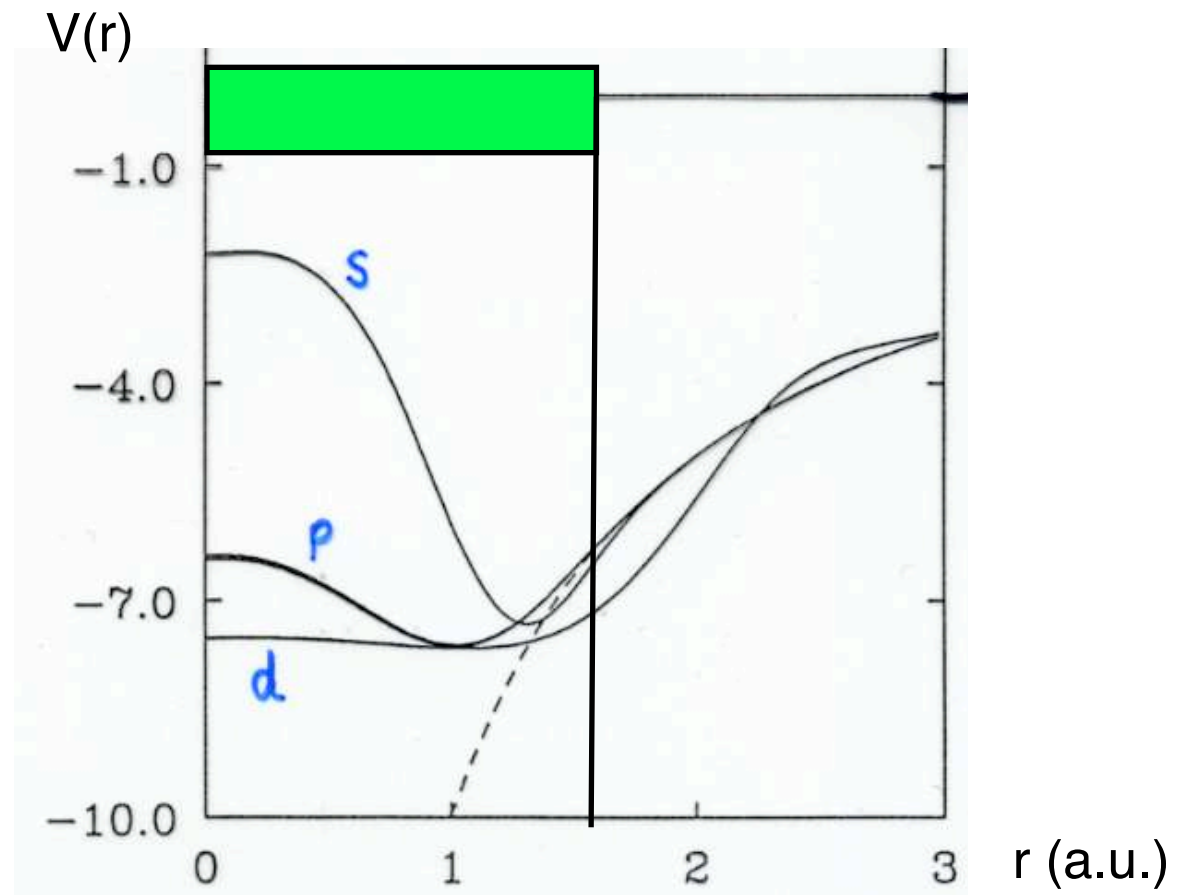
$$\{-\nabla^2 + V_{\text{eff}}[n](\mathbf{r})\}\psi_i = \varepsilon_i\psi_i \quad \text{One electron}$$

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

Internal electrons do not participate in the chemical bond



Effective potential for valence electrons
Pseudopotential

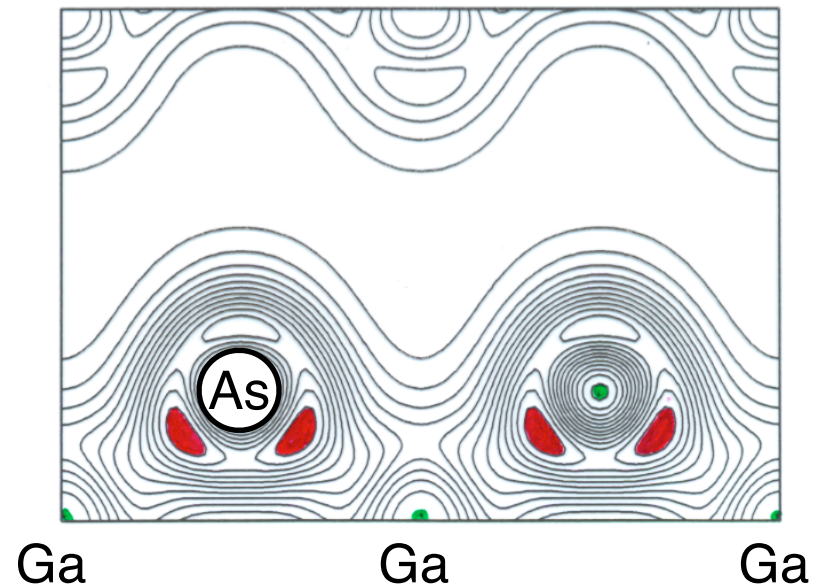
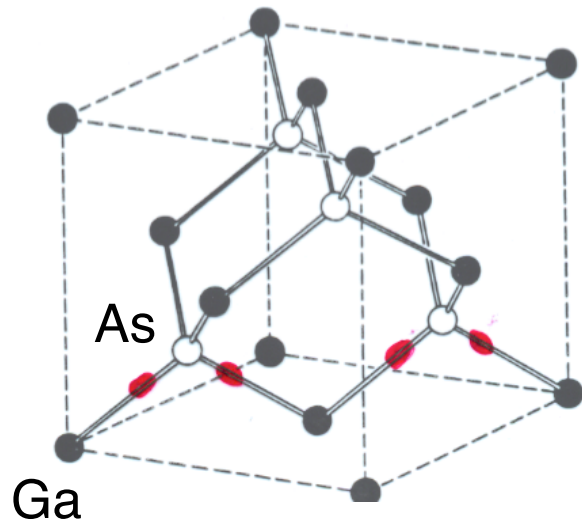


Density-functional theory
is a practical implementation
of the “ultimate model” for atomic aggregates

Reasonably accurate
Versatile

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
(accuracy)

- * *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)

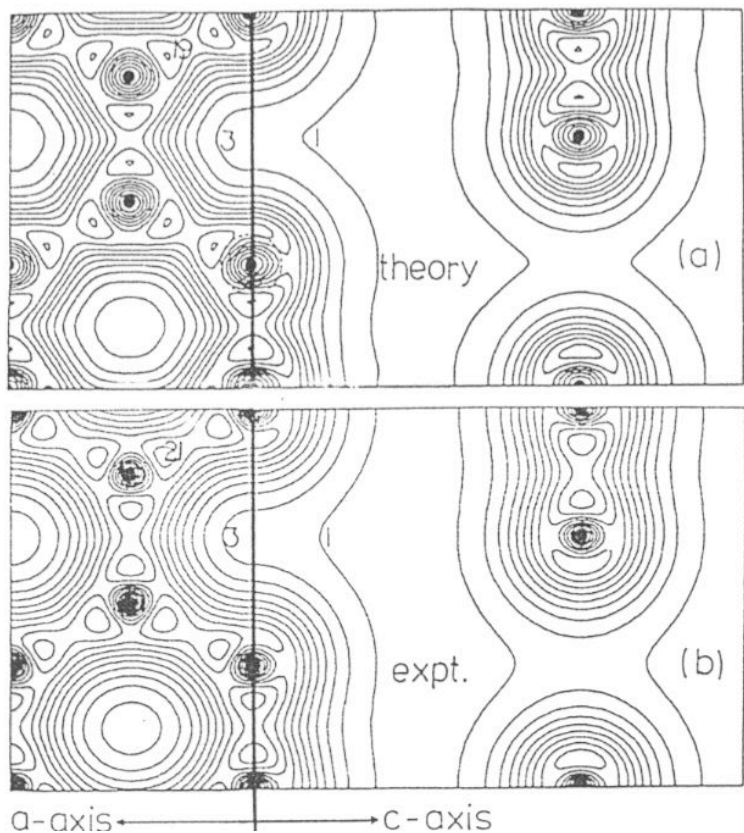
A simple model can shed more light on Nature's workings than a series of "ab-initio" calculations of individual cases, which, even if correct, are so detailed that they hide reality instead of revealing it. ...A perfect computation simply reproduces Nature, it does not explain it.

([P.W.Anderson](#))

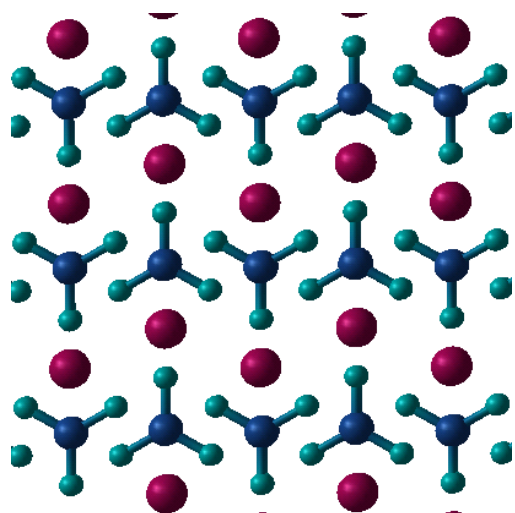


Uses in materials science

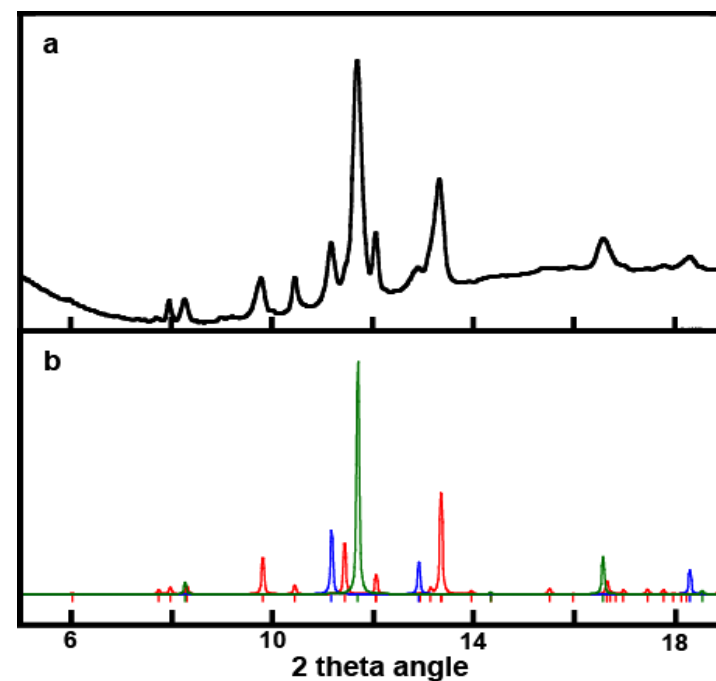
- **Exploration and prediction**, simulating experiments difficult or impossible in the laboratory.
- **Clarification/complement** of experimental information by means of the precise control of simulation conditions. (The computer is a perfect control machine)
- **Design of materials** with desired properties.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



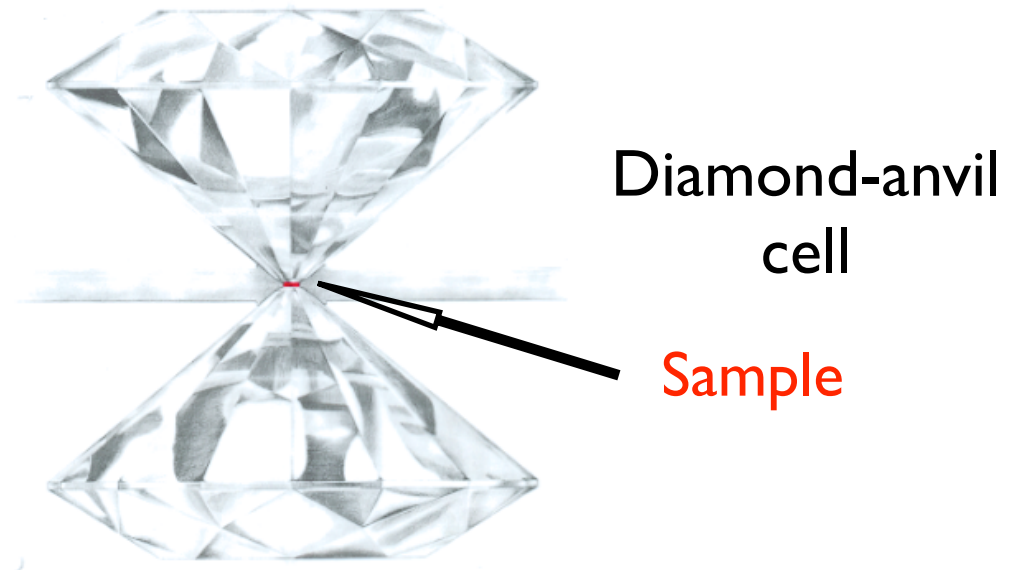
Calculation of electronic charge density
(Simulation of an X-ray experiment)



