# First-principles calculations: Exploration and understanding

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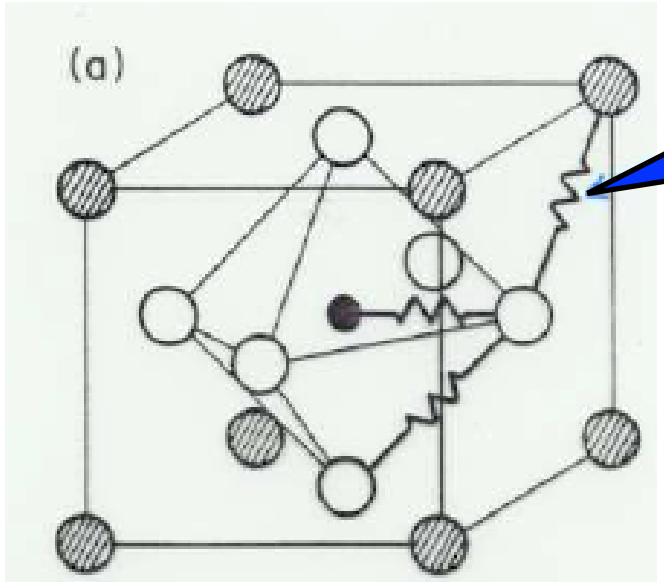
EXCELENCIA SEVERO OCHOA

- Scientific method: experiment, modelization, prediction, experiment, model refinement…

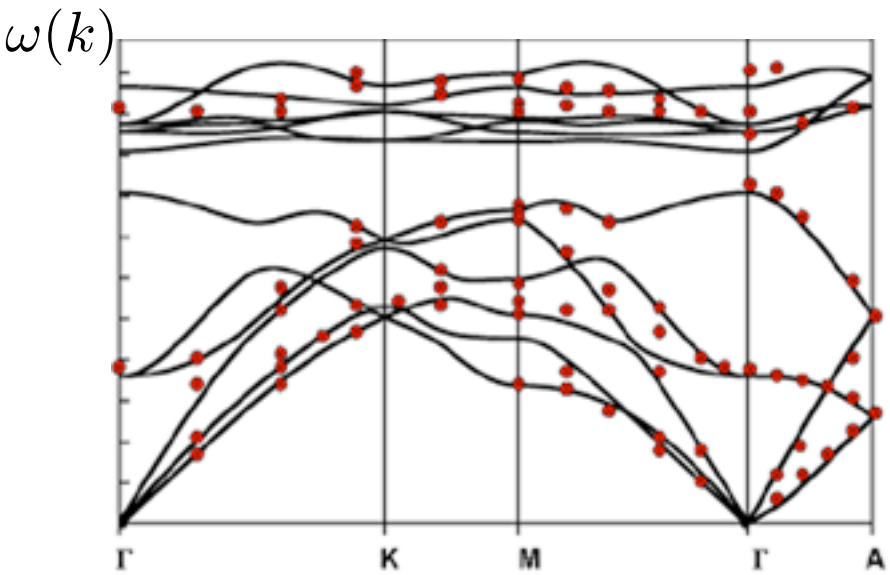
- We have the "ultimate model" for materials, and it involves the use of computers.

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



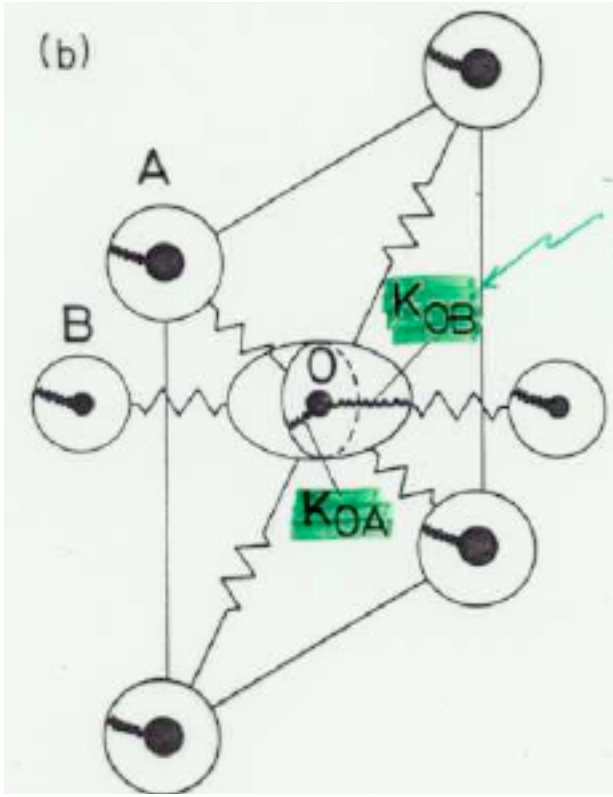

Spring constant

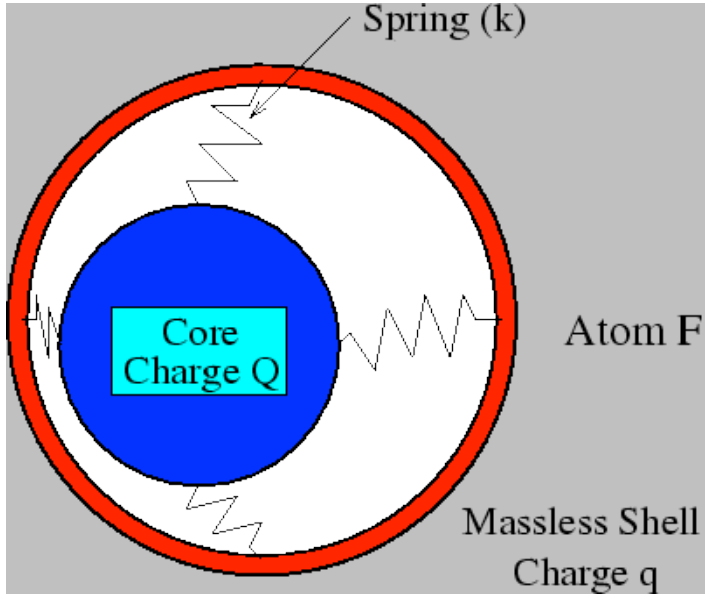
Basic idea: Vibrations around an equilibrium point




Parameters can be fitted to experiment

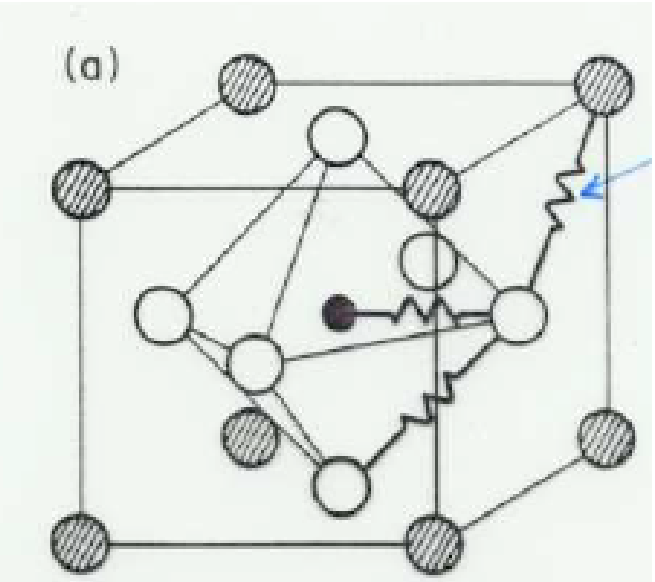
# Refinement of the model: polarizable electrons (shell model)

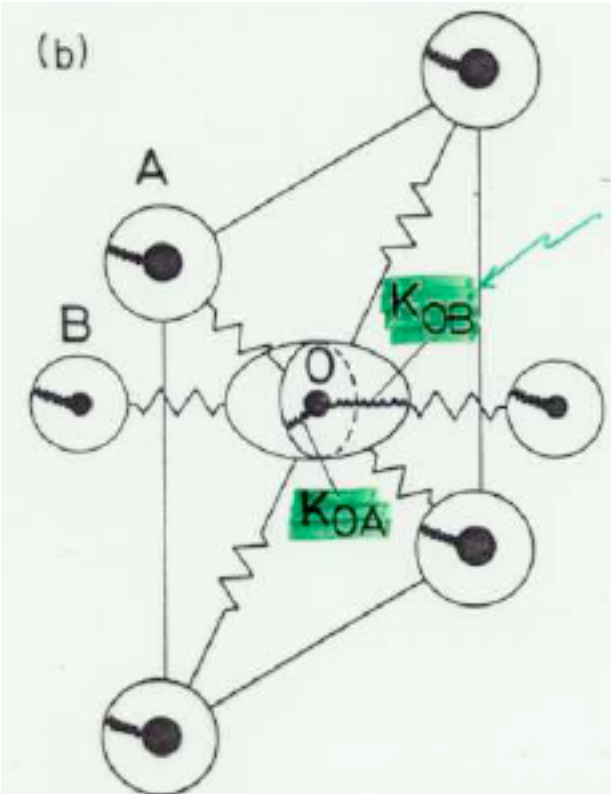



Internal structure of the atom acknowledged

Better fit to experiment
New phenomena



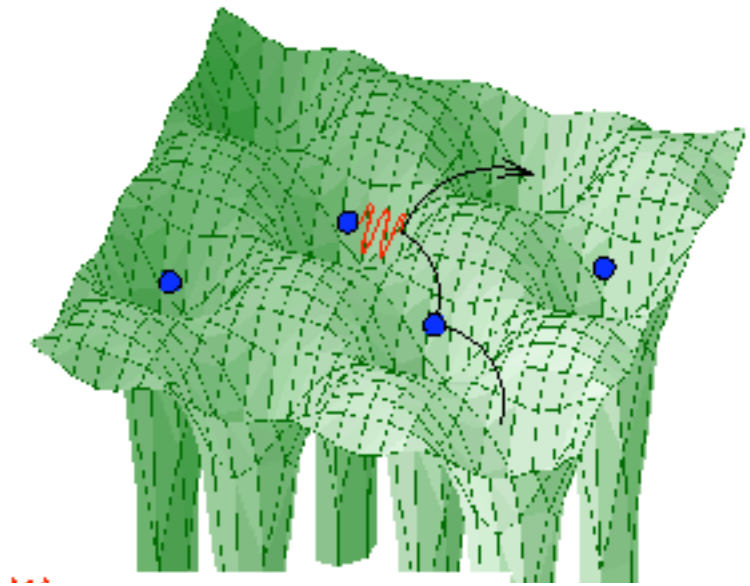

....

Electrons are the glue
holding solids together

We know the basic equations:
Quantum Mechanics and Electromagnetism

# The "ultimate model" for electrons in a material

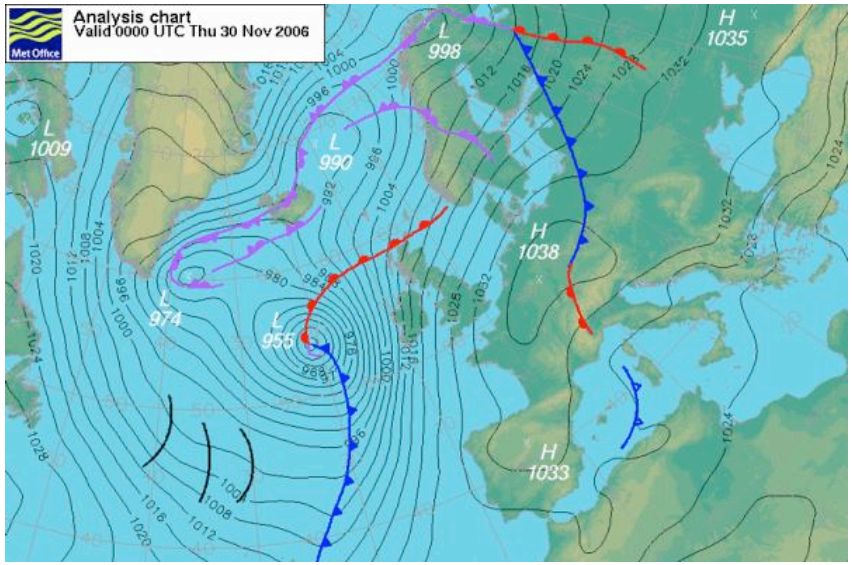
$$H = \sum_i \left[ -\frac{\hbar^2 \Delta_i}{2m_e} + \sum_I \frac{-e^2}{4\pi\epsilon_0} \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} \right] + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$



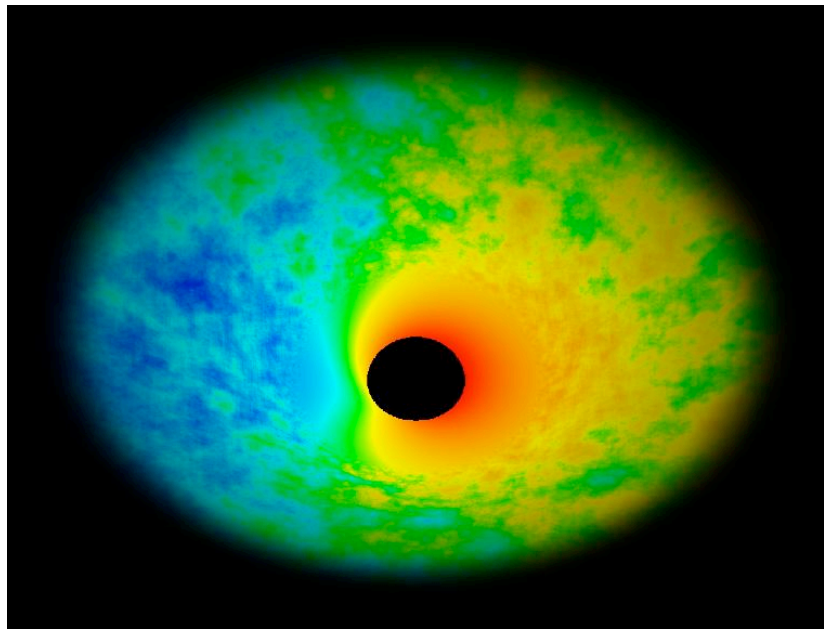
$$\hat{H}\Psi = E\Psi \qquad \Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n)$$

We could compute "everything"