Synthetic diffraction
diagram



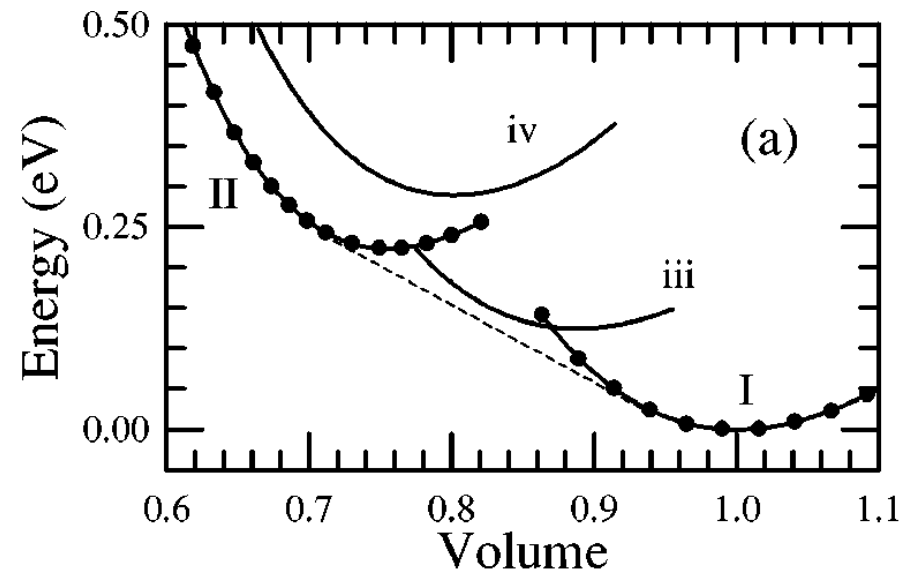
High-pressure experiment



Theoretical treatment

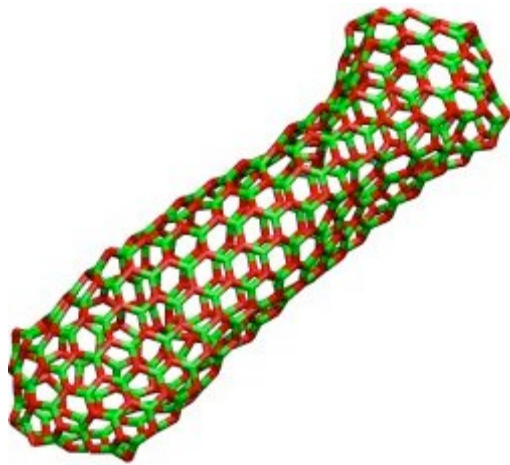
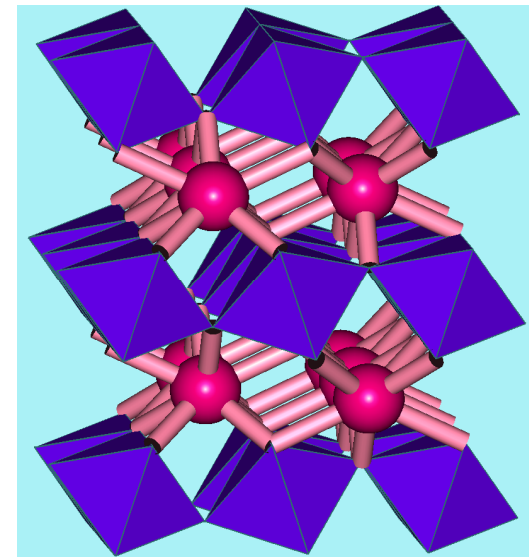
$$E = E(V), \quad p = -\frac{dE}{dV}, \quad p = p(V)$$

Equations of State
Phase transitions



Post-perovskite phase of MgSiO₃

Oganov et al, Nature (2004)

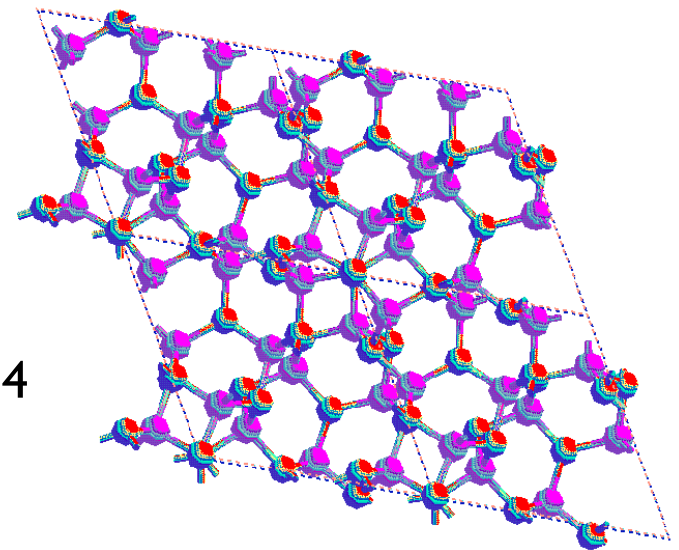
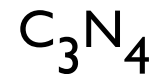


Prediction of BN nanotubes

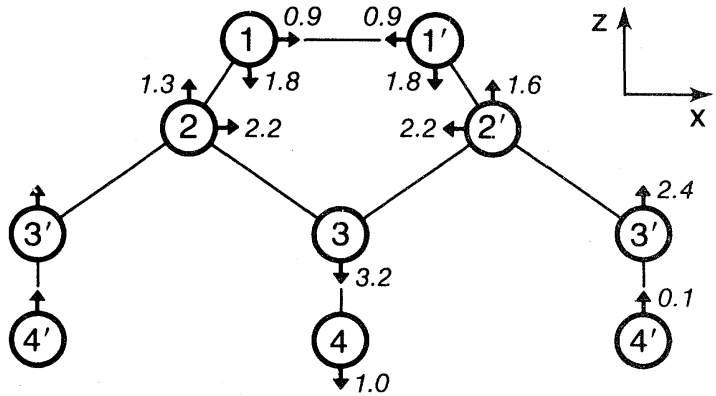
Rubio, Corkill, Cohen, PRB (1994)

Proposal for a super-hard material

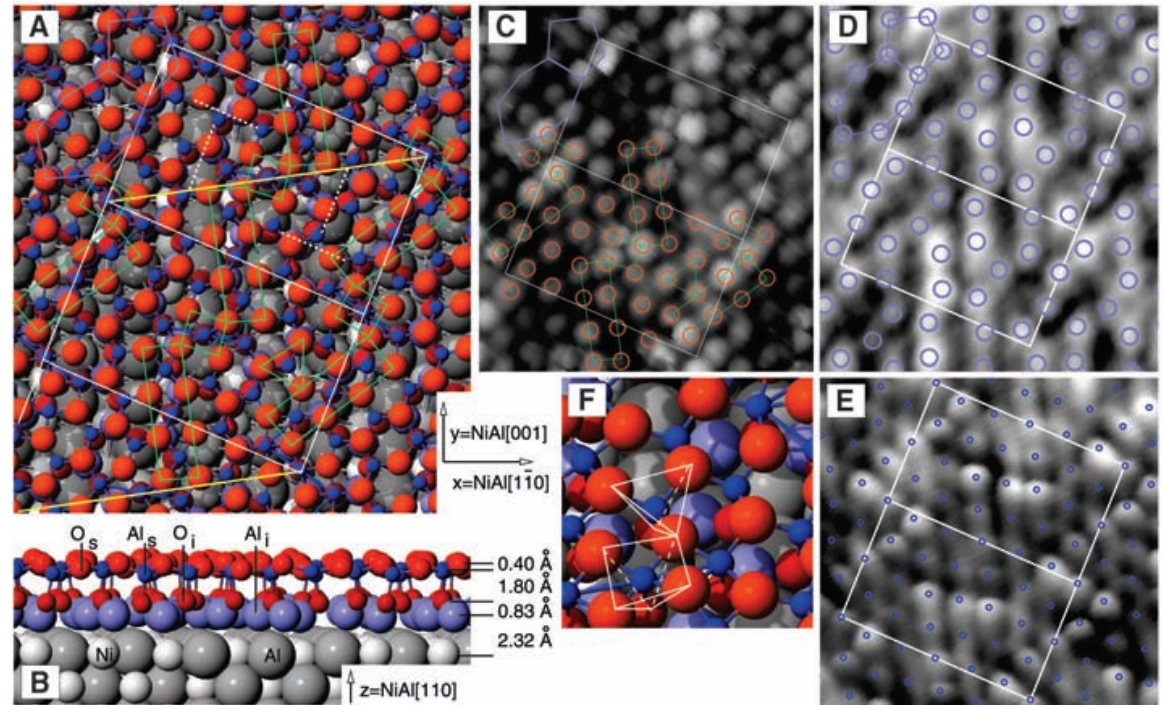
Liu, Cohen, Science (1989)



Surfaces



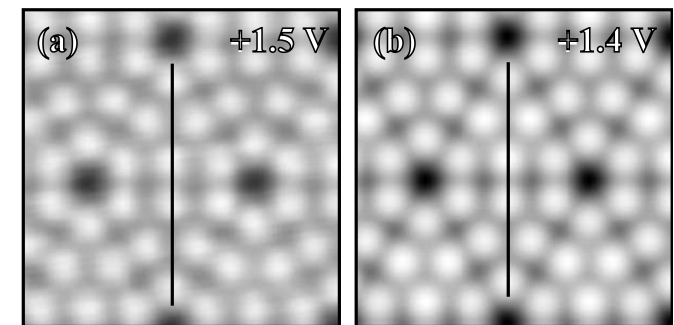
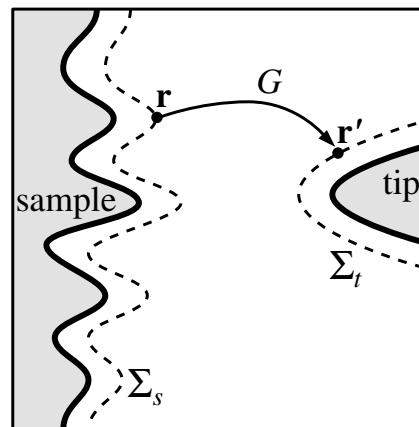
First work on Si(100)
Yin, Cohen, PRB (1981)



Oxidation of NiAl
Kresse et al, Science (2005)

Method for the simulation of
STM images

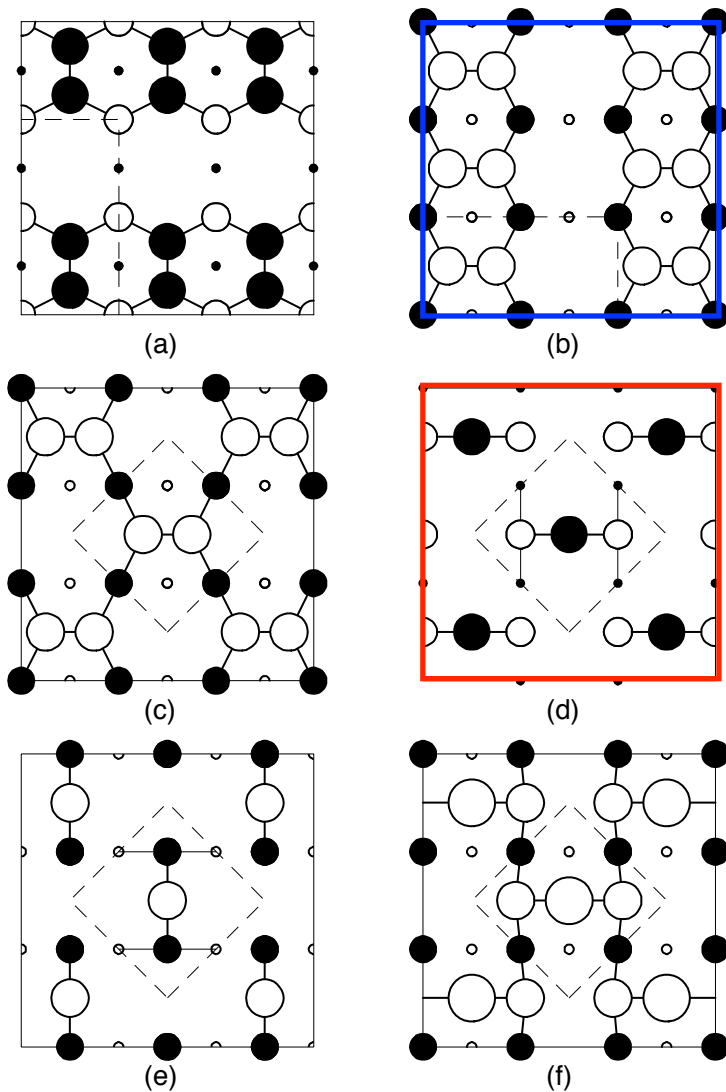
Paz et al, PRL (2005)



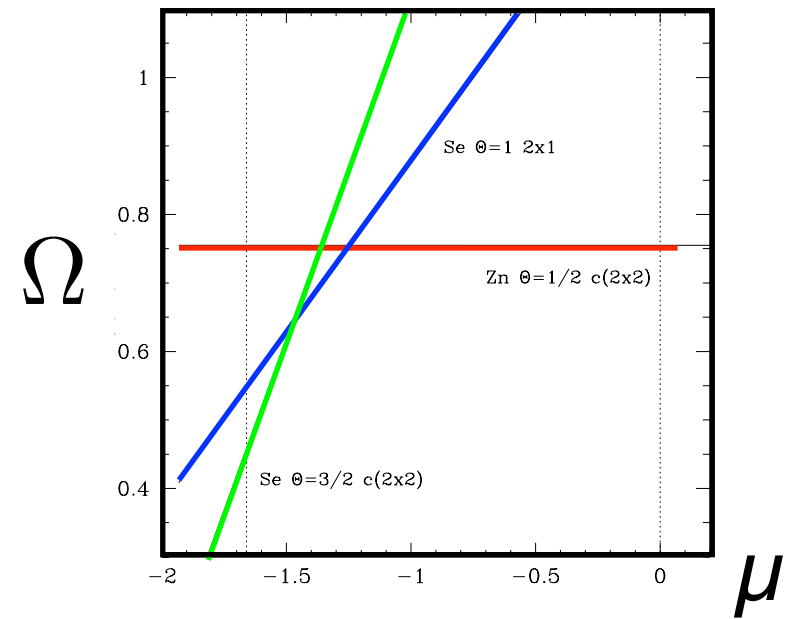
Exp

Theory

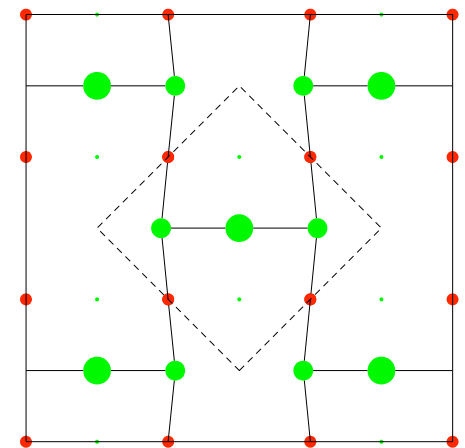
Clarification of the structure and prediction of a new surface phase of ZnSe



Zn ● ○ Se

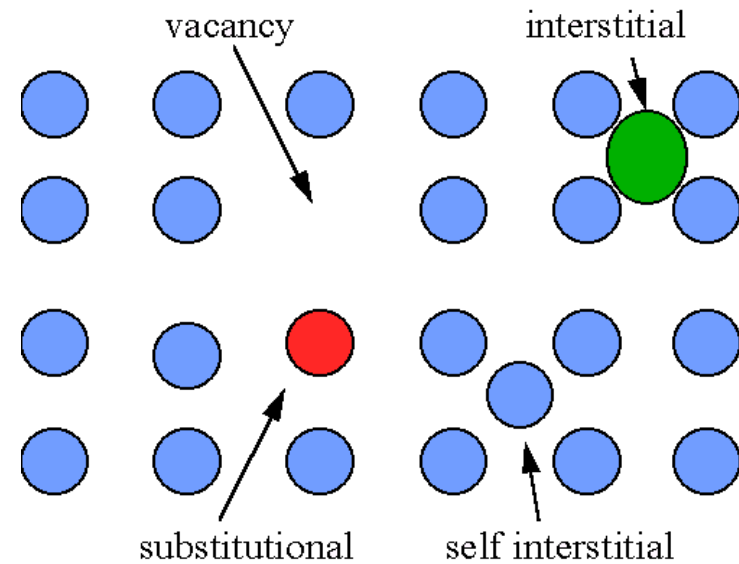


Garcia, Northrup, APL (1994)

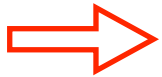


Precise control of simulation conditions

Point defects:
Great experimental
complexity

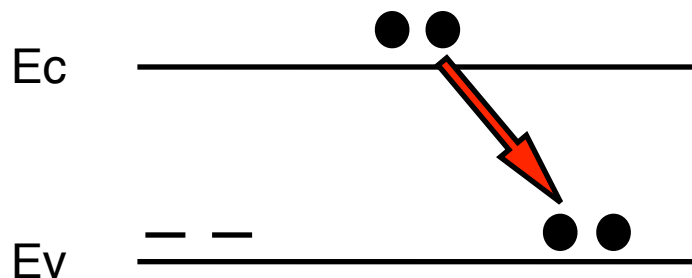
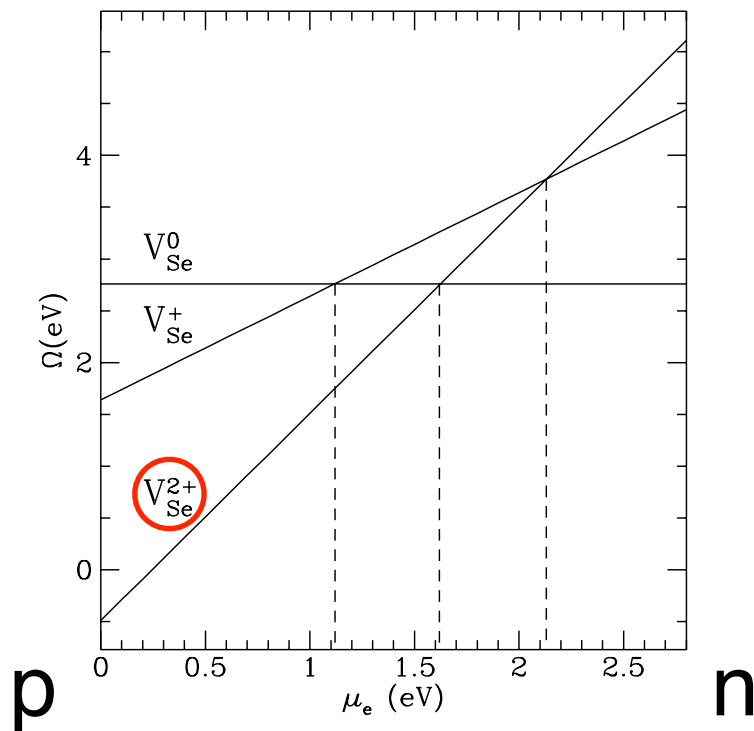


In a calculation they can be “prepared” (isolated or in complexes)
and their energies of formation and bonding computed



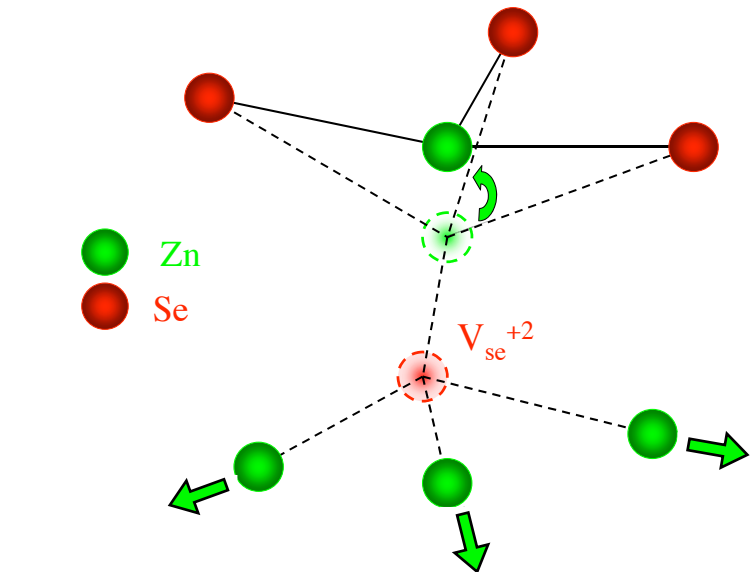
Help in the analysis of experiments,
and **direct testing of hypothesis**

Mechanism for p-doping saturation in ZnSe

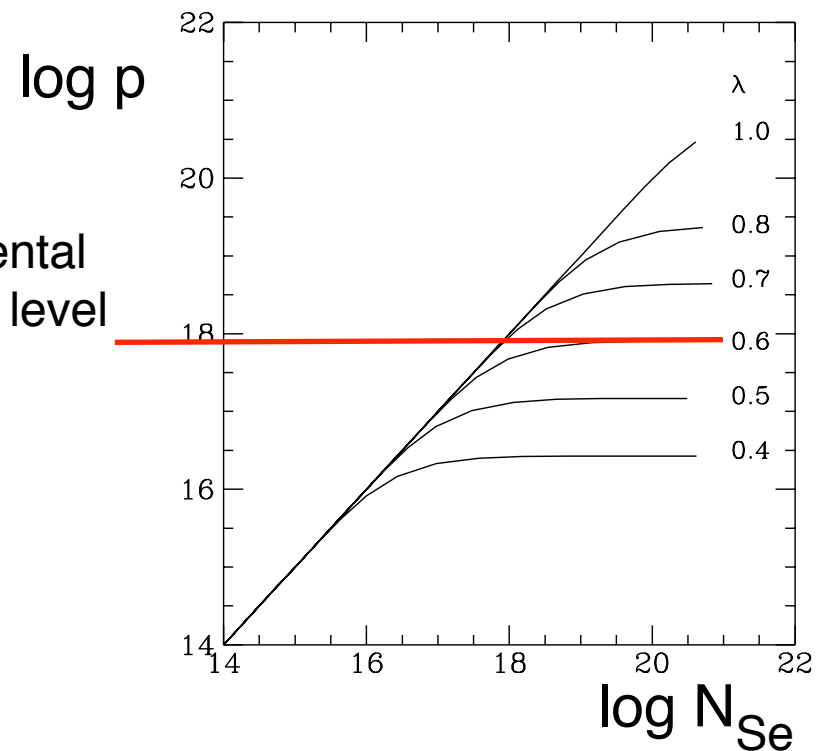


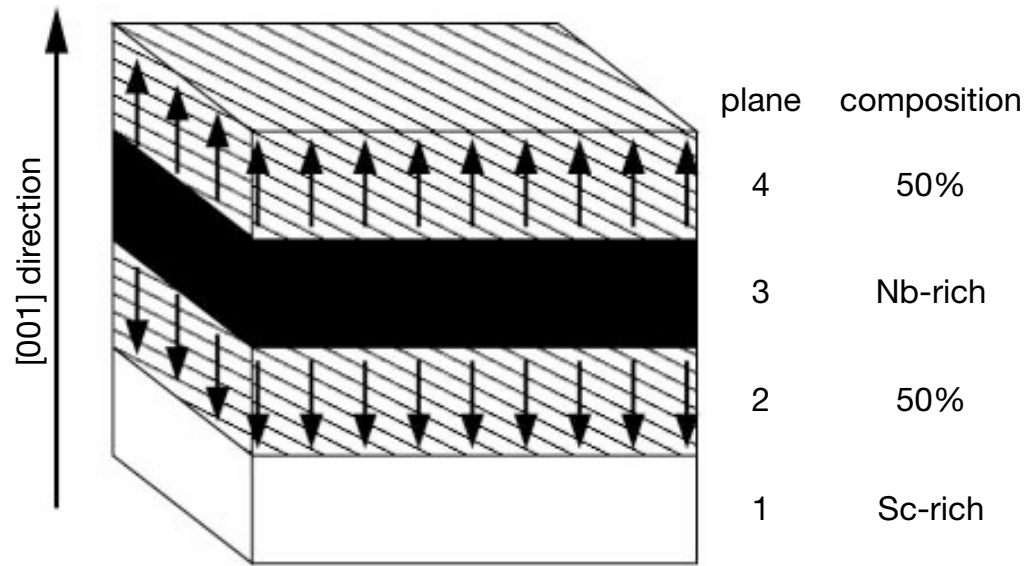
Compensation of two holes by V_{Se}^{+2}

Garcia, Northrup, PRL (1995)