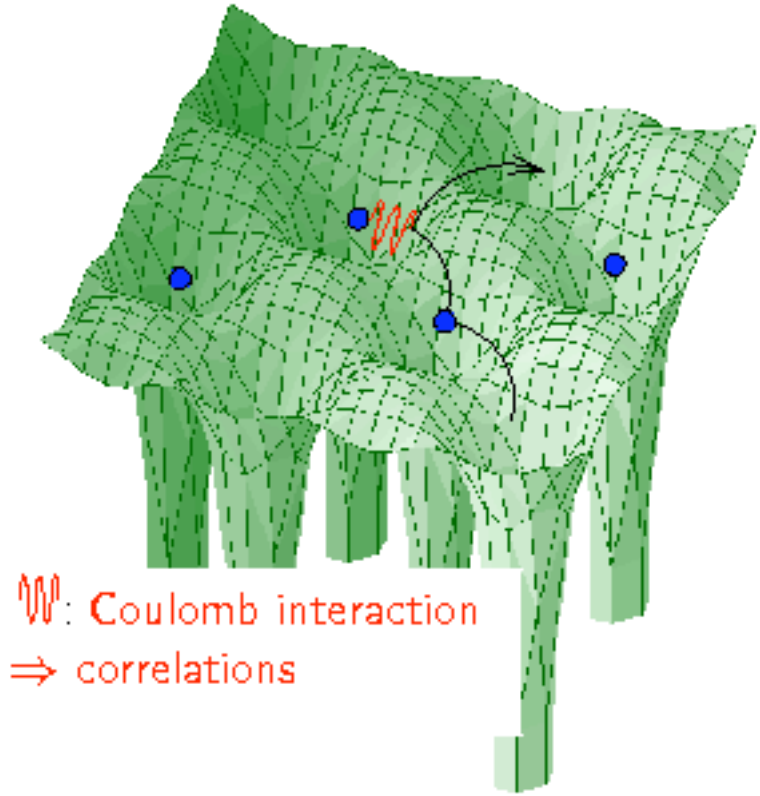
# *Simulation of reality*

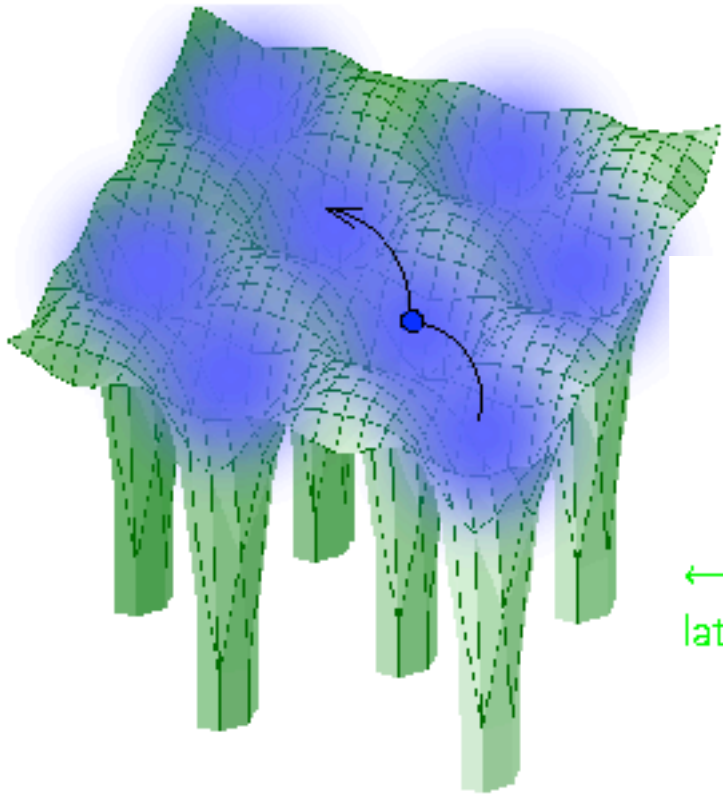



Meteorology:
We know the basic equations



Astrophysics:
We know the basic equations.
Little data



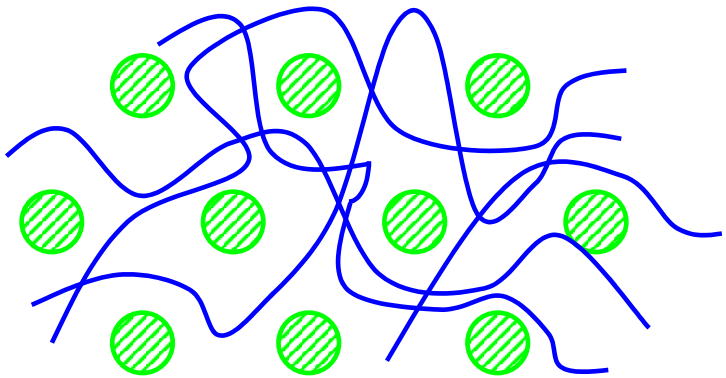



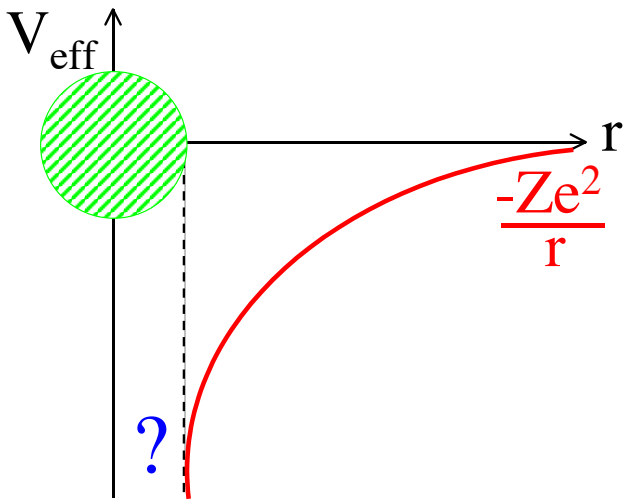

Density-functional theory $E = E[n] \quad n(\mathbf{r})$

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

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

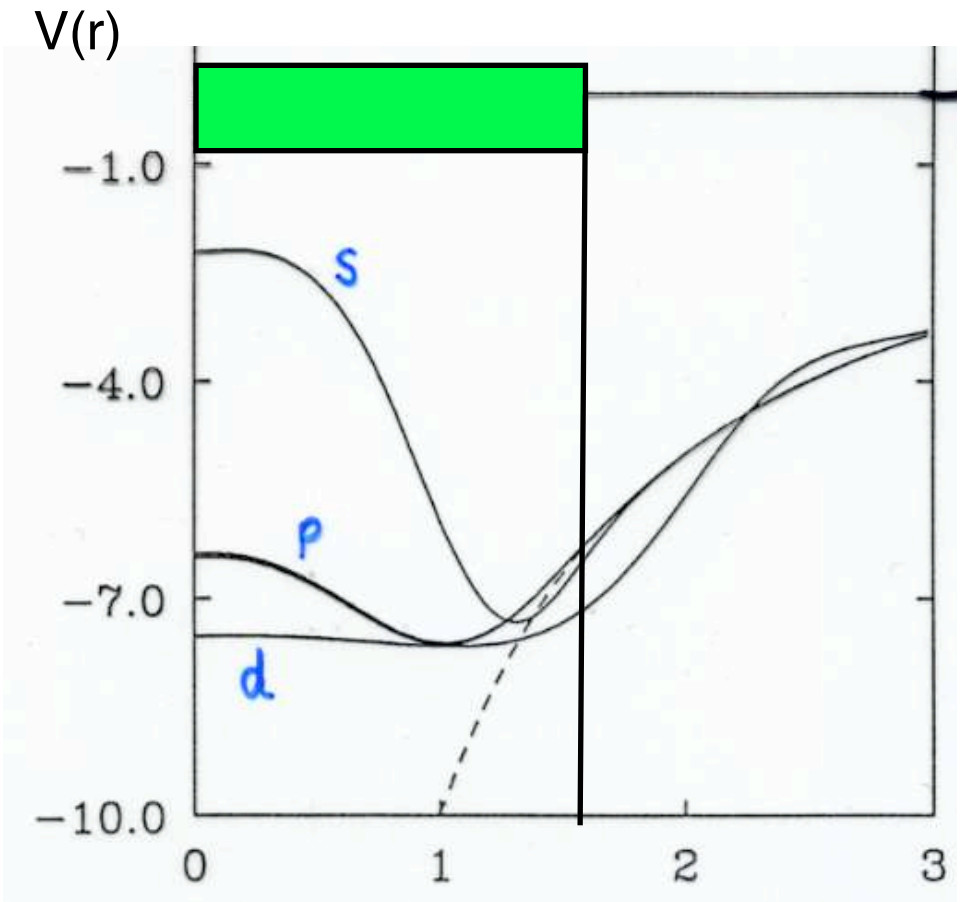
# Internal electrons do not participate in the chemical bond






Effective potential for valence electrons

Pseudopotential



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

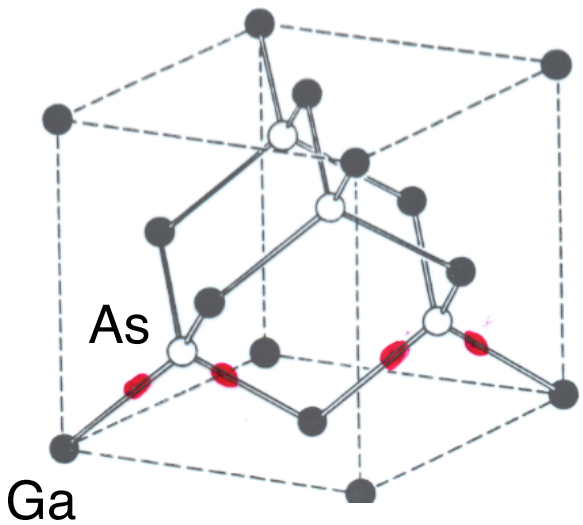
Reasonably accurate
Versatile

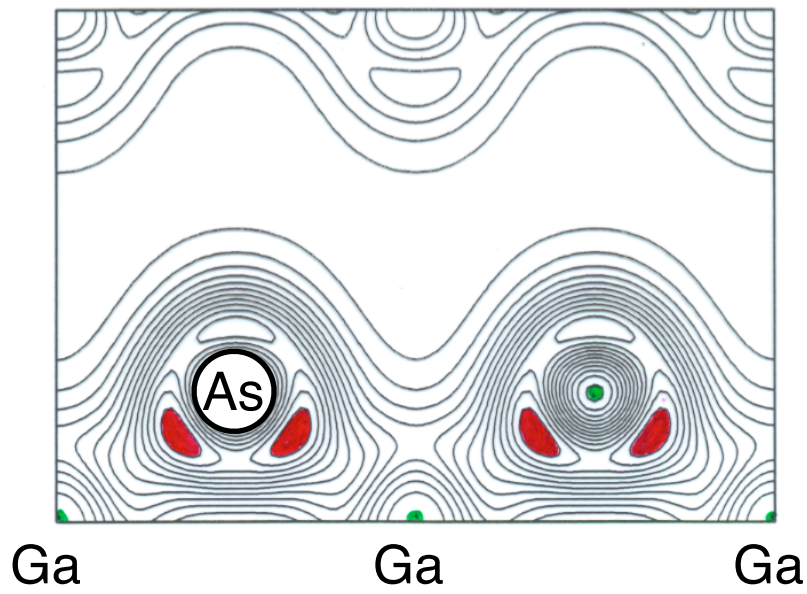
Dozens of codes available

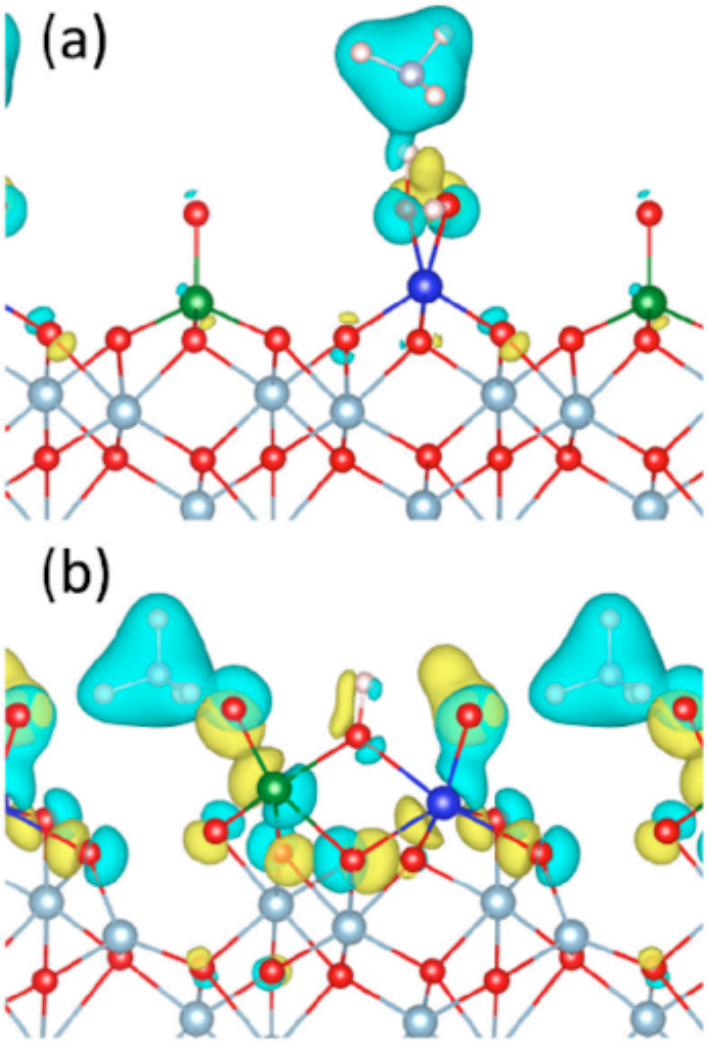
*Siesta, Espresso, Abinit, Fleur, Vasp, BigDFT, FHI-Aims, Wien2k, CP2K, Dmol, ADF, Castep, OpenMX, ….*

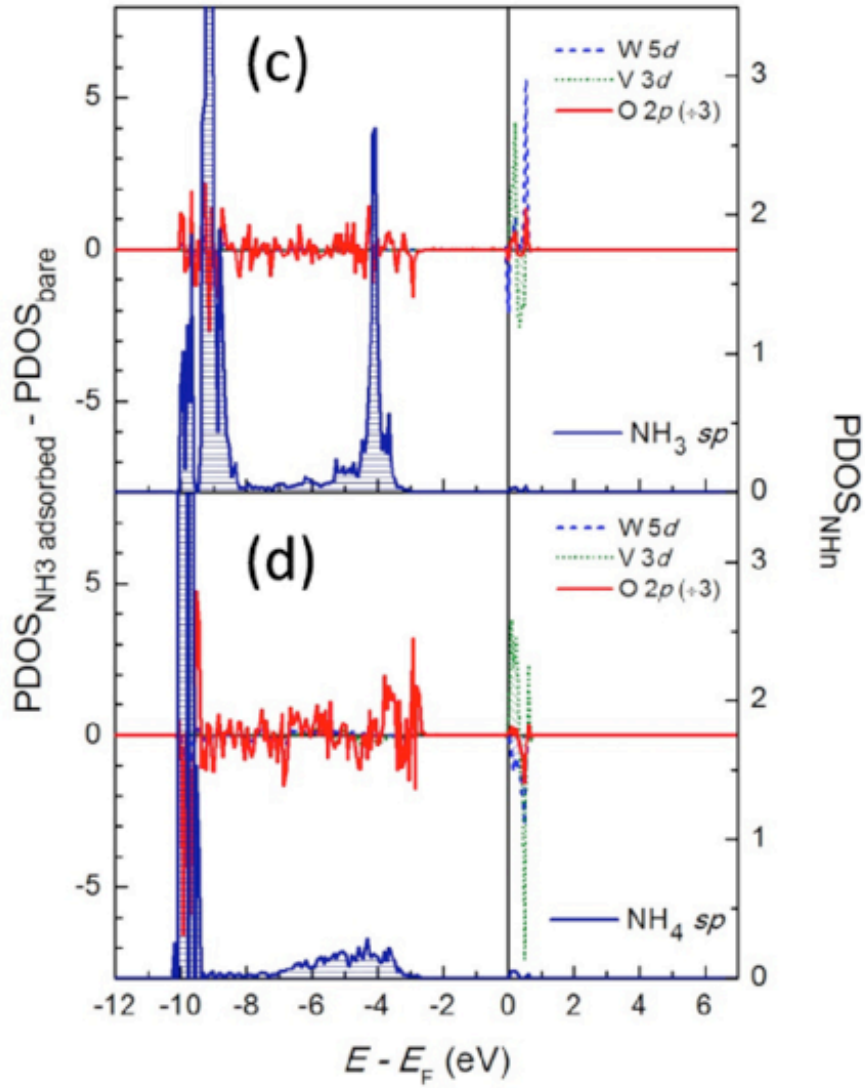
# Output of the program

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




(a)
(b)