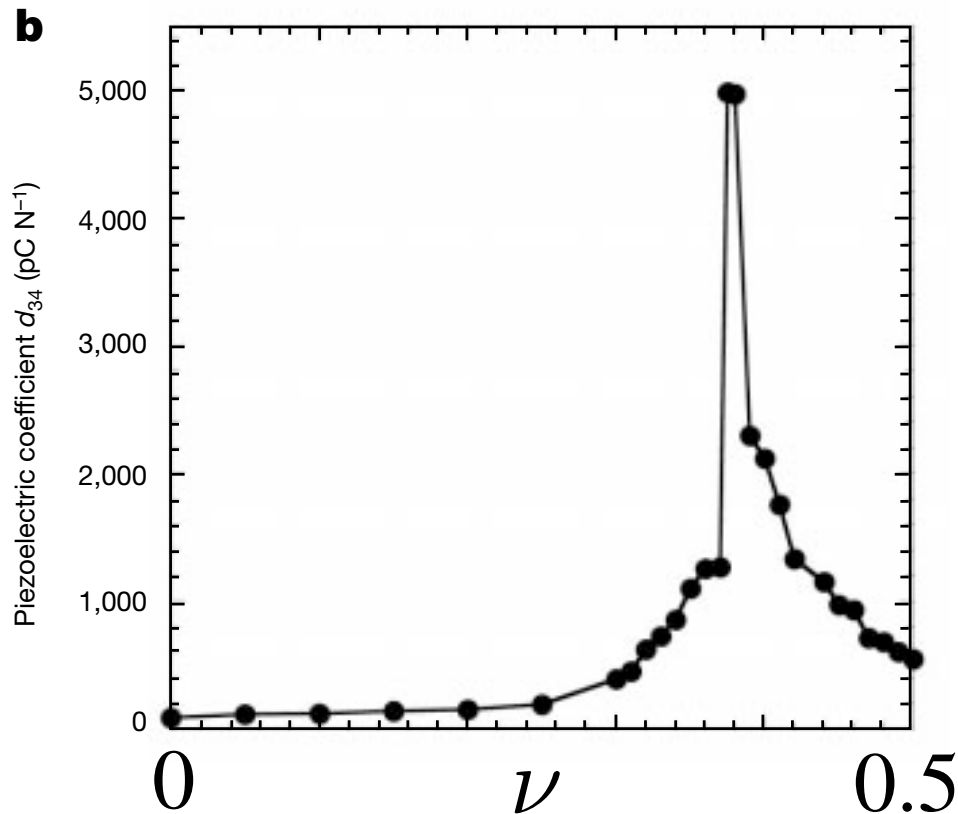
Experimental
saturation level





$$x = 0.5 - \nu$$

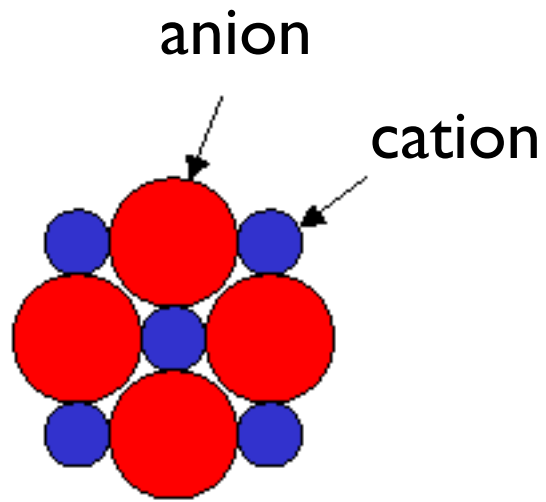
$$x = 0.5 + \nu$$



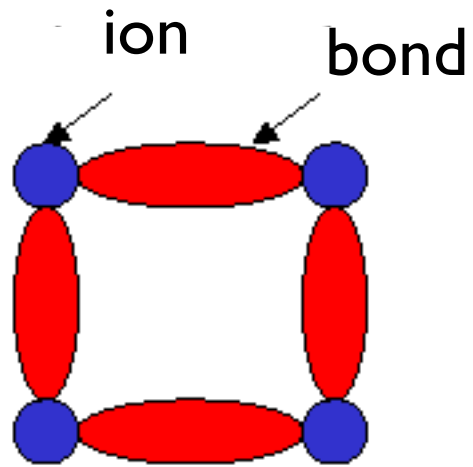
Design of materials
with optimized
piezoelectric response

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

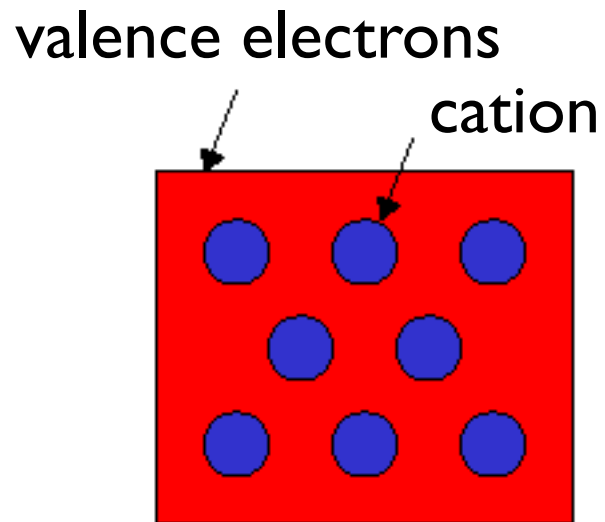
What of Anderson's claim?
Do we understand more?



Ionic

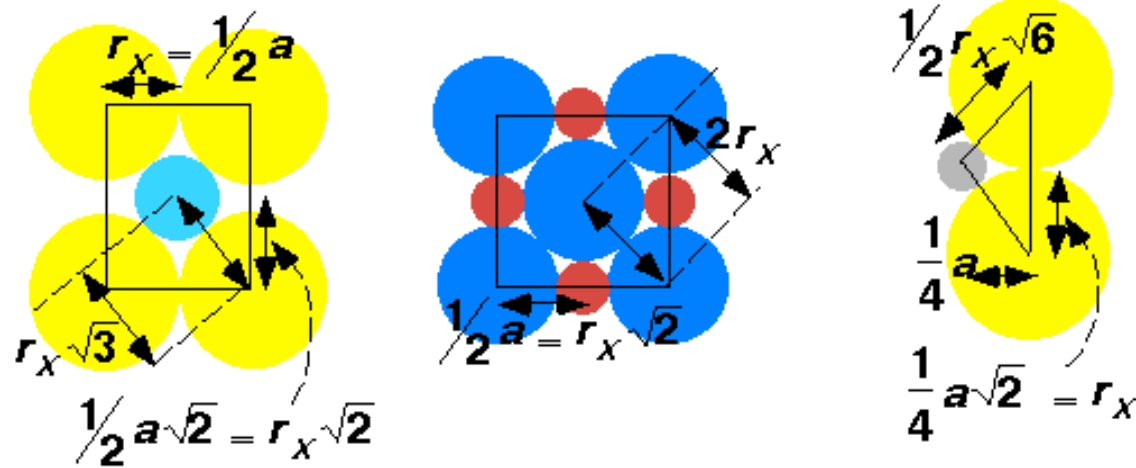


Covalent

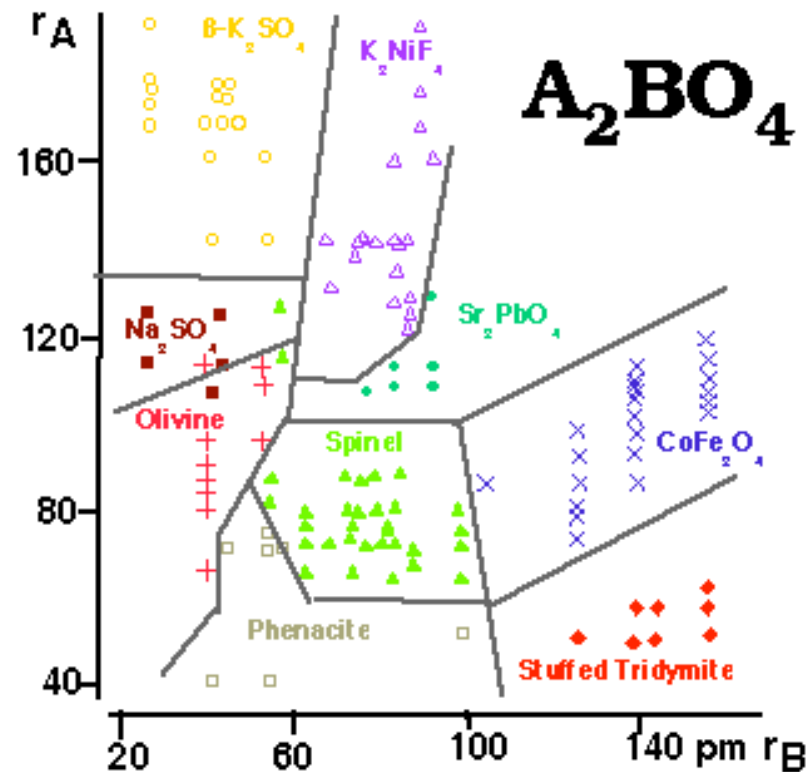


Metallic

Electronegativity
difference
is enough!



Classification involving ionic radii



Simulation as a route for comprehension (I)

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

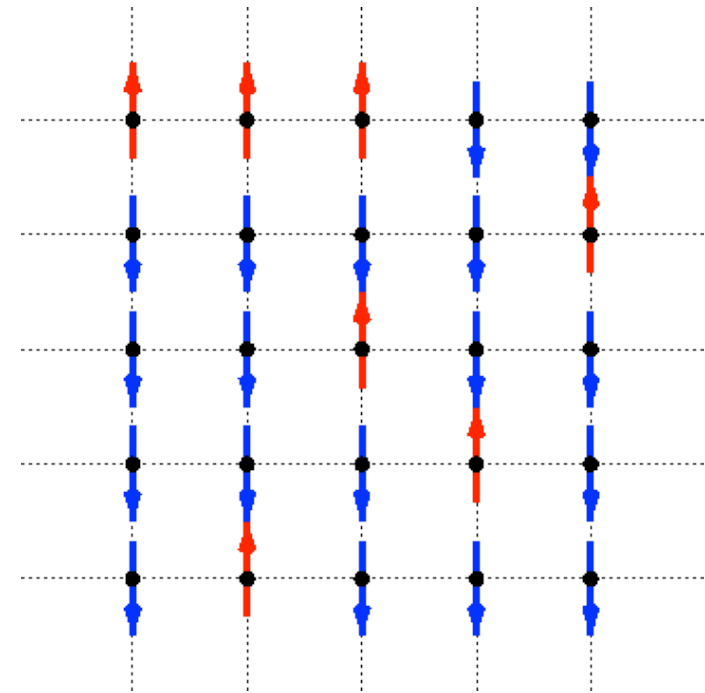
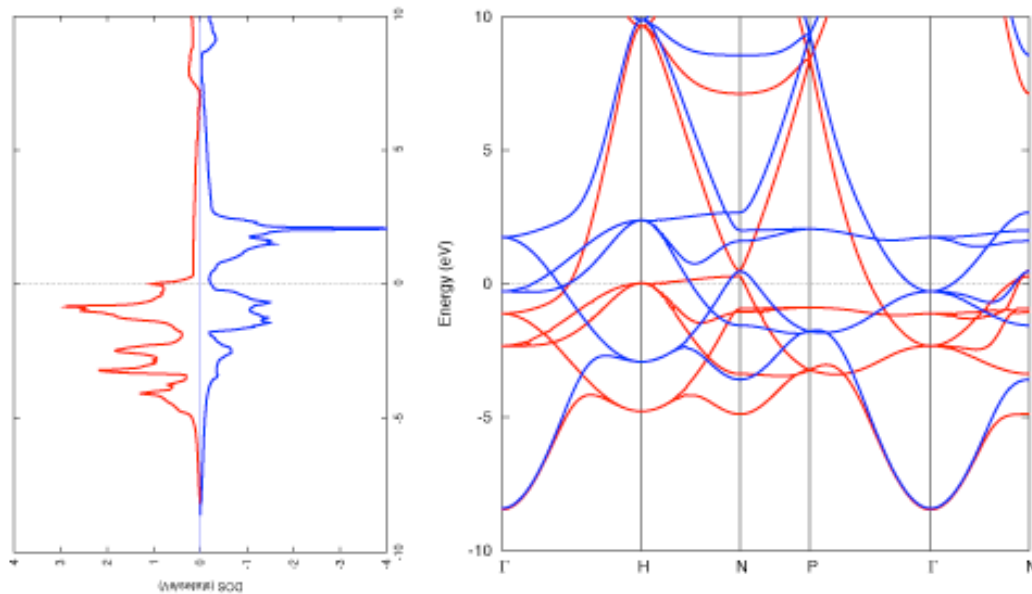
High-level
physical concepts

Electronegativity
Bonding
Parametrization of
simple models

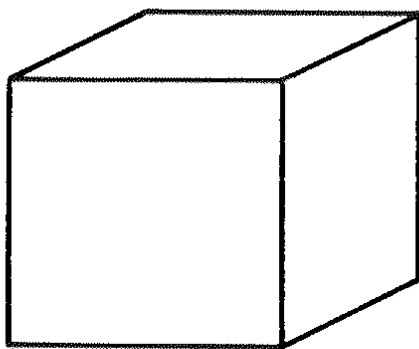
One can use first-principles methods to compute **parameters** for **simple** but **relevant and realistic** models

Parametrization of a Heisenberg model from the electronic structure.

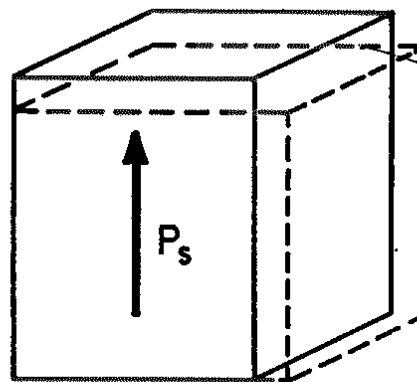
Relevant for magnetic properties



Ferroelectricity

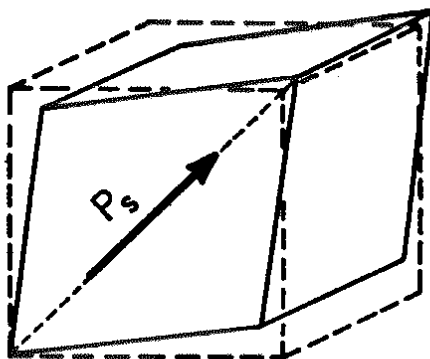


Cubic

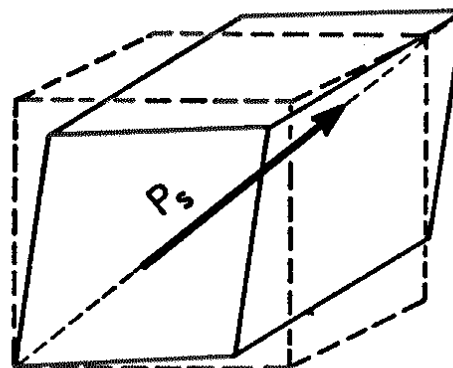


Tetragonal

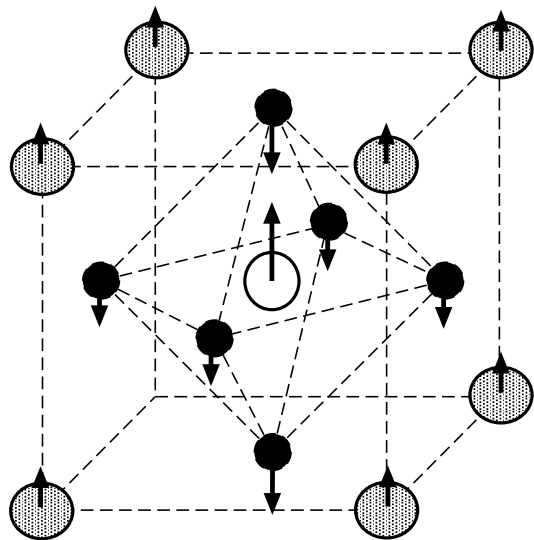
BaTiO₃



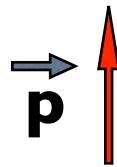
Orthorhombic



Rhombohedral

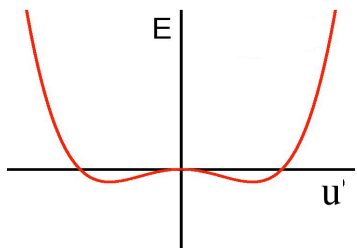


+ ○ Ti
 ● Ba
 - ● O

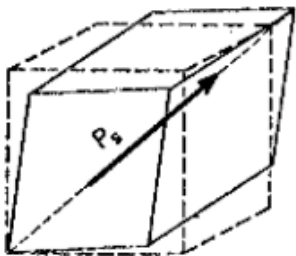


Basic distortion
 involved in ferroelectricity
 (soft mode)

Relevant degree of freedom

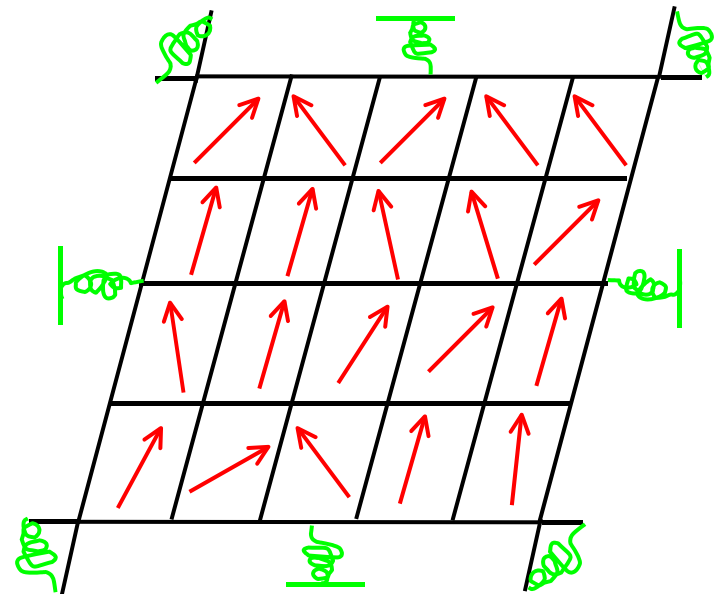


Local mode u

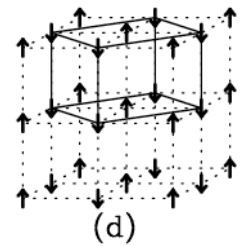
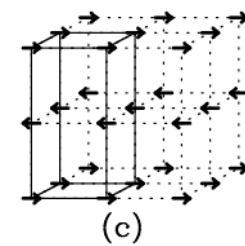
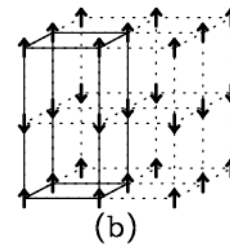
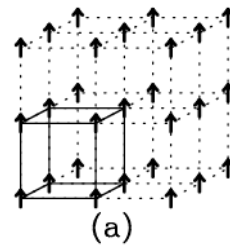
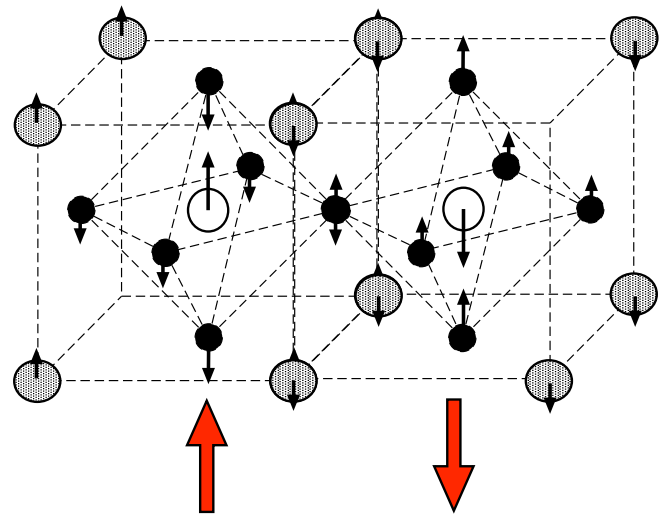


Lattice Strain

Model system



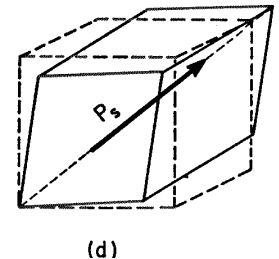
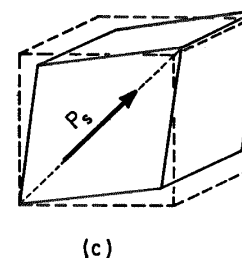
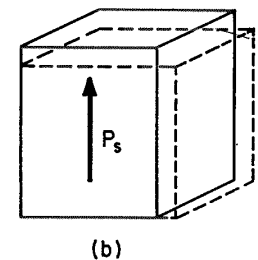
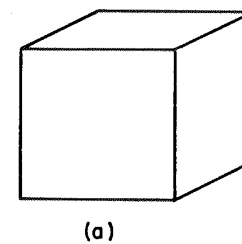
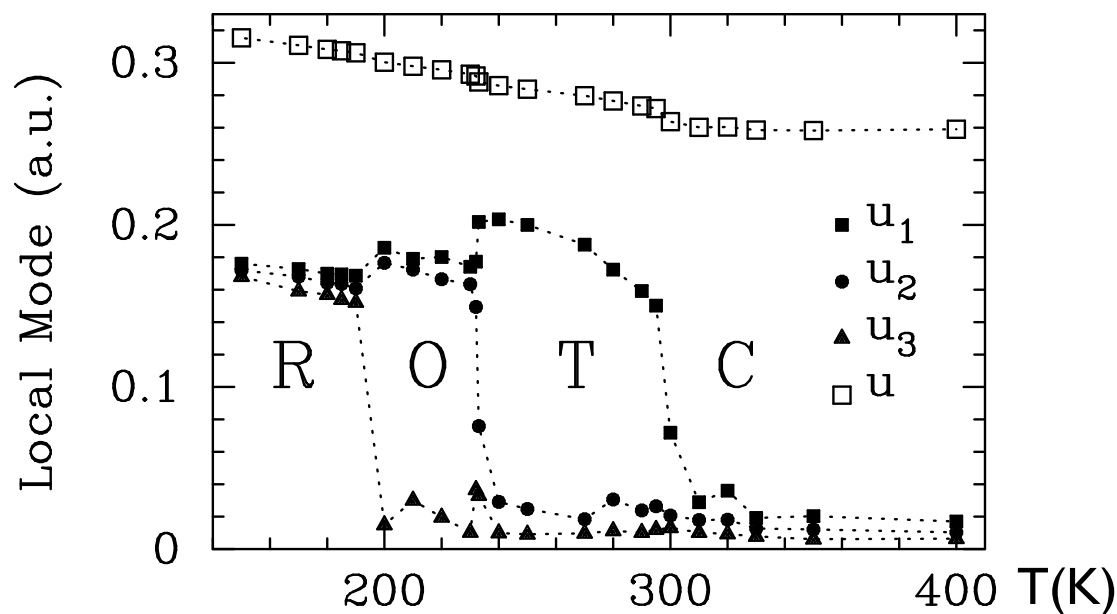
Zhong, Vanderbilt, Rabe, PRL 73, 1861 (1994)



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

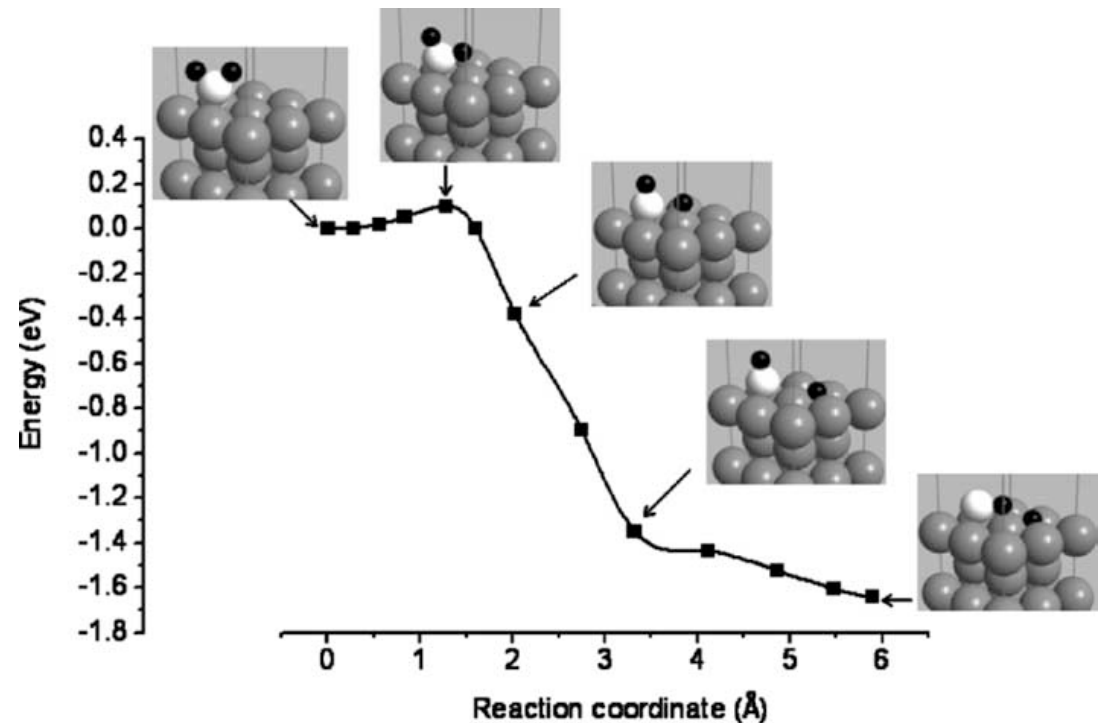
Effective-Hamiltonian parametrized **ab-initio**