(c)
(d)
W 5d
V 3d
O 2p (÷3)
NH3 sp
NH4 sp
PDOSNH3 adsorbed - PDOSbare
PDOSNHn
E - EF (eV)
-12 -10 -8 -6 -4 -2 0 2 4 6
5 0 -5
3 2 1 0

* *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.*

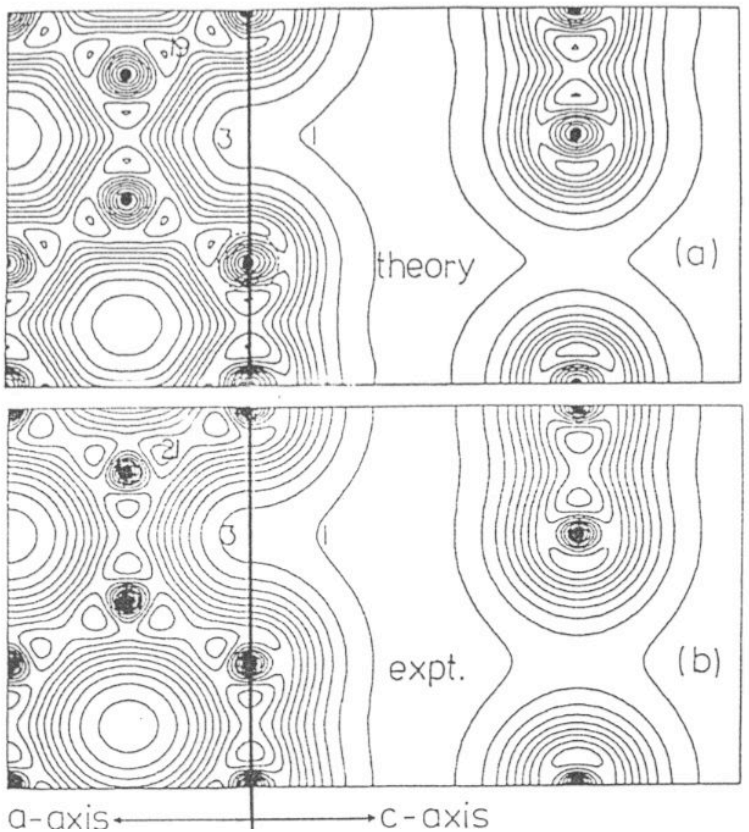
*(Headings from the essay: "The Computer: Ruin of Science and Threat to Mankind", by Clifford Truesdell, in "An Idiot's Fugitive Guide to Science", Springer, 1984)*

*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.*

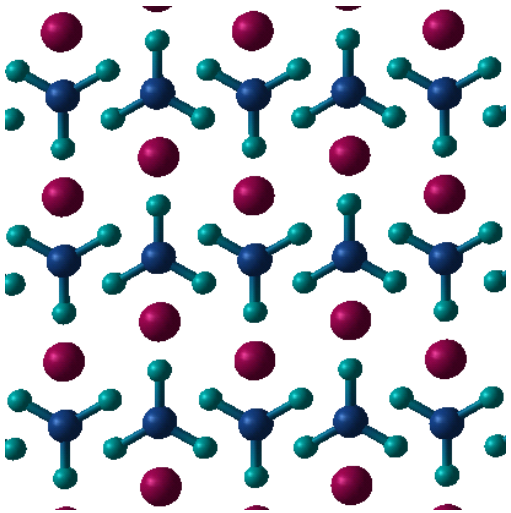
*(P.W. Anderson)*

# Uses in materials science

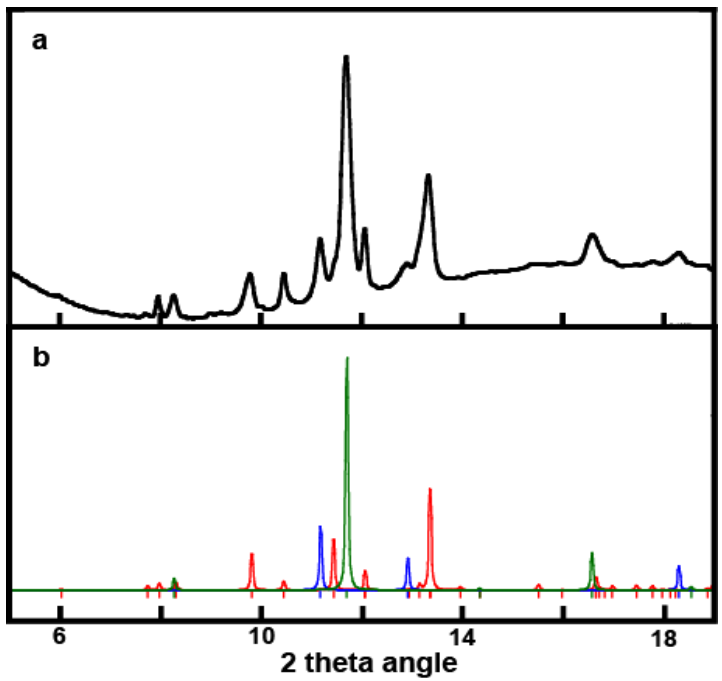
- Exploration and prediction, simulating experiments difficult or impossible in the laboratory.
- Clarification/complement of experimental information by means of the precise control of simulation conditions. (The computer is a perfect control machine)
- Design of materials with desired properties. Reduction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



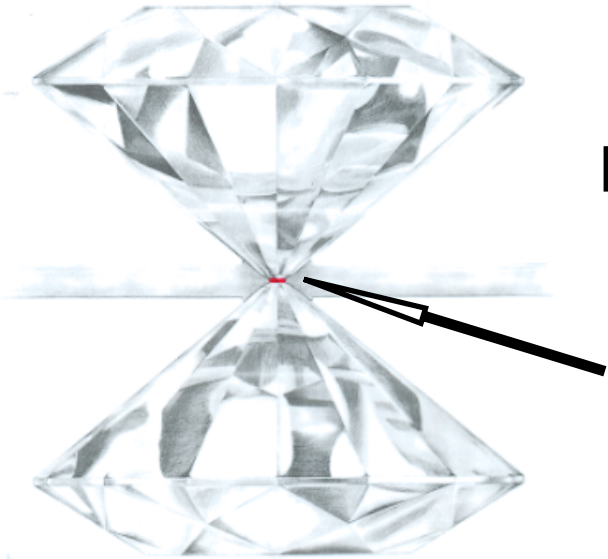

Calculation of electronic charge density
(Simulation of an X-ray experiment)



Synthetic diffraction diagram



## High-pressure experiment

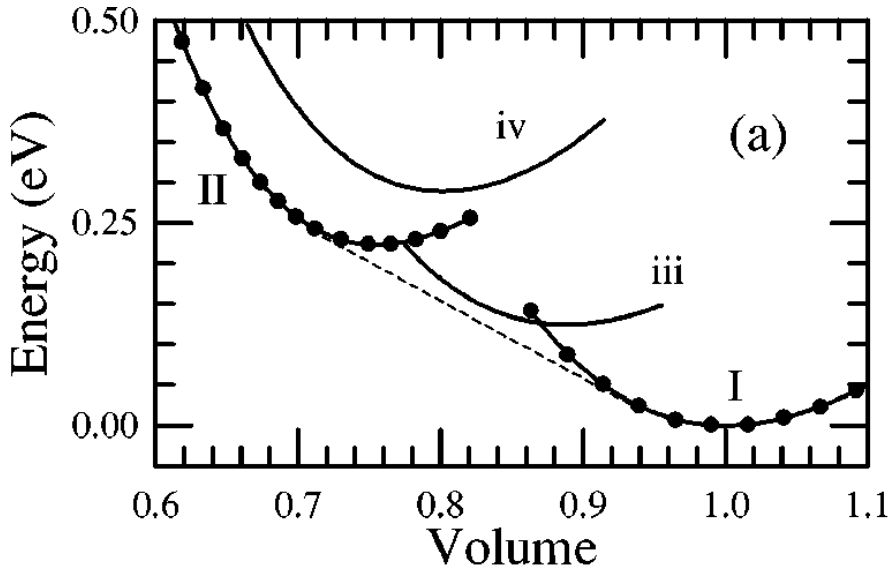



Diamond-anvil cell

## Theoretical treatment

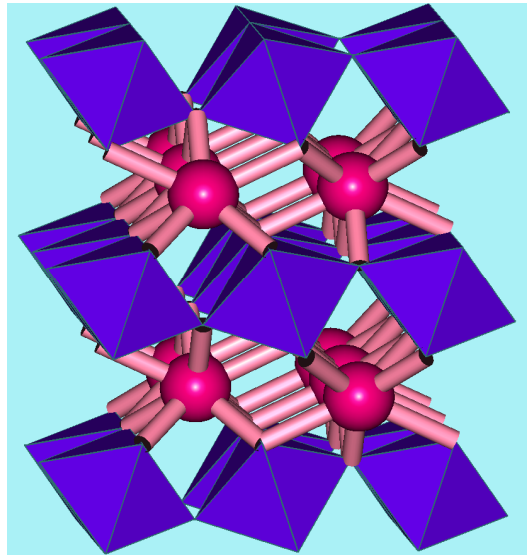
$$E = E(V), \quad p = -\frac{dE}{dV}, \quad p = p(V)$$

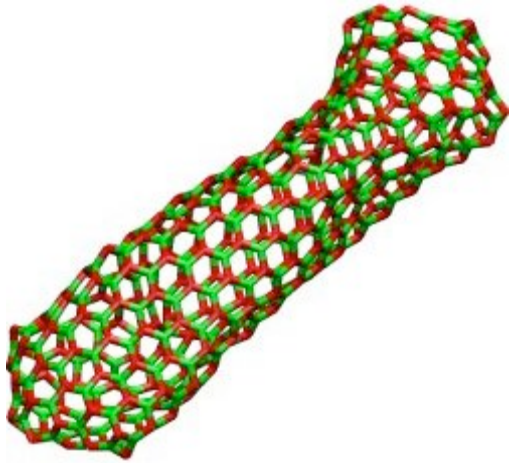
Equations of State
Phase transitions



Post-perovskite phase of MgSiO3

Oganov et al, Nature (2004)





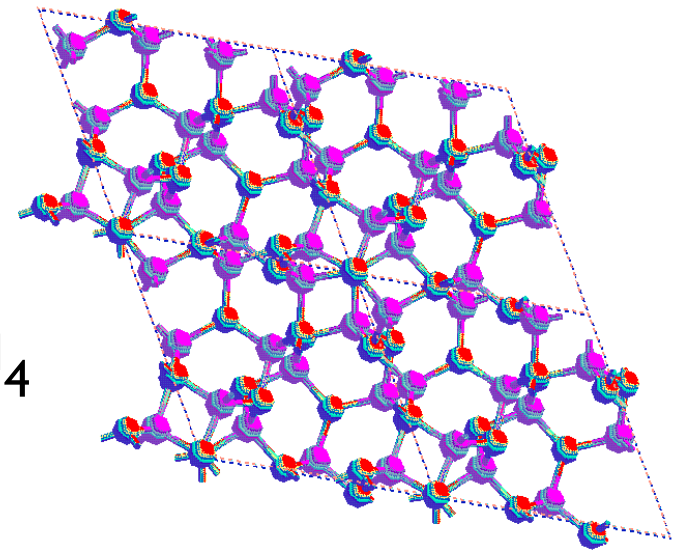
Prediction of BN nanotubes

Rubio, Corkill, Cohen, PRB (1994)

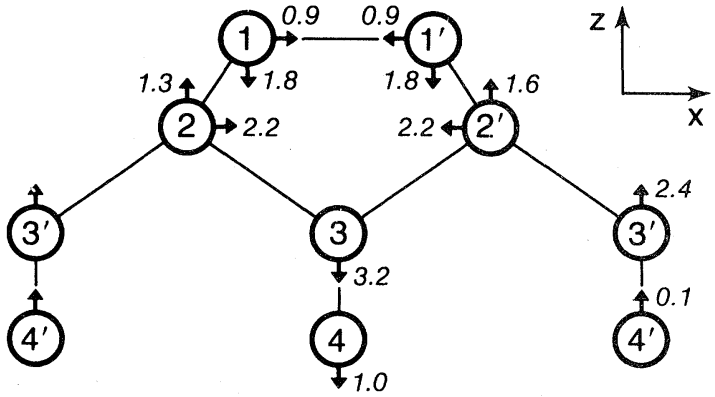
Proposal for a super-hard material

Liu, Cohen, Science (1989)

$C_3N_4$

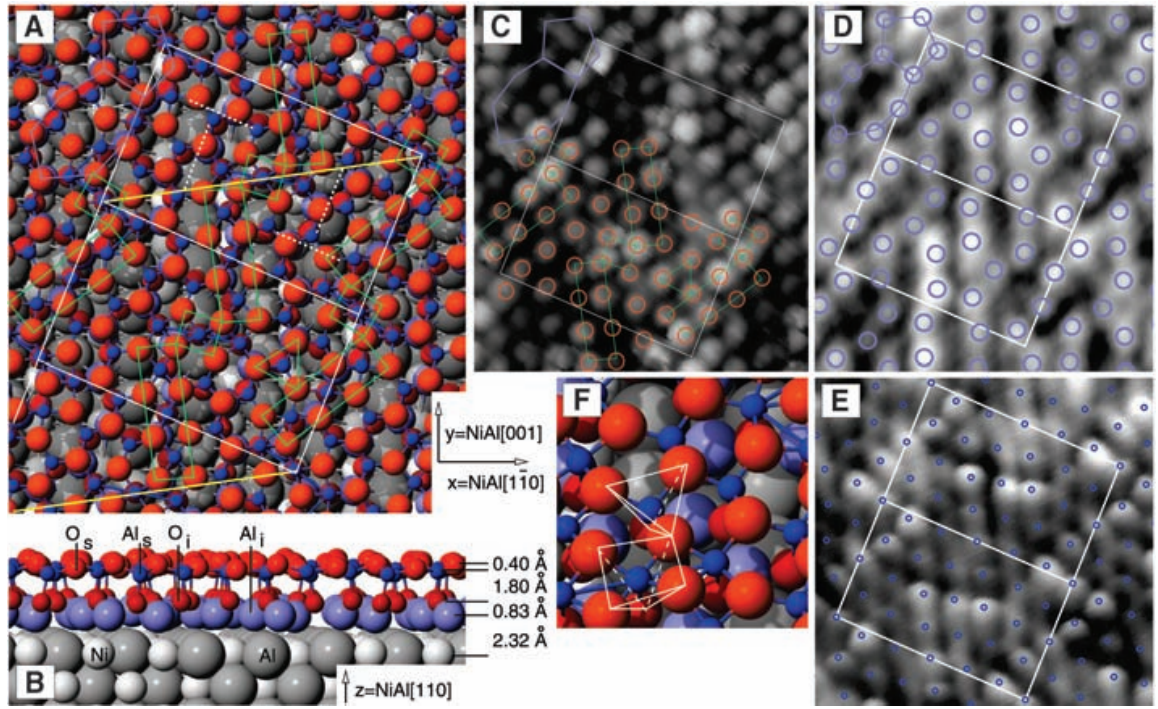


# Surfaces




First work on Si(100)