Phase transition sequence obtained from Monte Carlo simulations

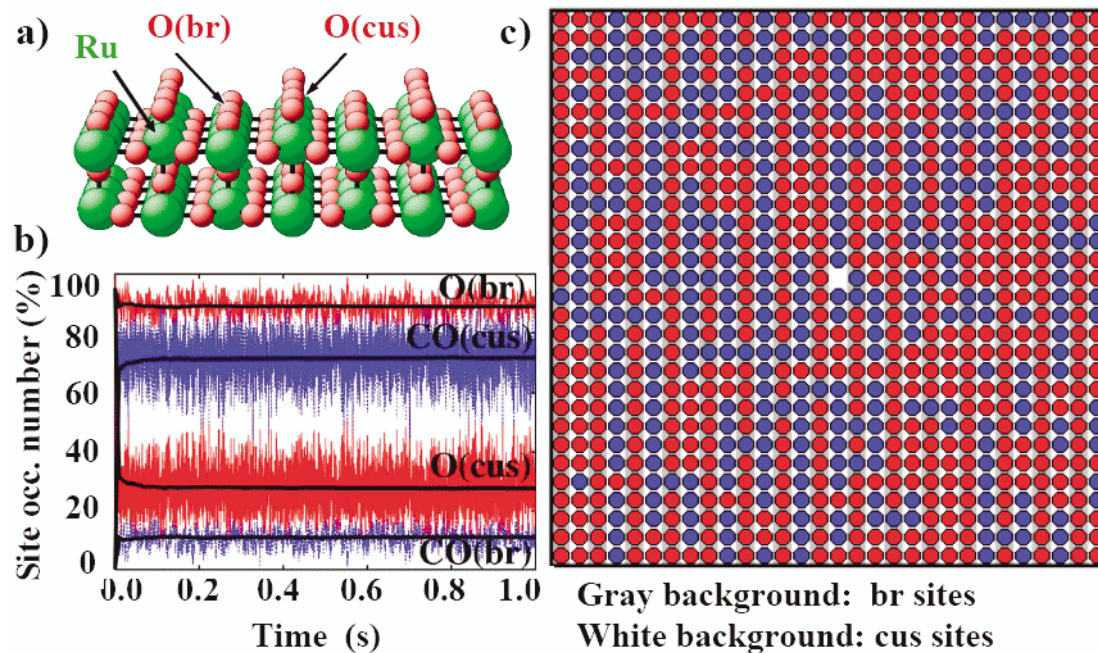


Disociation of H_2S in $\text{Fe}(110)$

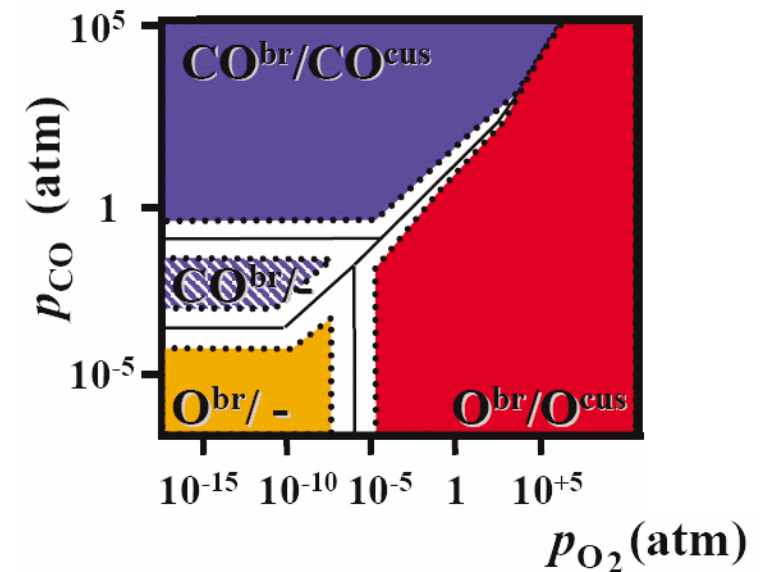
Jiang, Carter, Surf. Sci (2005)



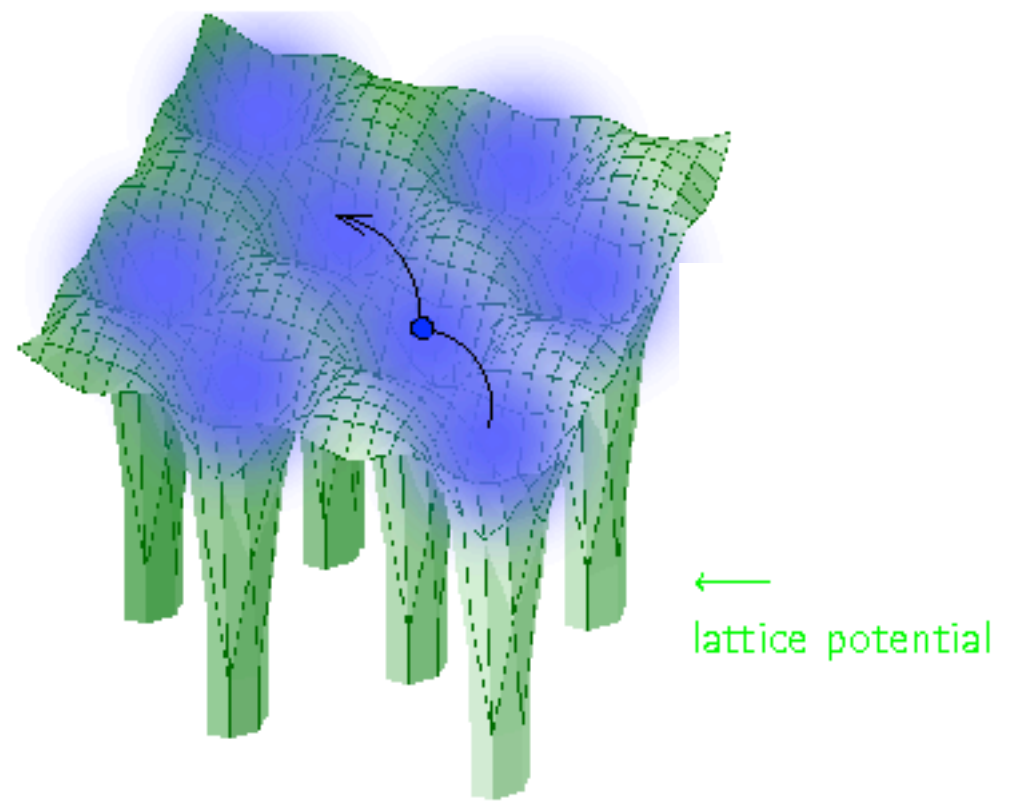
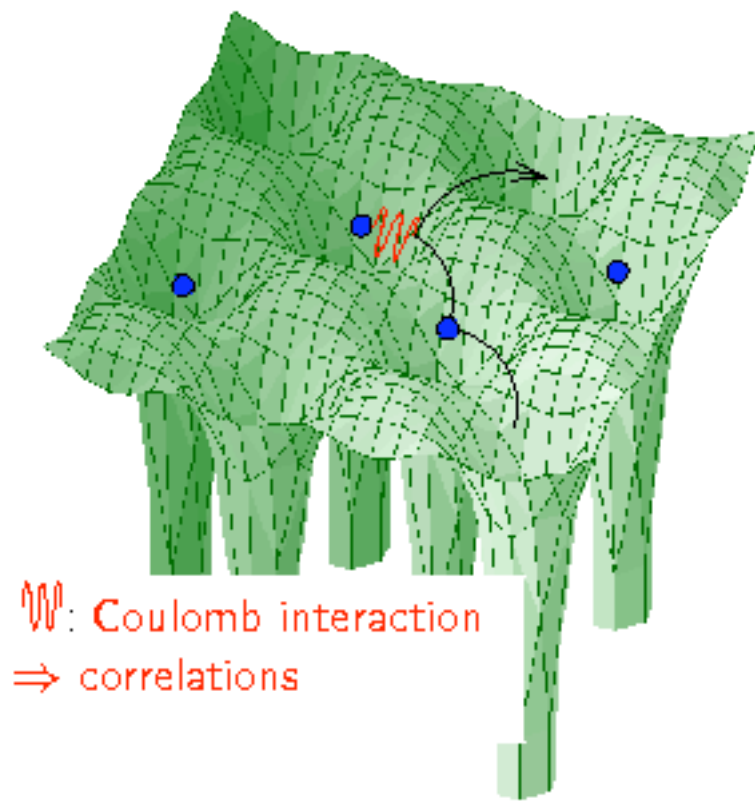
Kinetic-Monte Carlo method for catalysis -- parametrization



Reuter et al, PRL (2004)

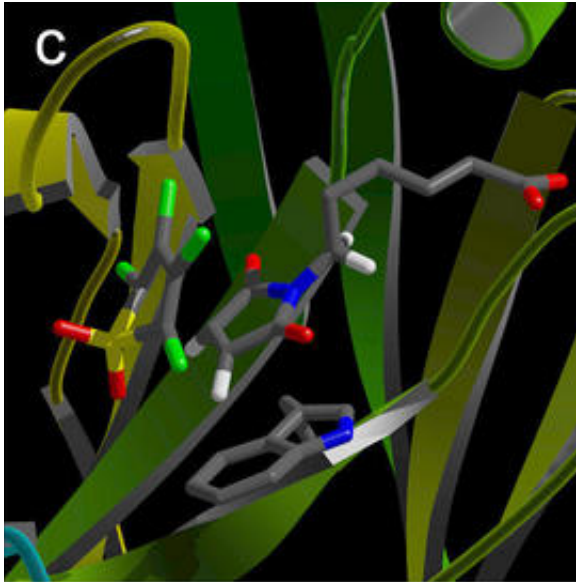


Challenges



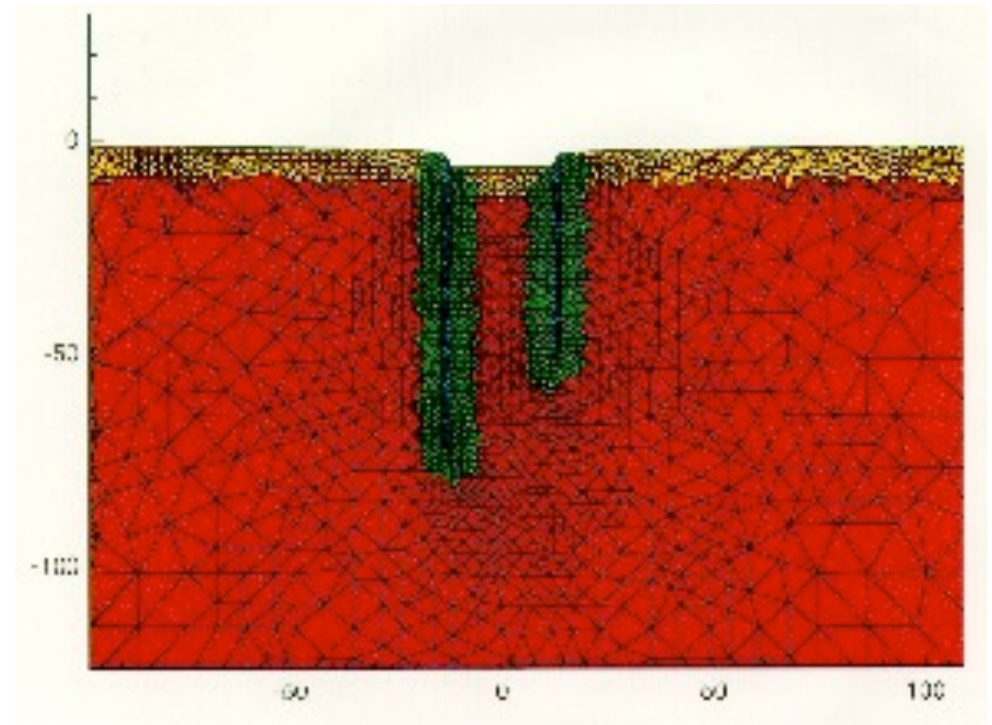
Better treatment of electronic correlation,
essential to describe localized states
in transition metals and rare earths

Hybrid methods to bridge length scales



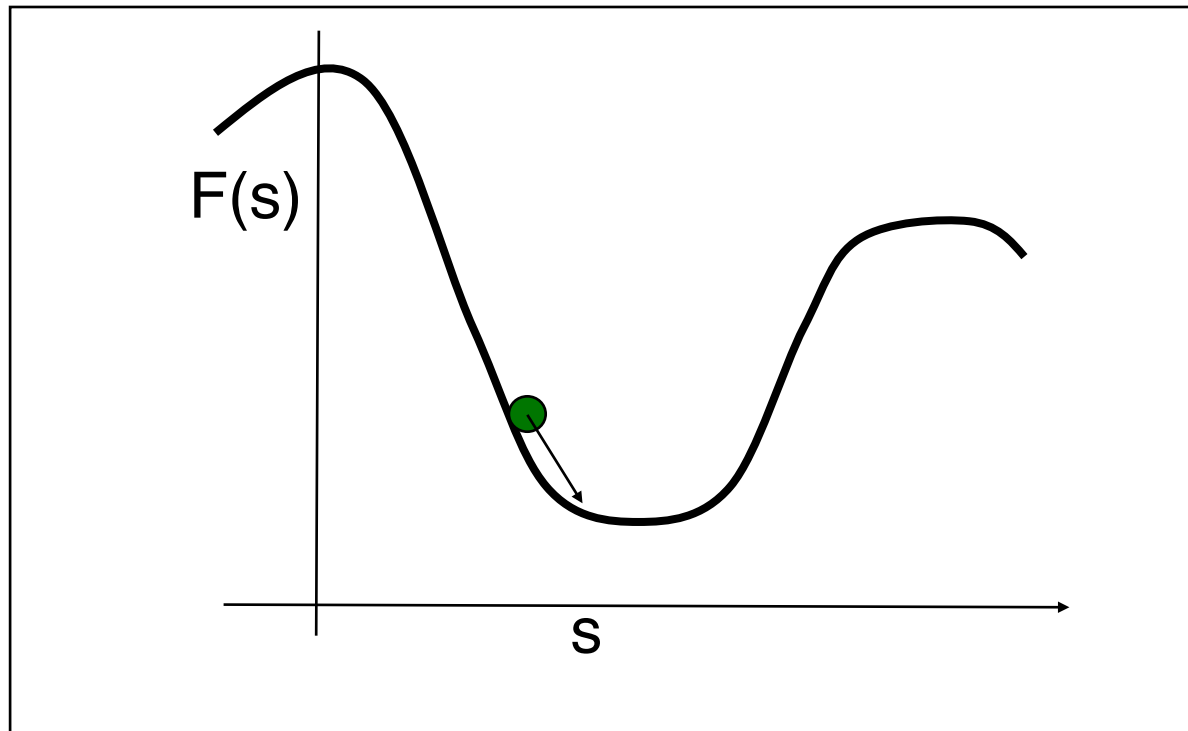
QM-MM: Precise treatment (QM) of a special part of the system. Rest treated at a lower level of quality.