Yin, Cohen, PRB (1981)

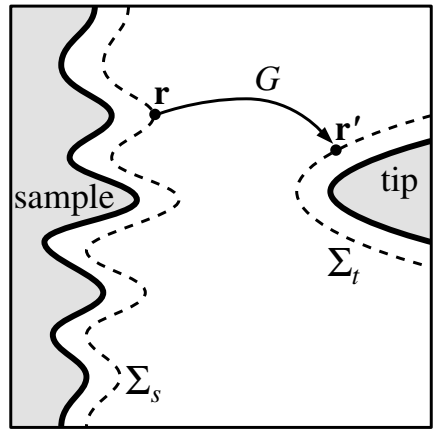


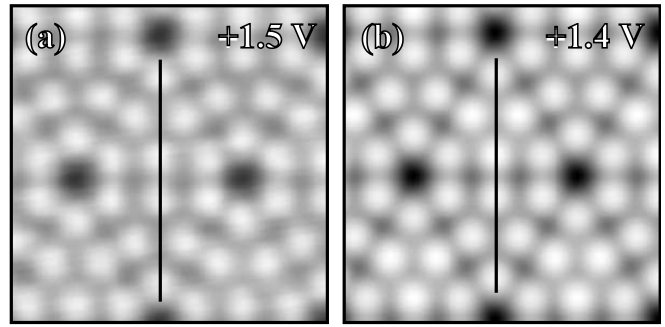

Oxidation of NiAl

Kresse et al, Science (2005)

Method for the simulation of STM images

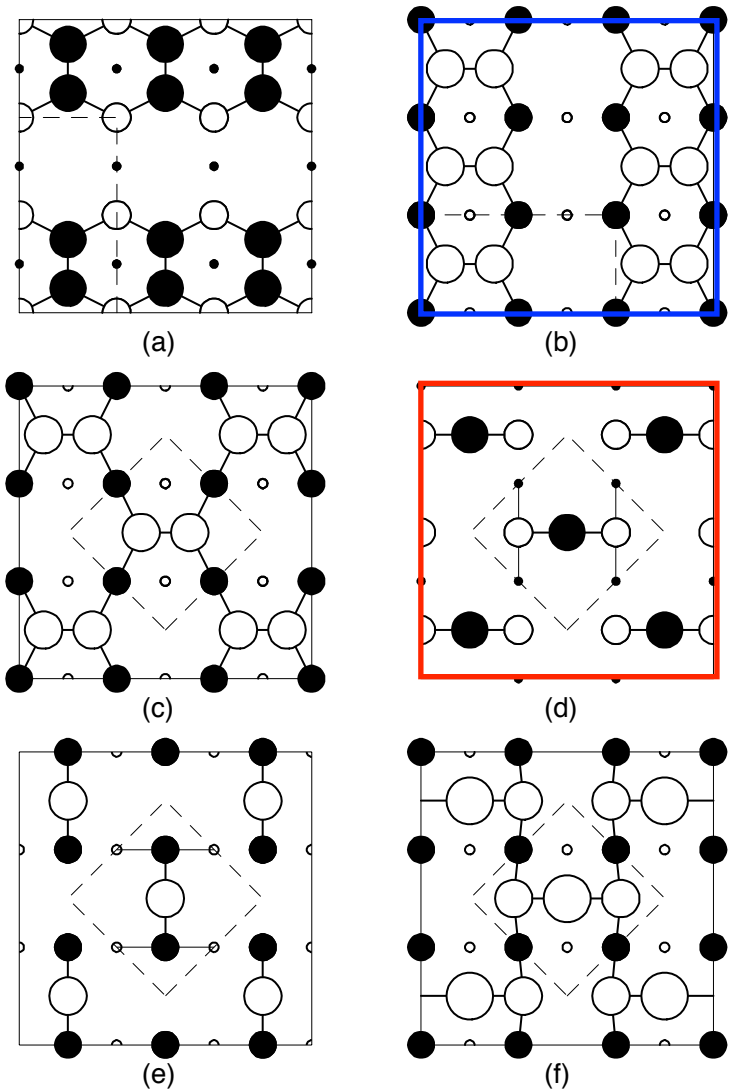
Paz et al, PRL (2005)

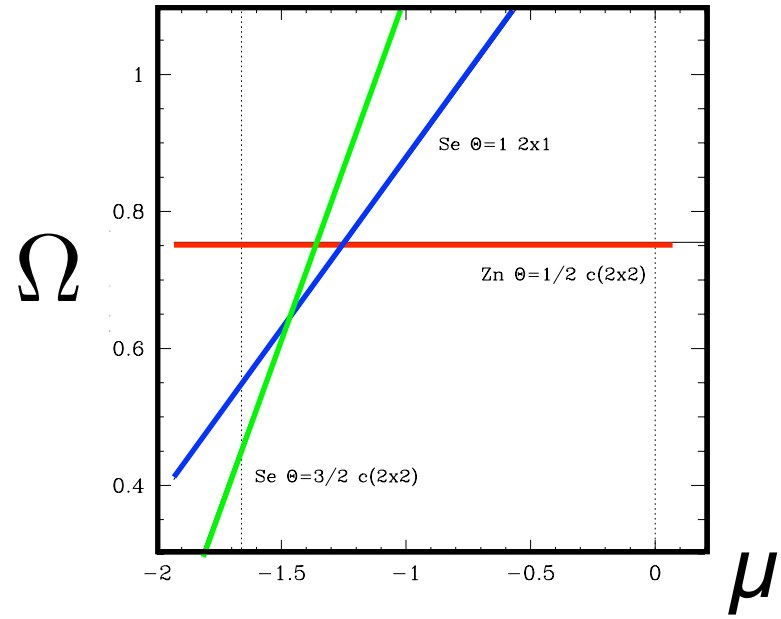


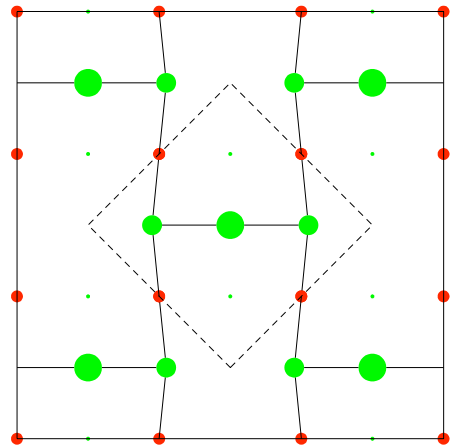

Exp Theory

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



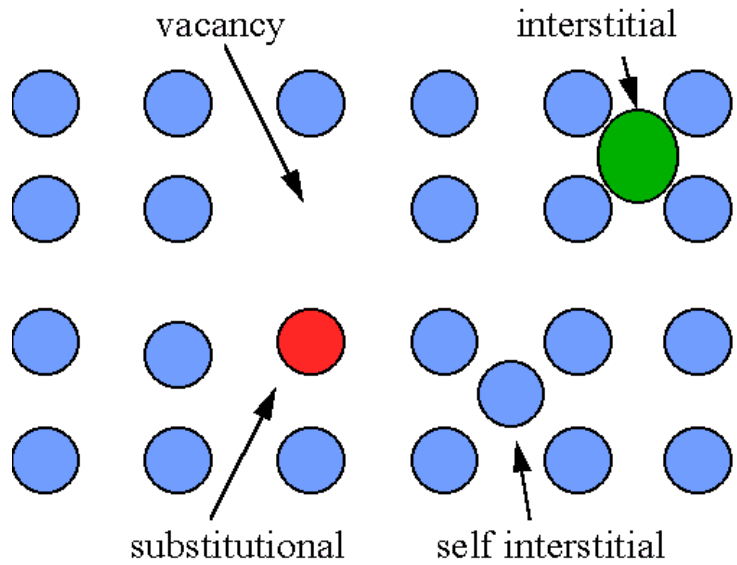




Garcia, Northrup, APL (1994)



# Precise control of simulation conditions

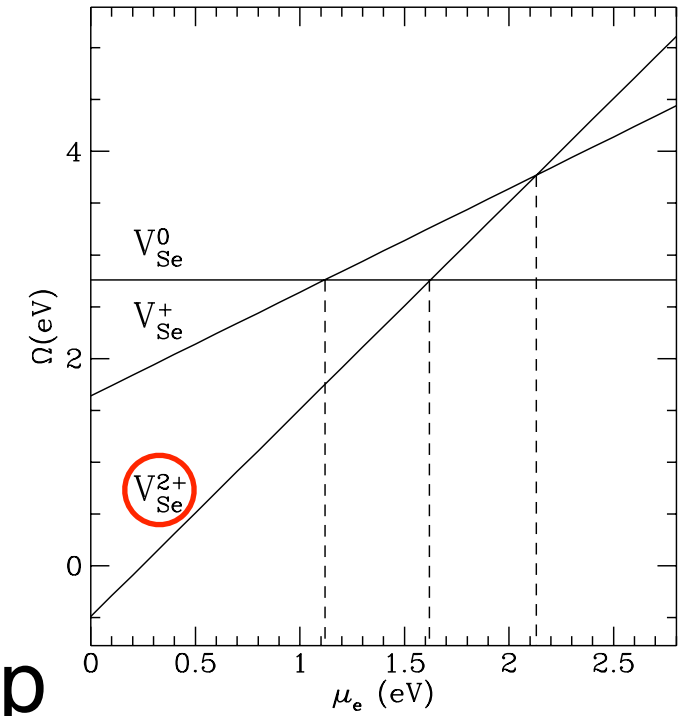
Point defects:
Great experimental complexity



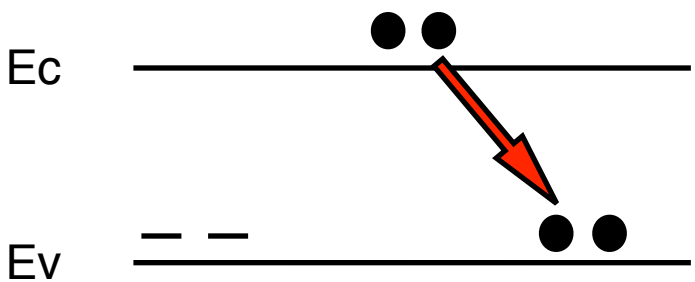

In a calculation they can be “prepared” (isolated or in complexes) and their energies of formation and bonding computed

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

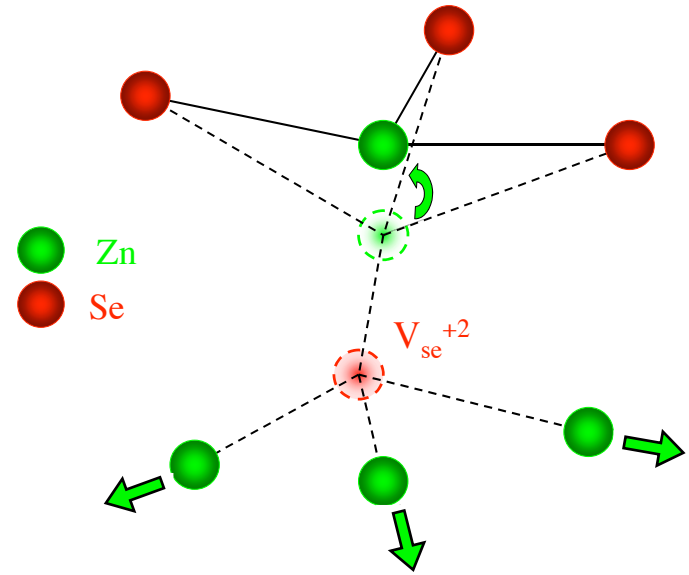
# Mechanism for p-doping saturation in ZnSe




p n

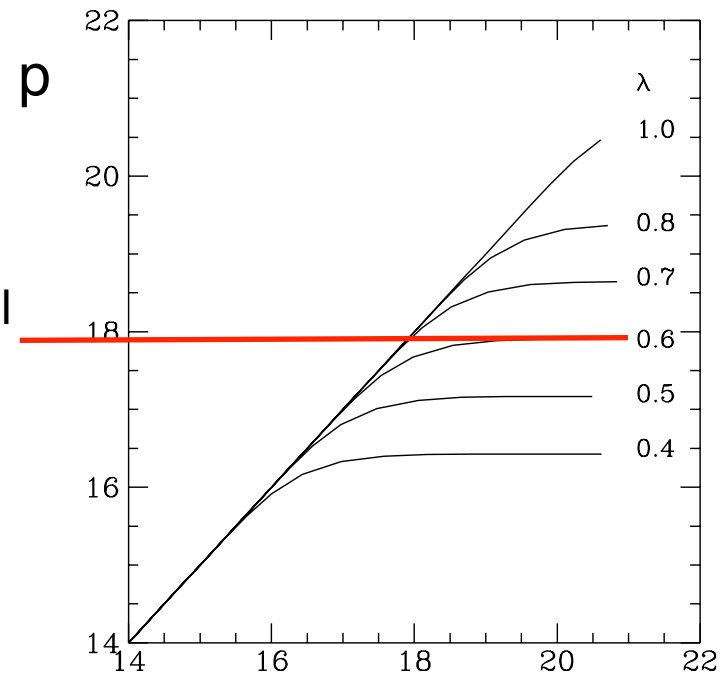



Compensation of two holes by $V_{Se}^{+2}$

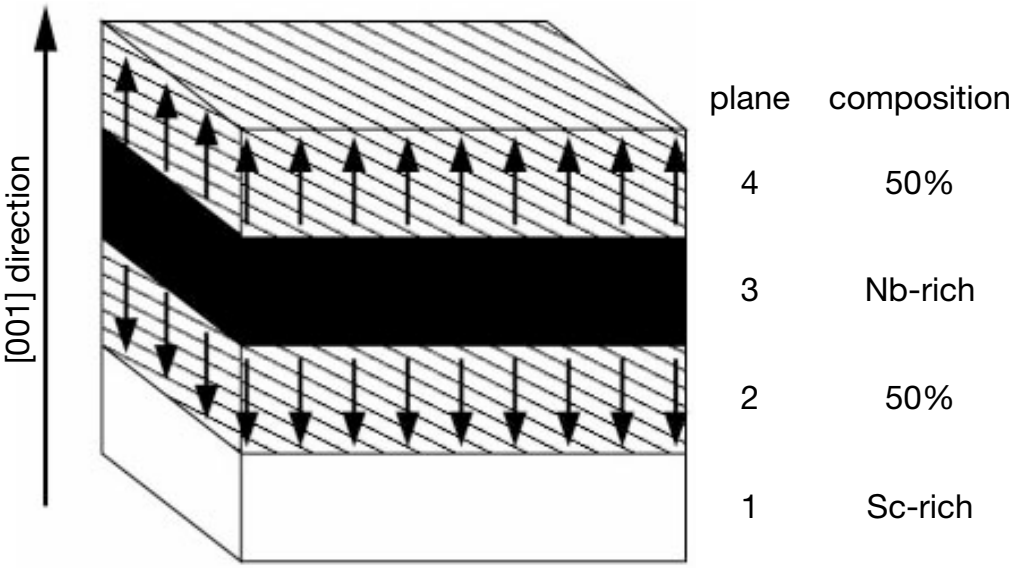



log p

Experimental saturation level



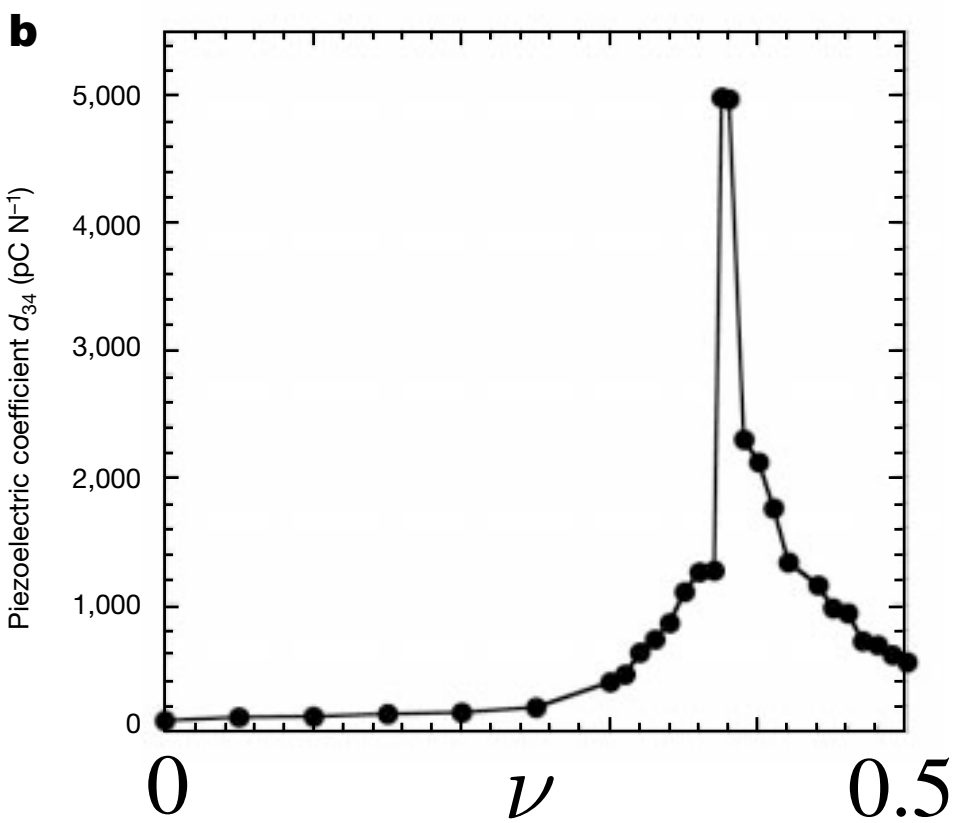

Garcia, Northrup, PRL (1995)




$$\mathrm{Pb}(\mathrm{Sc}_x\mathrm{Nb}_{1-x})\mathrm{O}_3$$

$$x = 0.5 - \nu$$

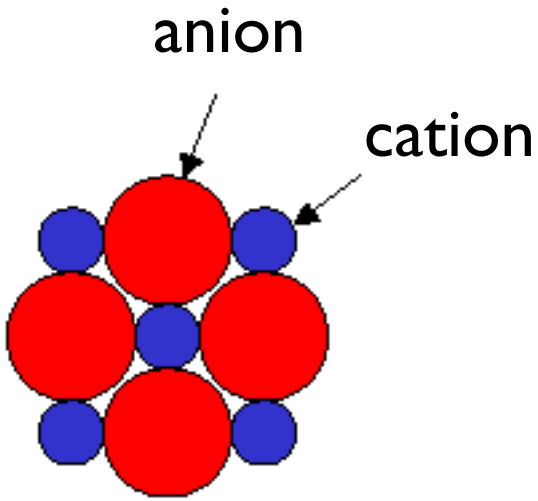
$$x = 0.5 + \nu$$



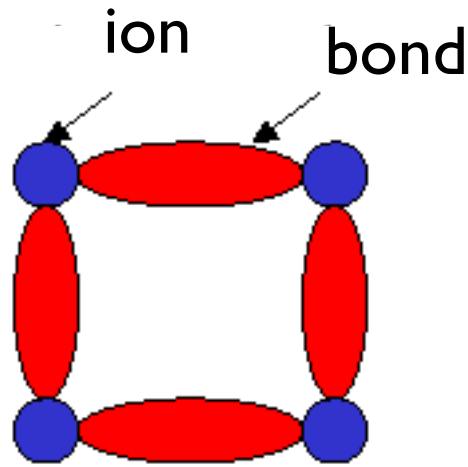

Design of materials with optimized piezoelectric response

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

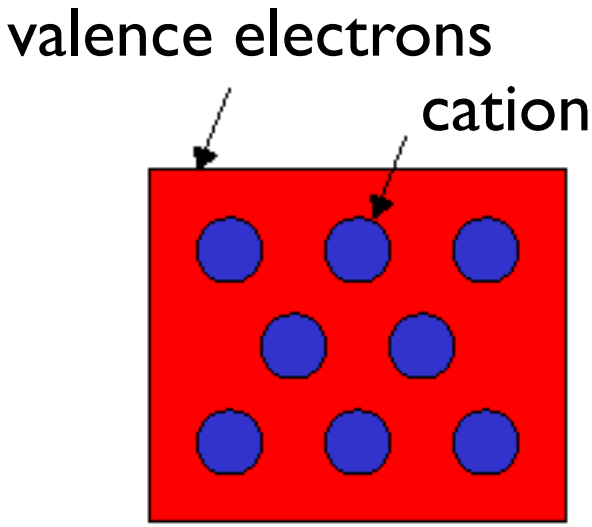
What of Anderson’s claim?
Do we understand more?




Ionic

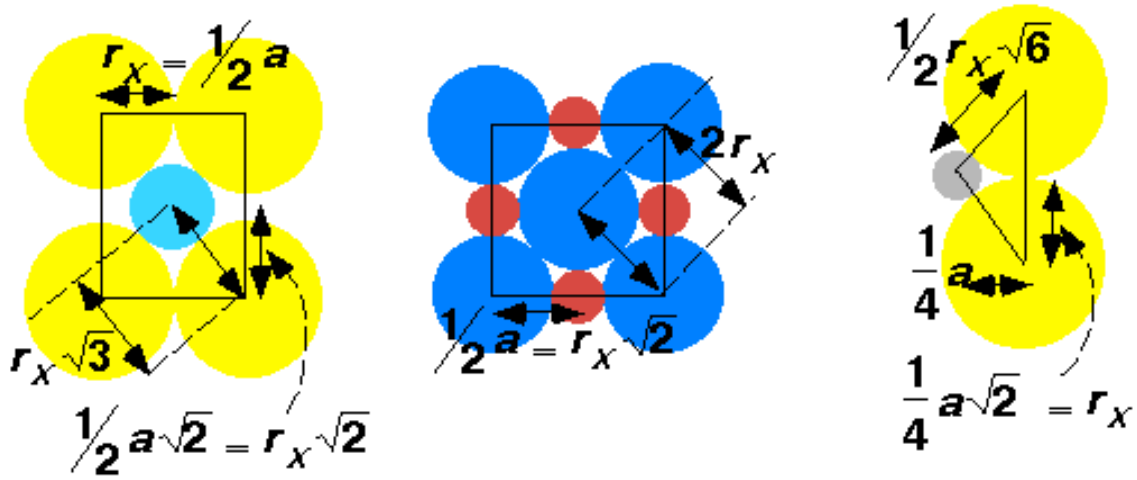



Covalent

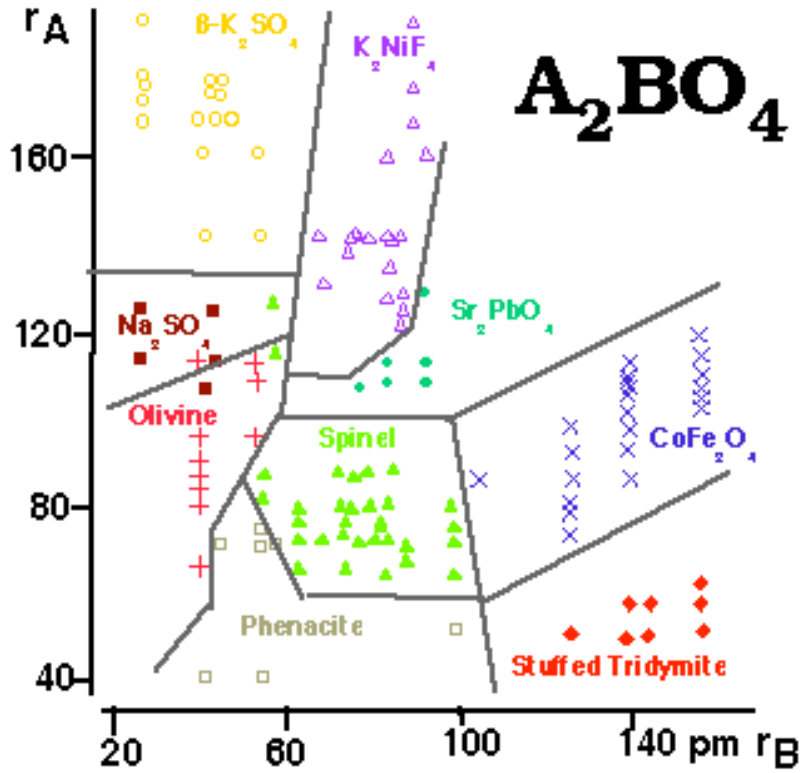



Metallic

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

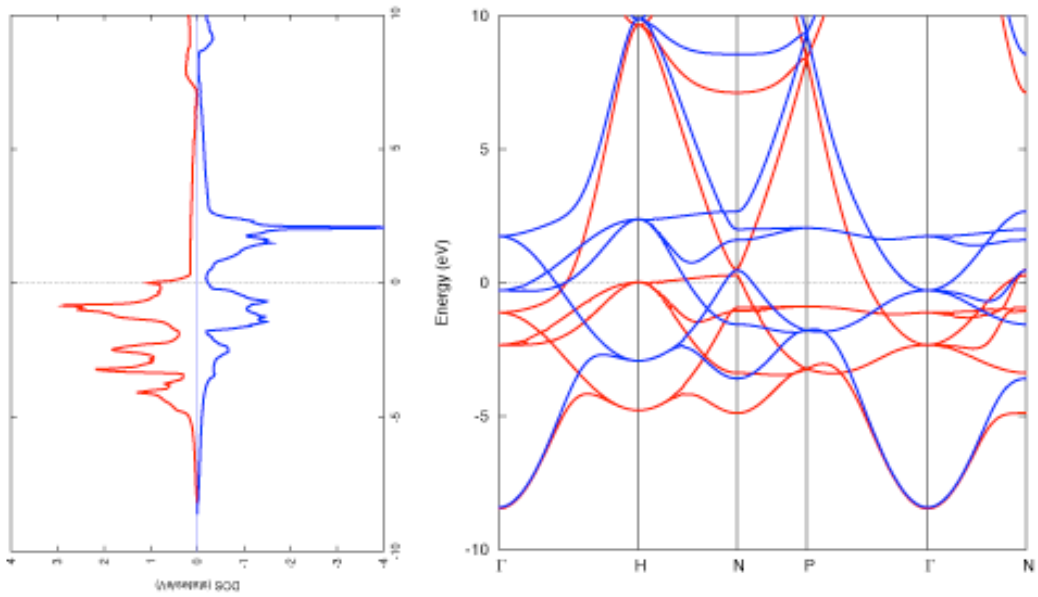
High-level
physical concepts

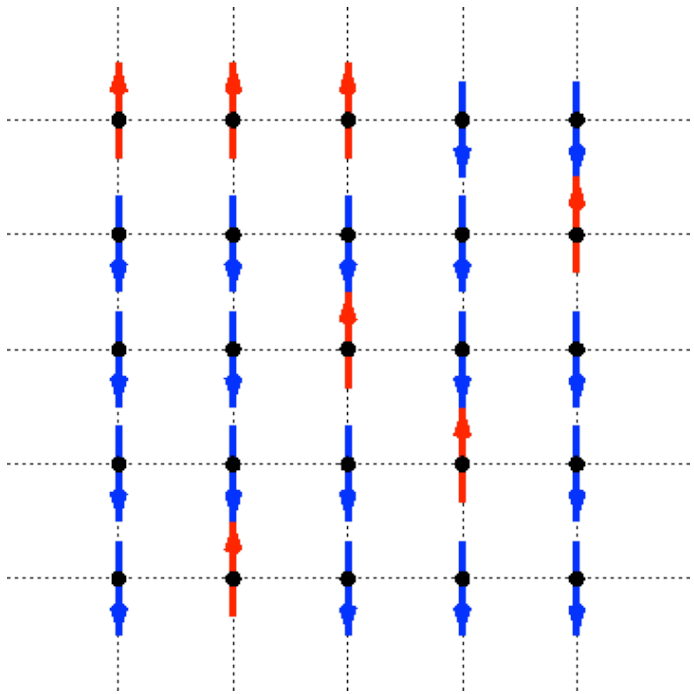
Electronegativity
Bonding
Parametrization of
simple models

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

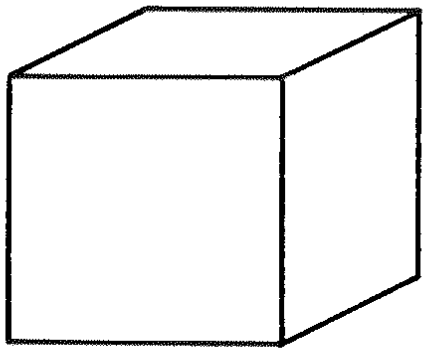
# Parametrization of a Heisenberg model from the electronic structure.