Matching of atomistic methods with the continuum approximation



Escaping free-energy minima

Phase transition mechanisms, new crystal structures

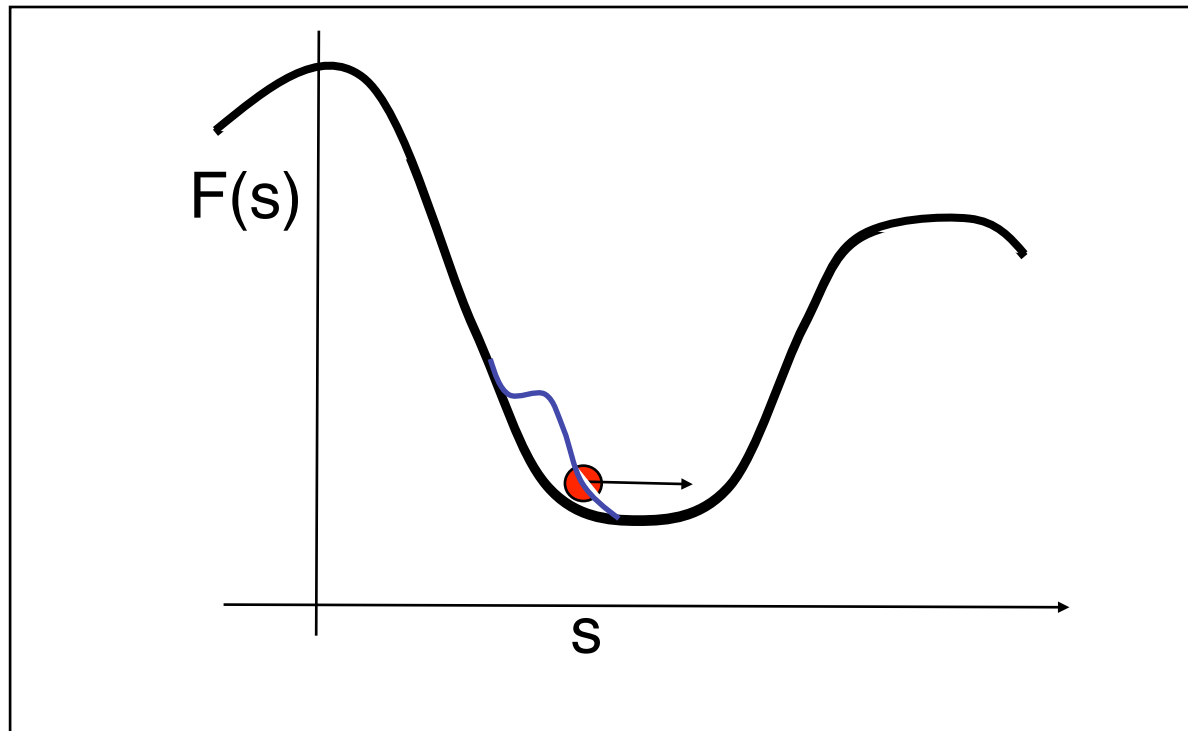


Metadynamics

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

Escaping free-energy minima

Phase transition mechanisms, new crystal structures

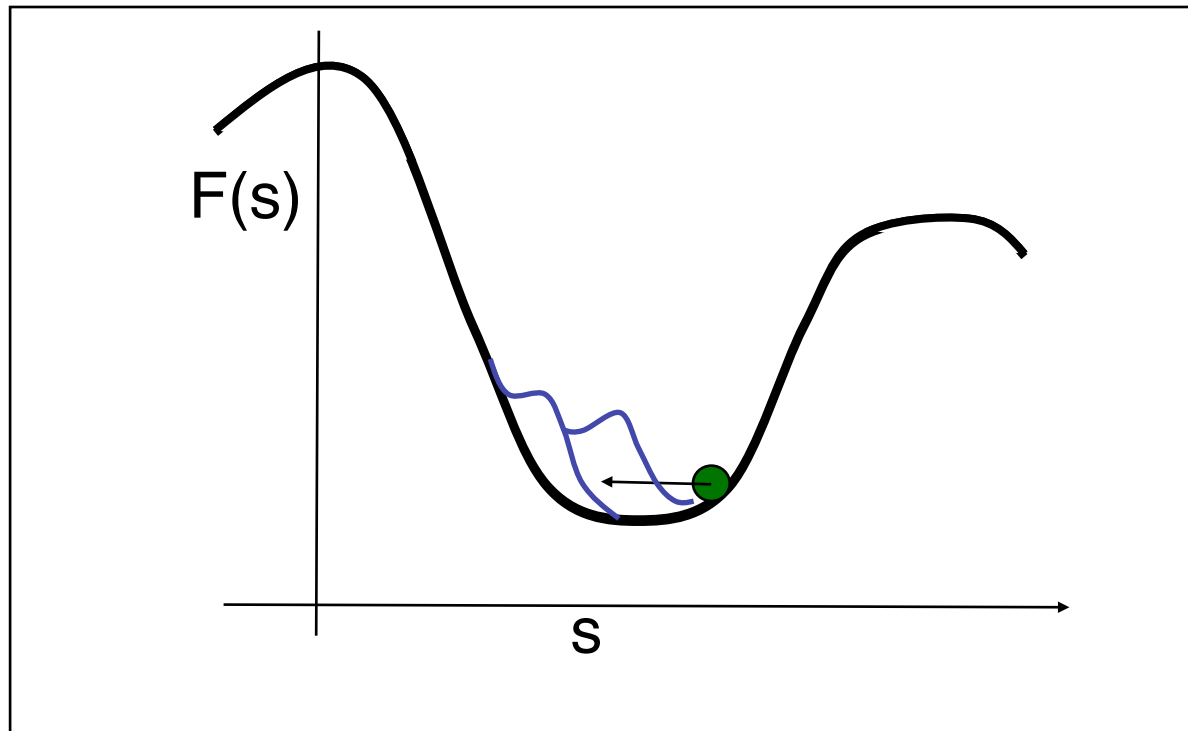


Metadynamics

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

Escaping free-energy minima

Phase transition mechanisms, new crystal structures

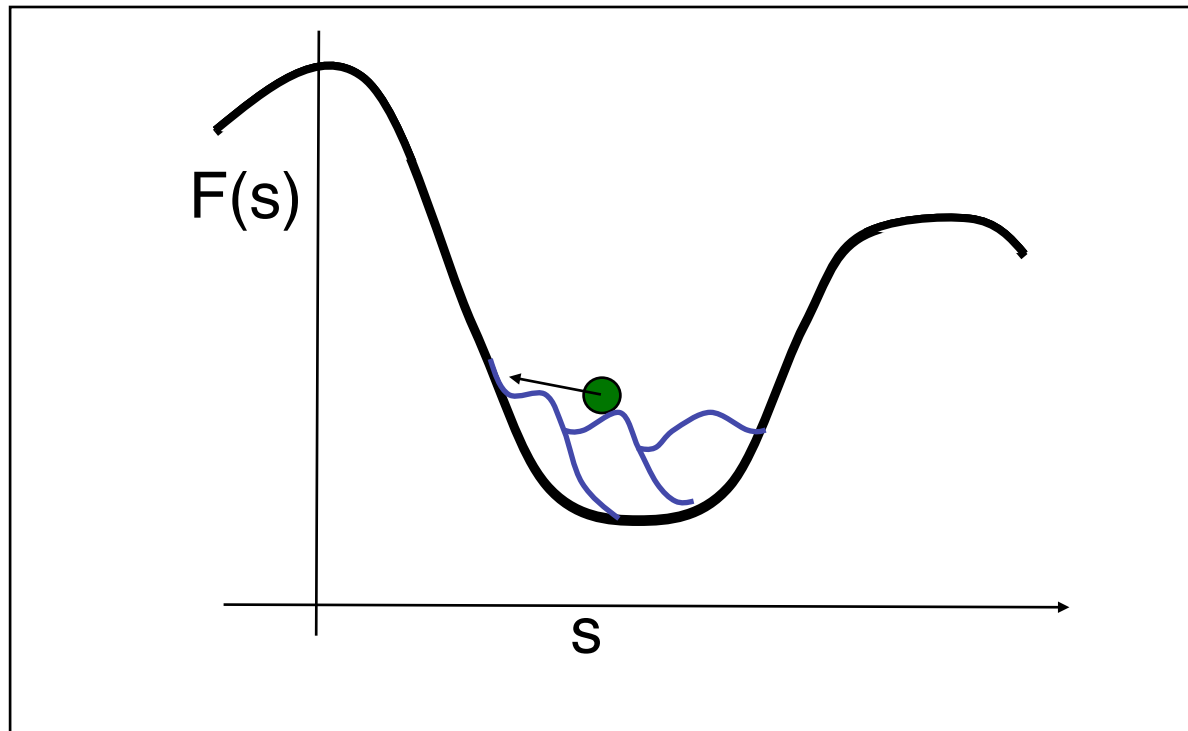


Metadynamics

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

Escaping free-energy minima

Phase transition mechanisms, new crystal structures

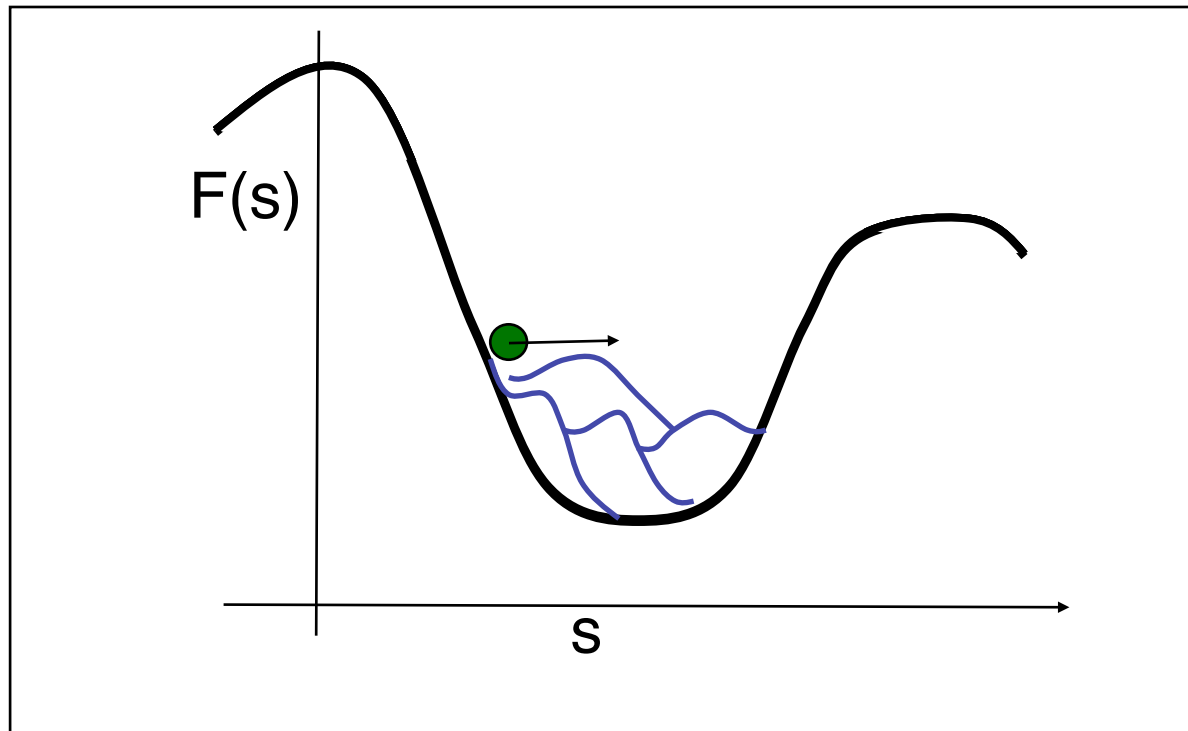


Metadynamics

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Escaping free-energy minima

Phase transition mechanisms, new crystal structures

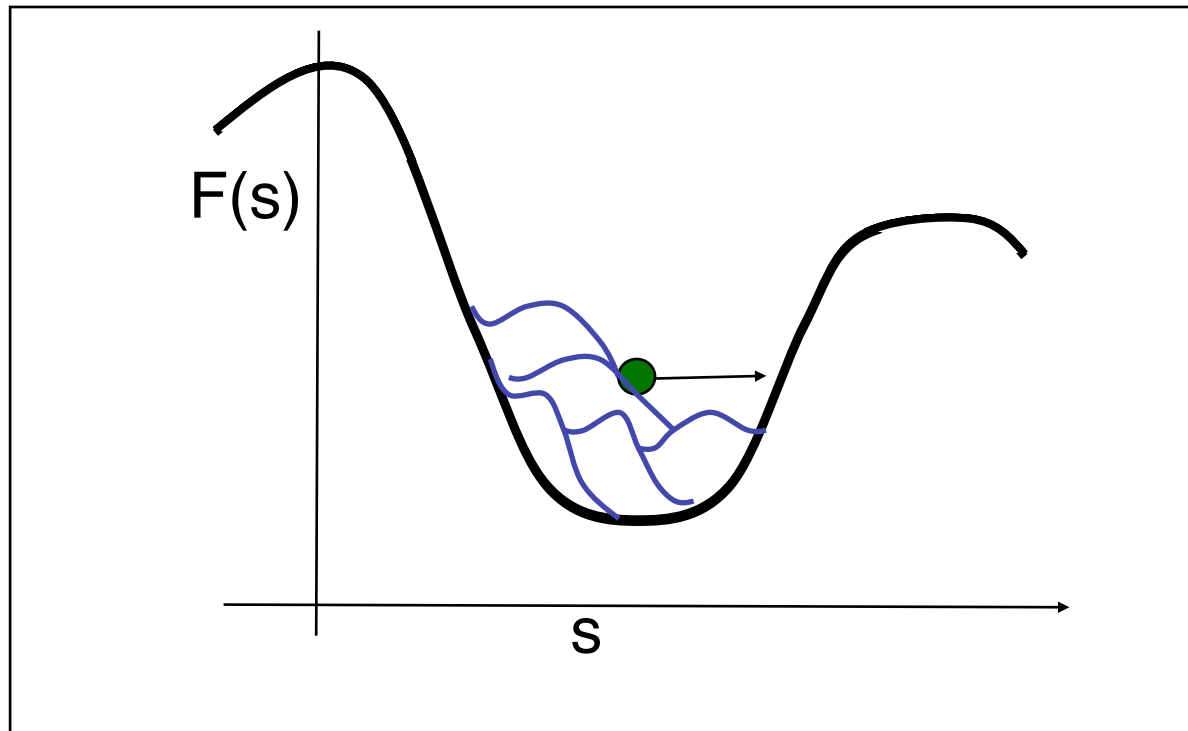


Metadynamics

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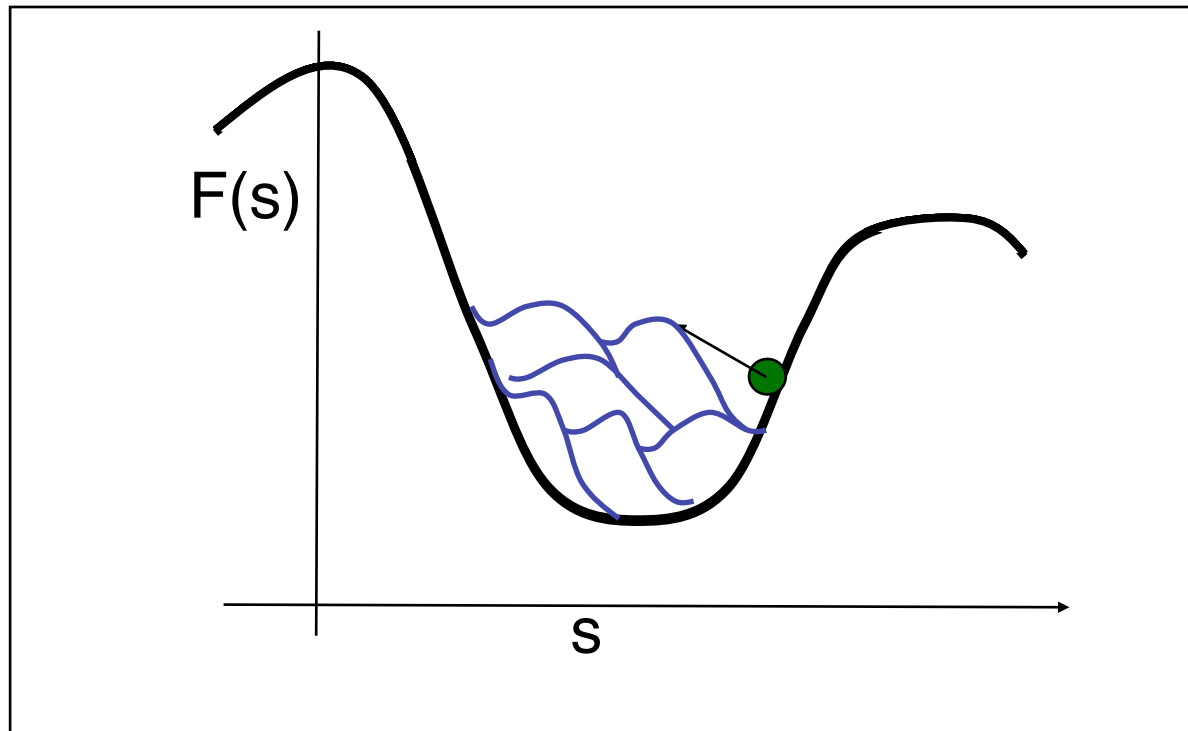


Metadynamics

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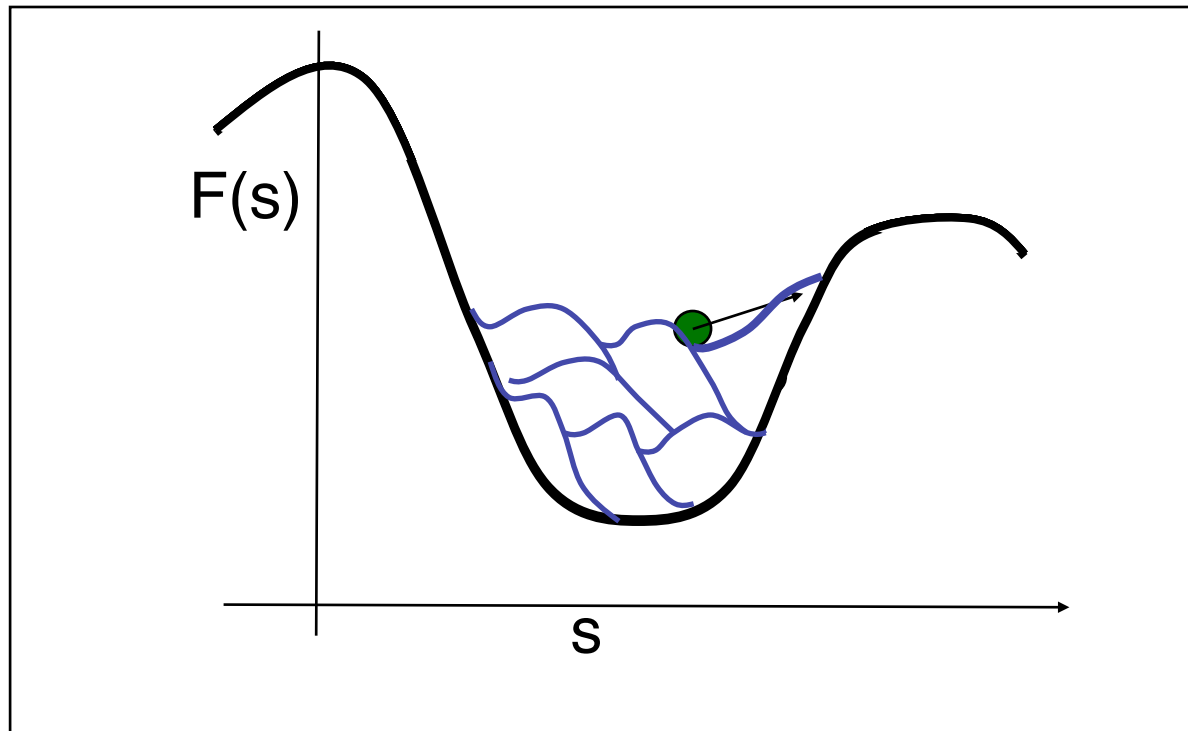


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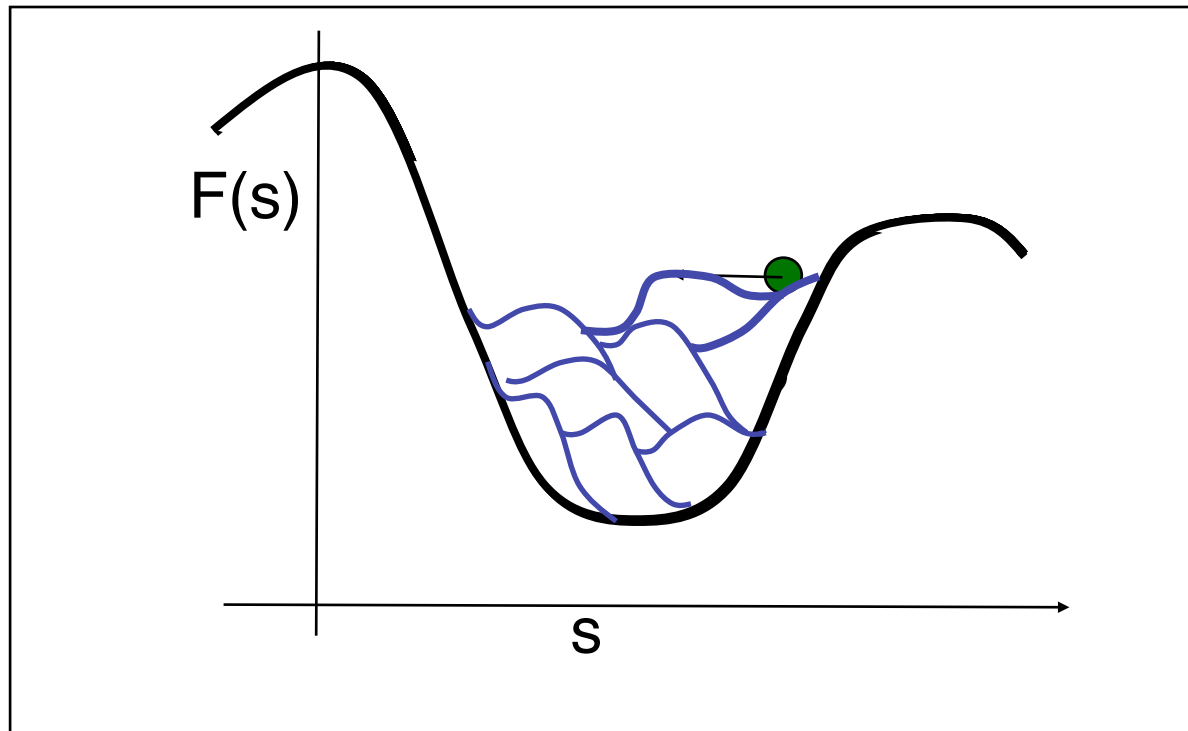


Metadynamics

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

Escaping free-energy minima

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Metadynamics

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

The Torii Analogy

(Prof. H. Nakamura)

First-principles calculations



Theory Experiment