Relevant for magnetic properties

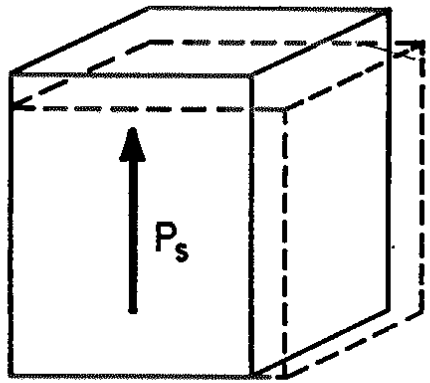


# Ferroelectricity

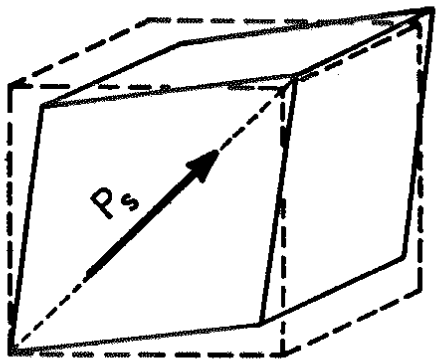


Cubic

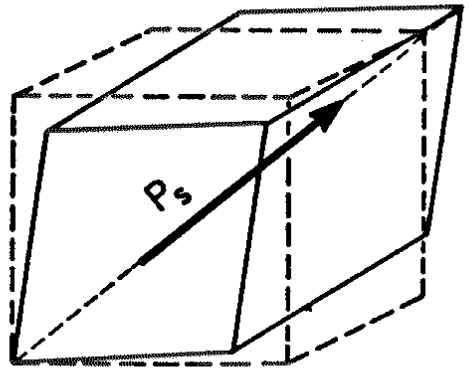



Tetragonal

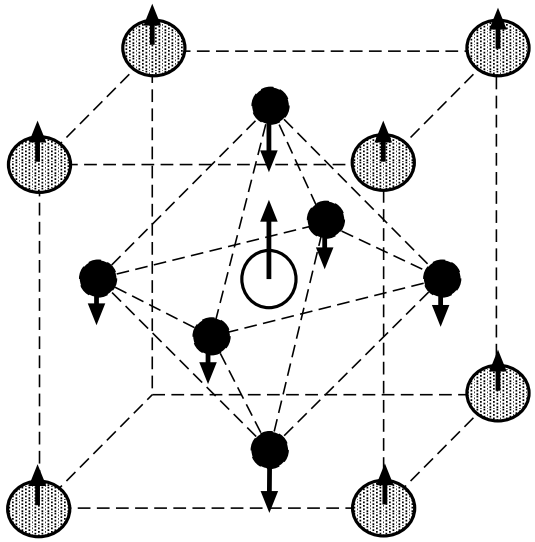
$BaTiO_3$




Orthorhombic




Rhombohedral

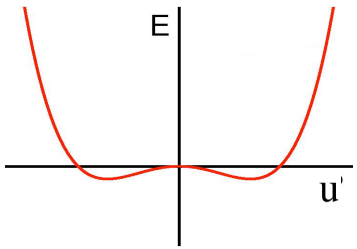


+ Ti
Ba
− O

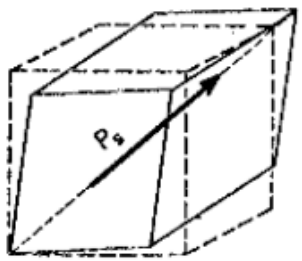
## Basic distortion involved in ferroelectricity (soft mode)

$\vec{p}$

Relevant degree of freedom

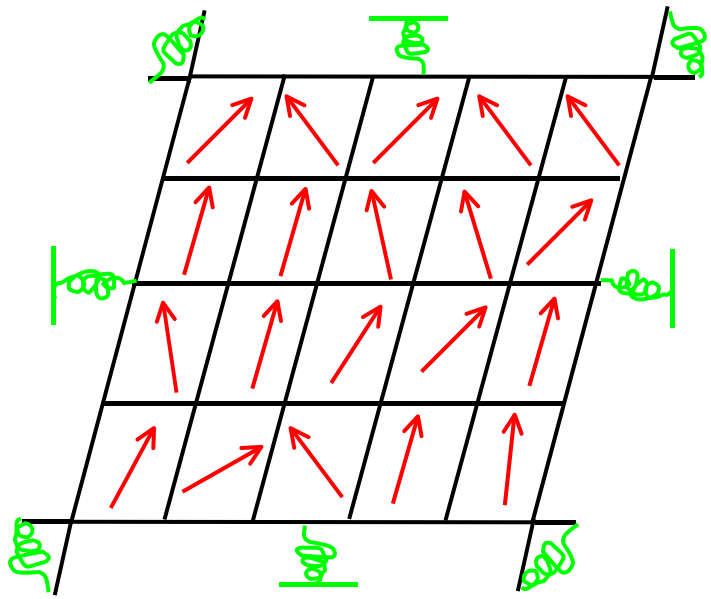



Local mode u

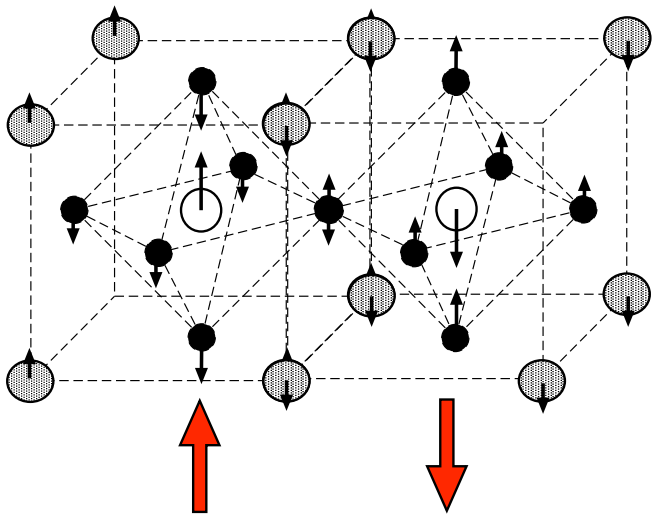


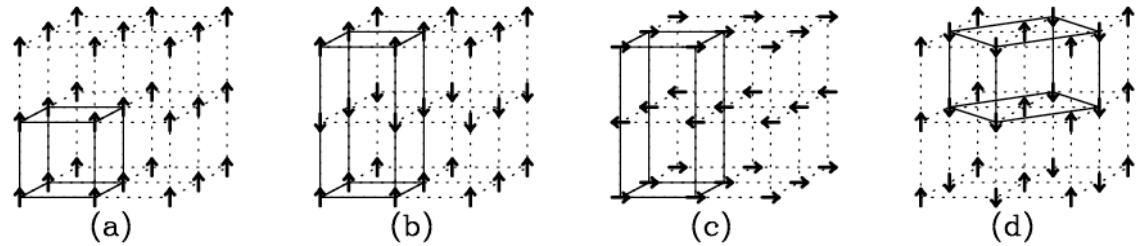

Lattice Strain

## Model system



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

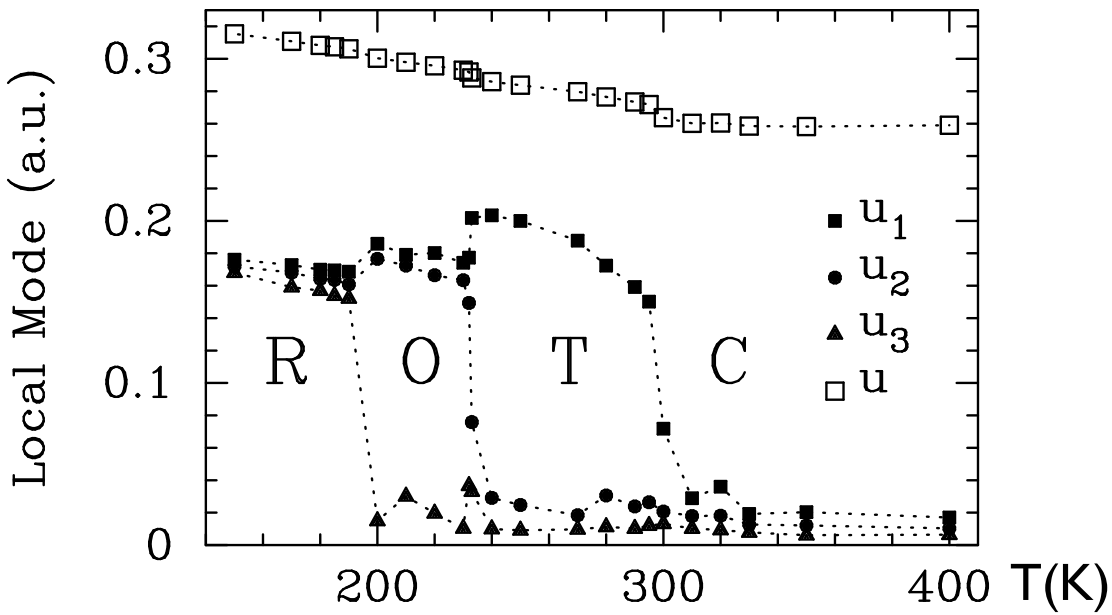


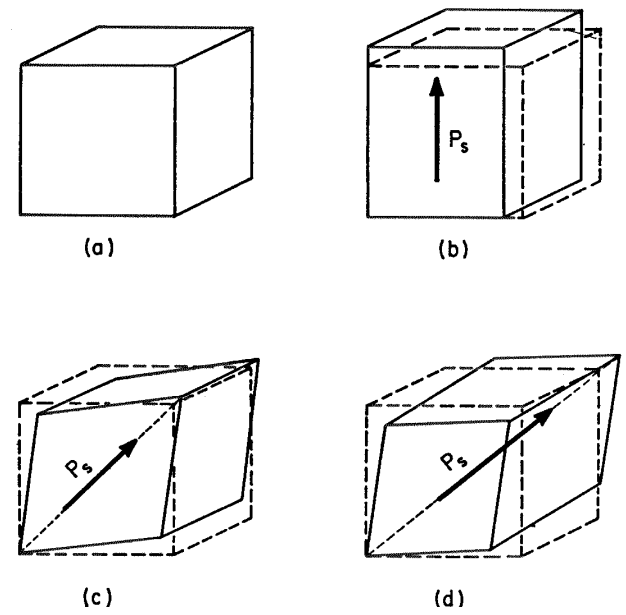



$$E_{\text{short}}(\{\mathbf{u}_i\}) = \frac{1}{2}\sum_{i\neq j}\sum_{\alpha\beta} J_{ij,\alpha\beta}u_{i\alpha}u_{j\beta}$$

Effective-Hamiltonian parametrized ab-initio

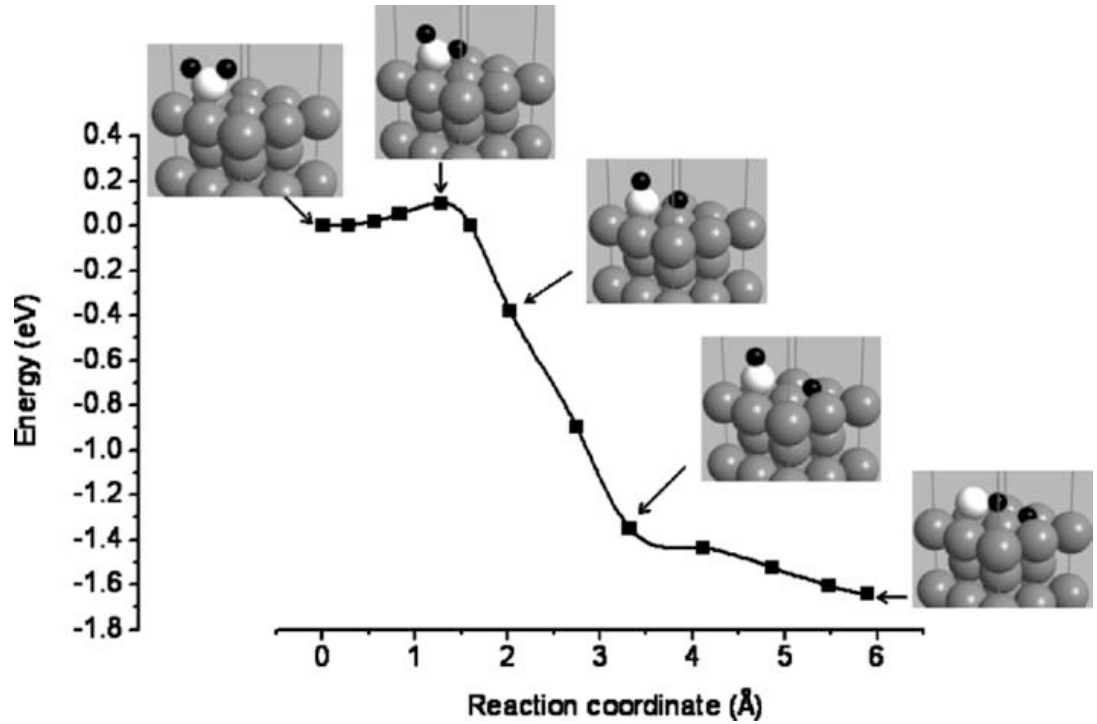
Phase transition sequence obtained from Monte Carlo simulations



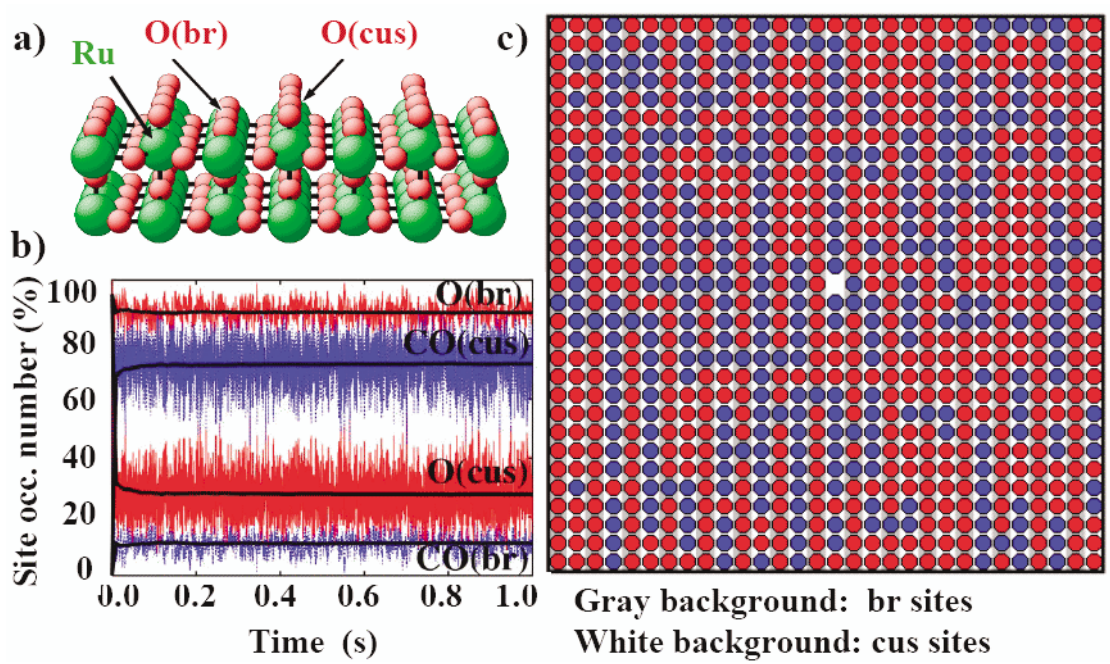



# Disociation of $H_2S$ in Fe(110)

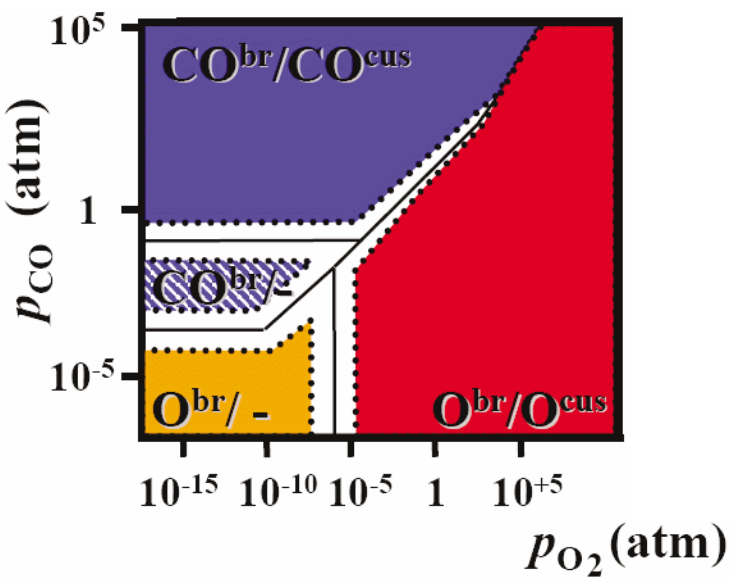
Jiang, Carter, Surf. Sci (2005)



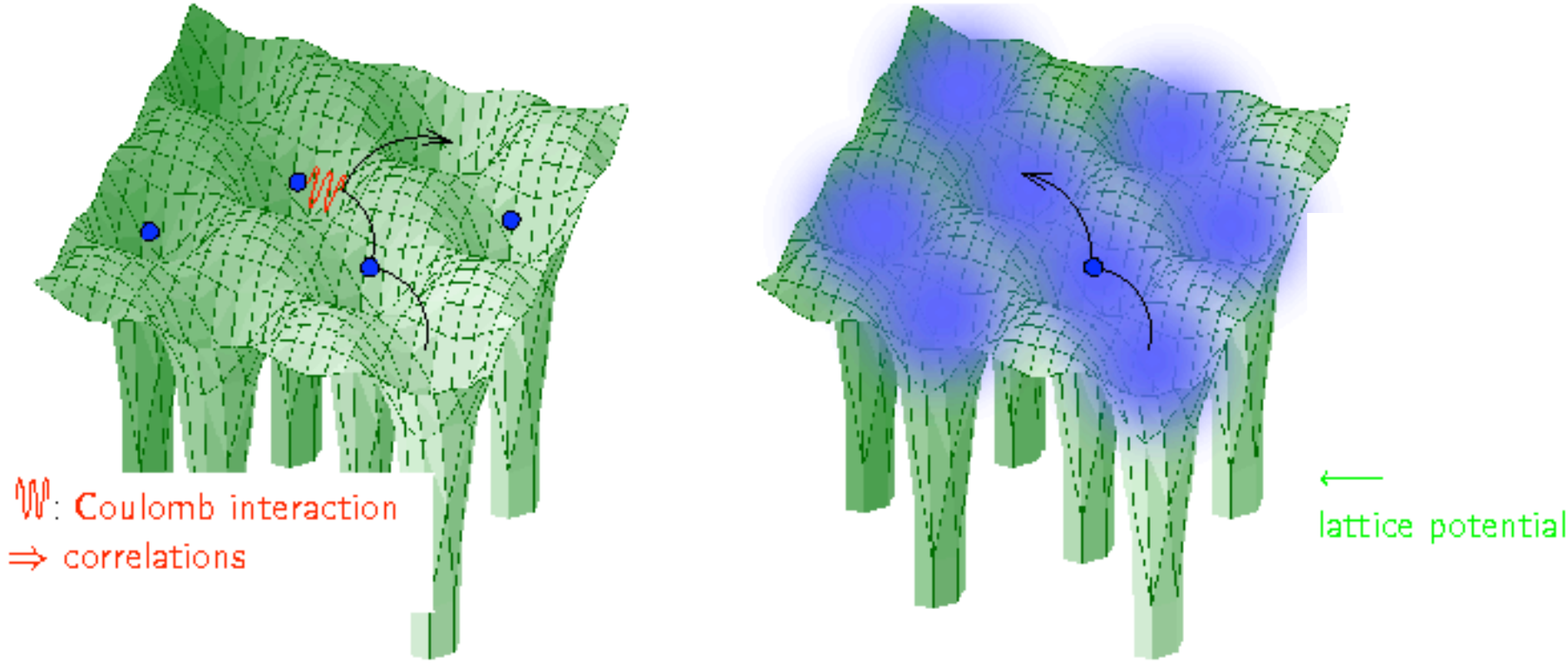

# Kinetic-Monte Carlo method for catalysis -- parametrization




Reuter et al, PRL (2004)

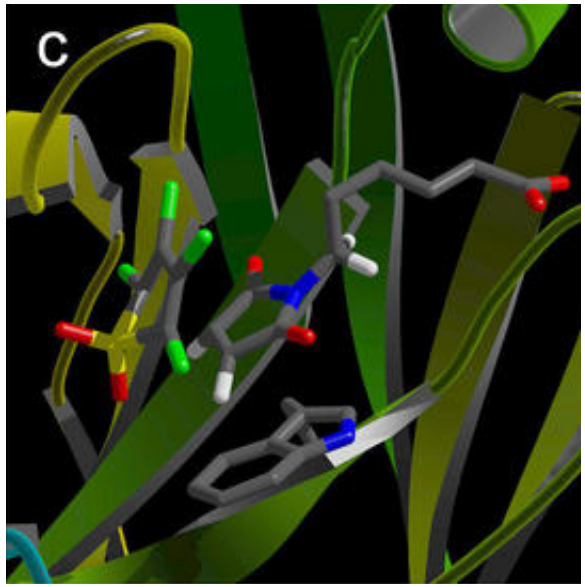


# Challenges



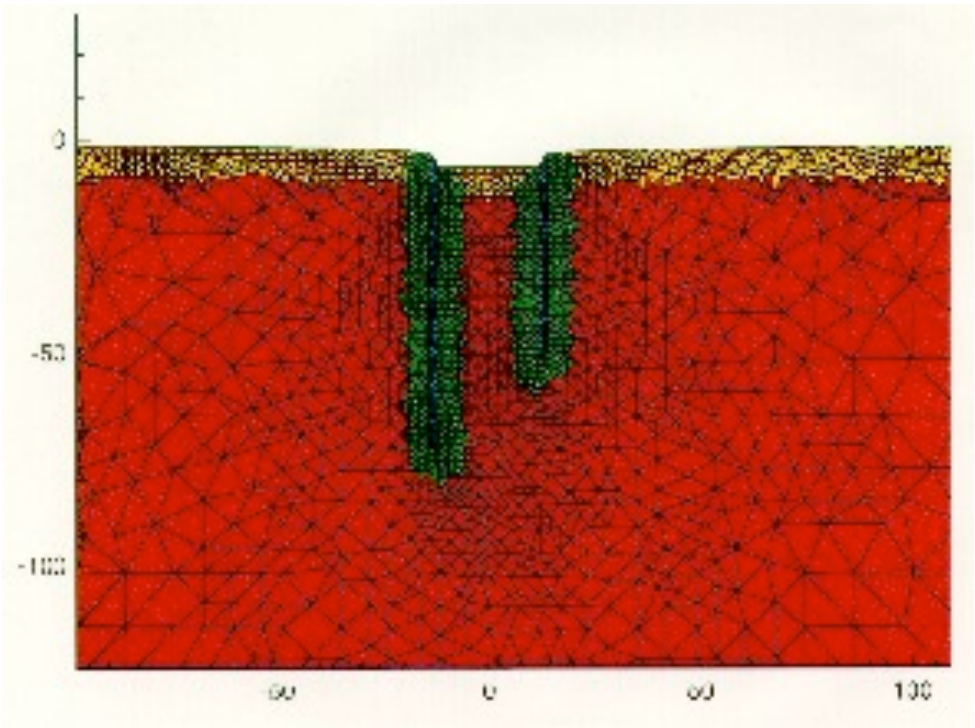

Better treatment of electronic correlation,
essential to describe localized states
in transition metals and rare earths

# Hybrid methods to bridge length scales



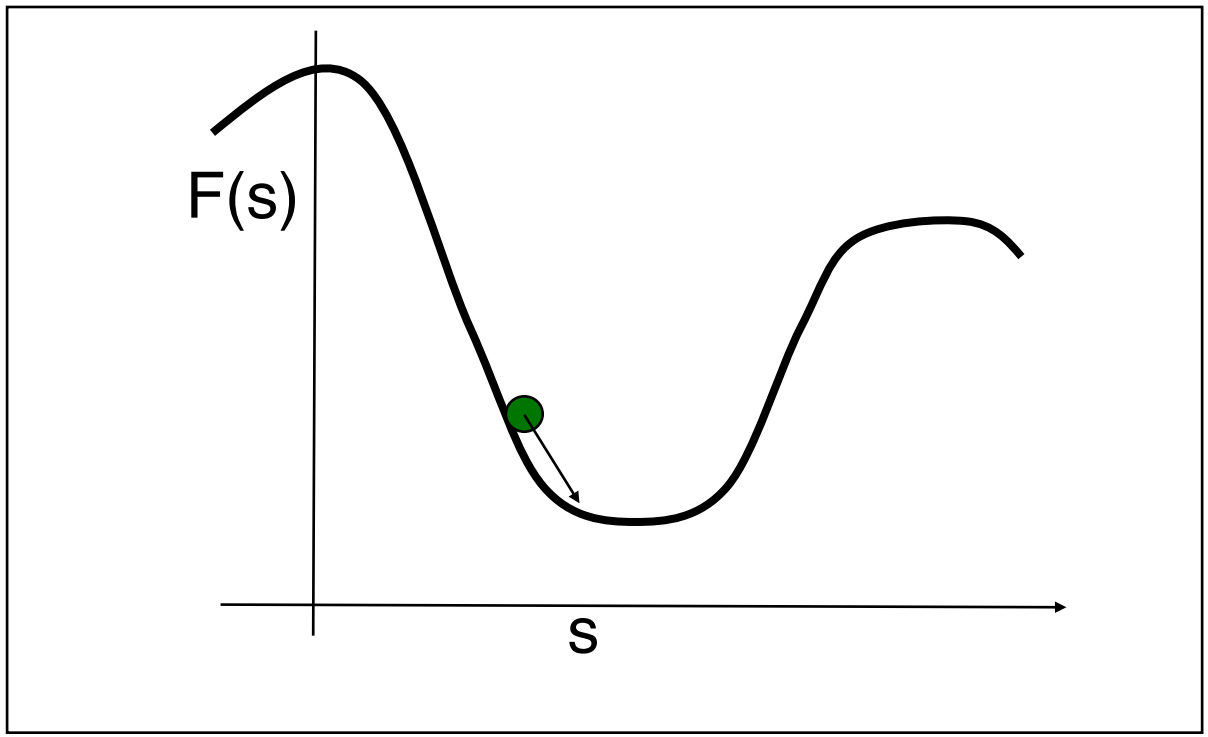

QM-MM: Precise treatment (QM) of a special part of the system. Rest treated at a lower level of quality.

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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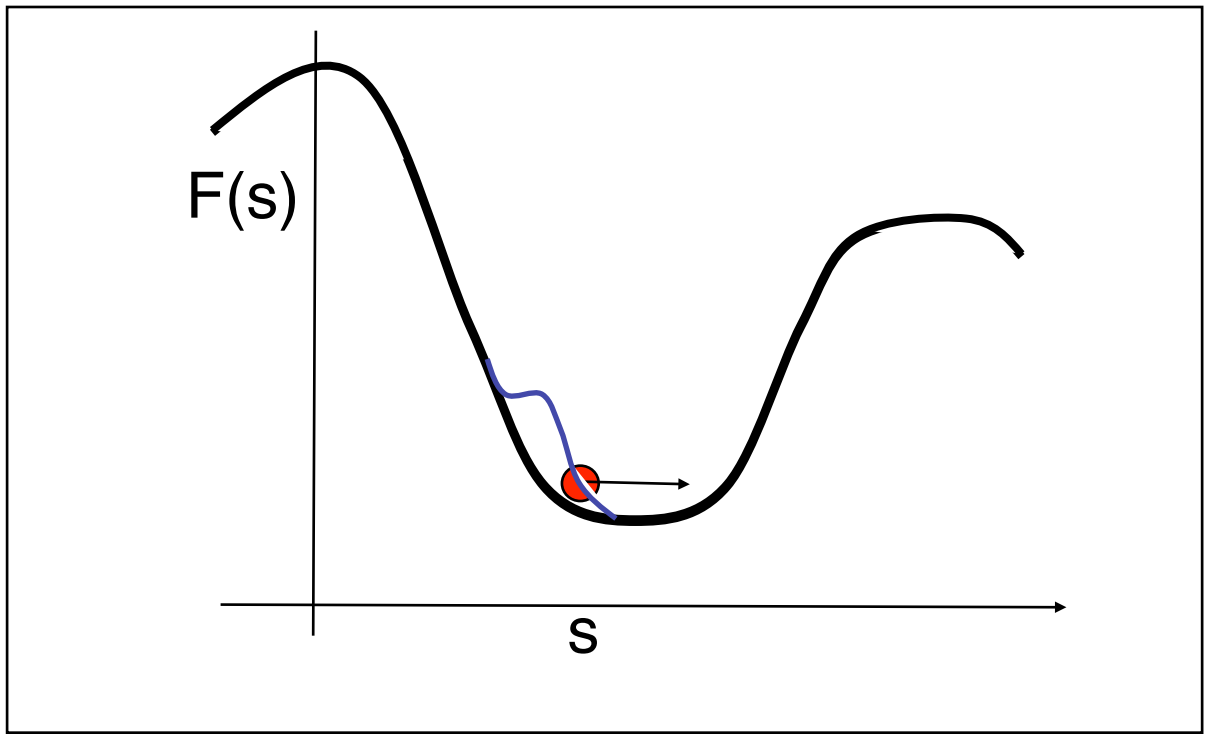
Phase transition mechanisms, new crystal structures

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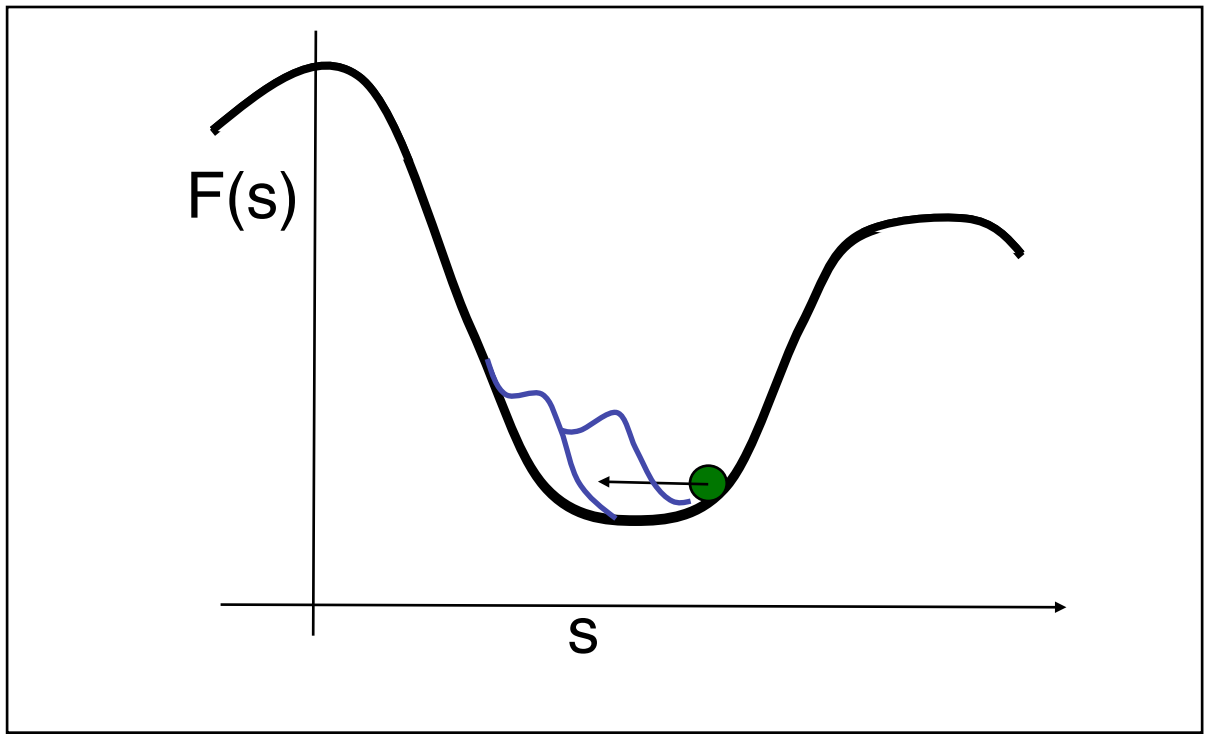


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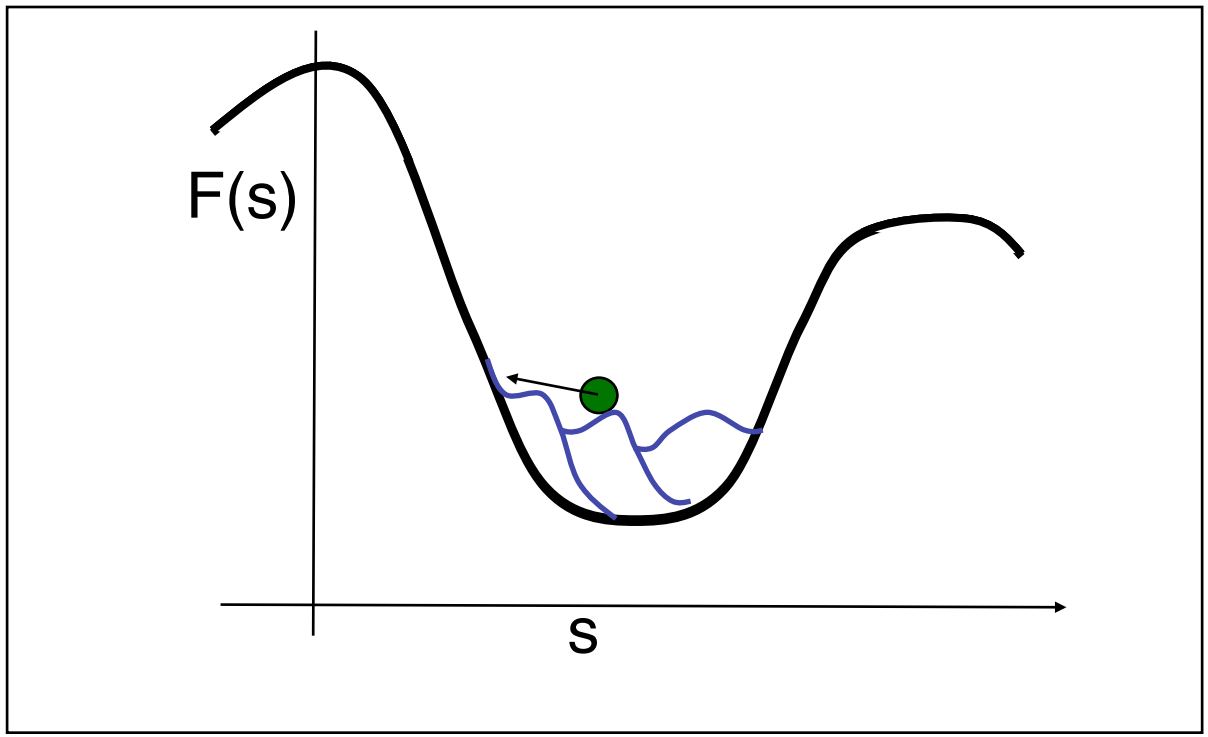


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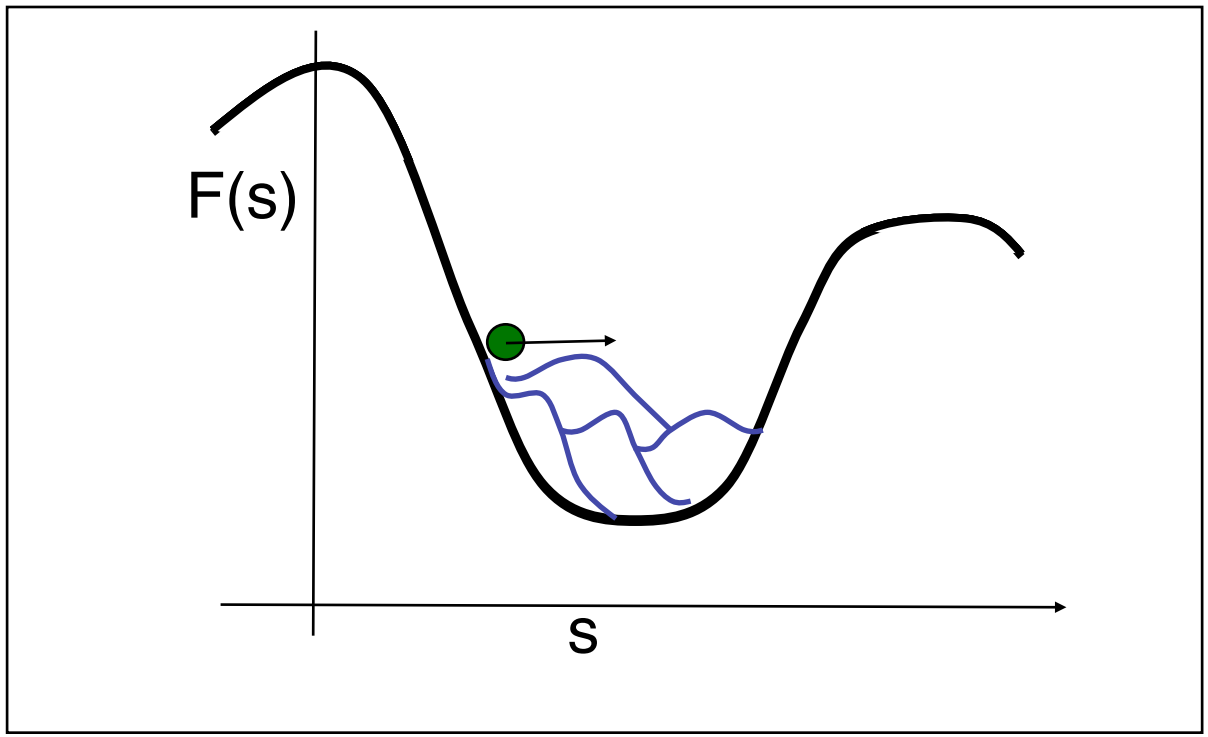


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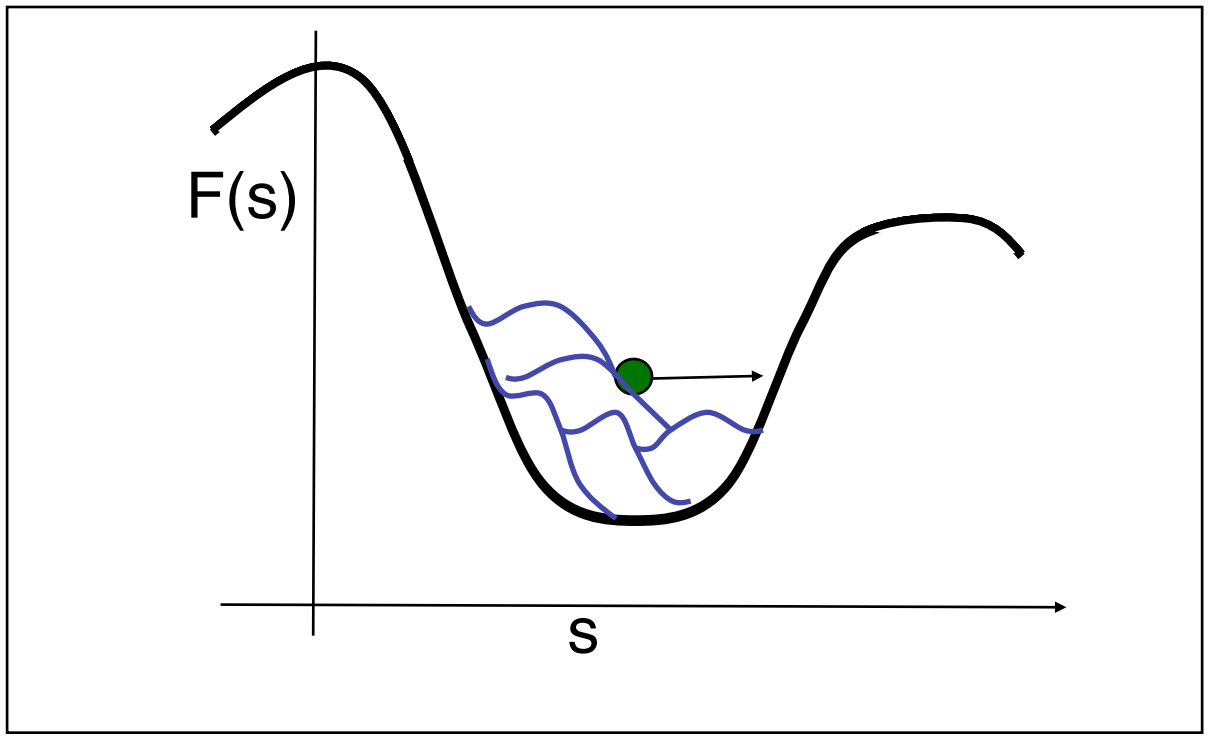
Phase transition mechanisms, new crystal structures

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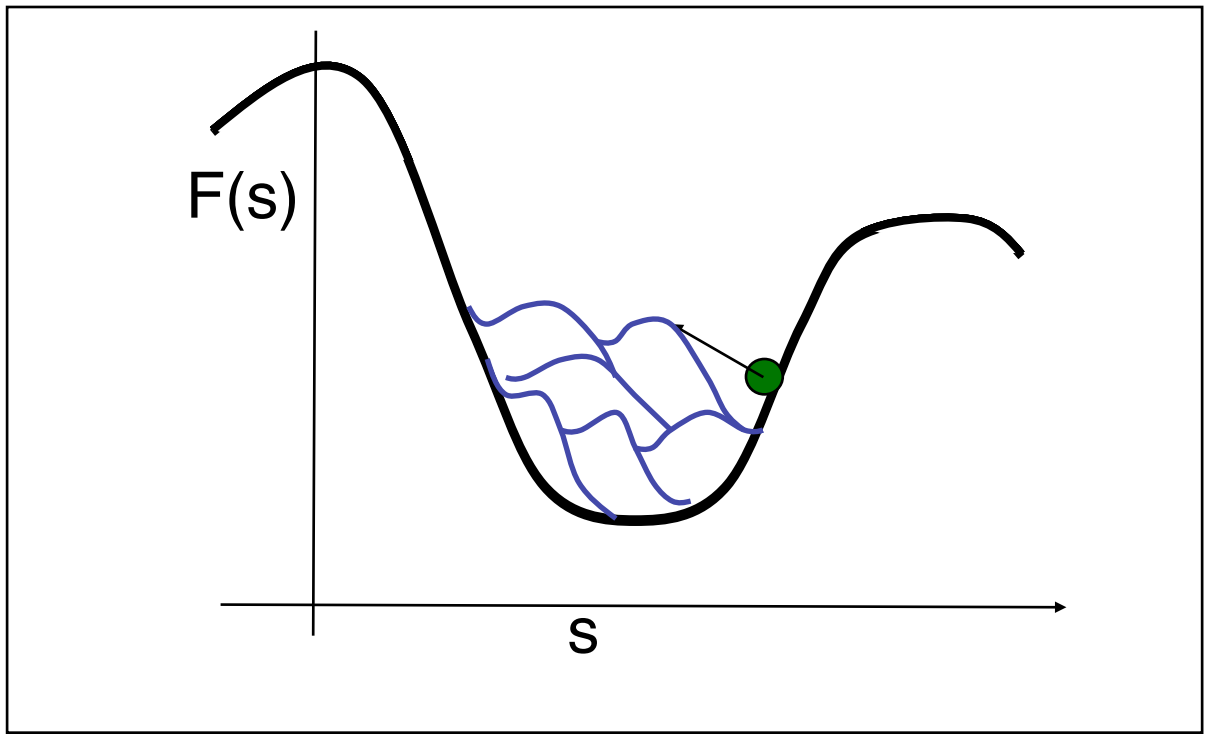


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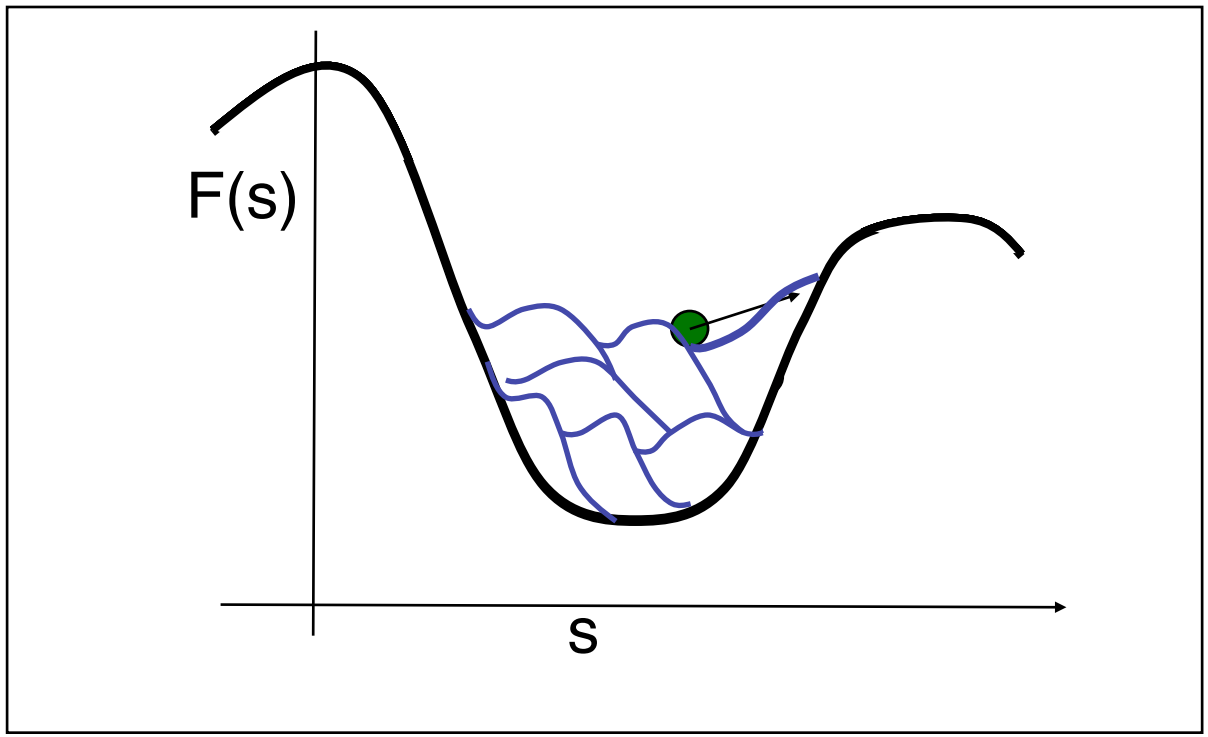


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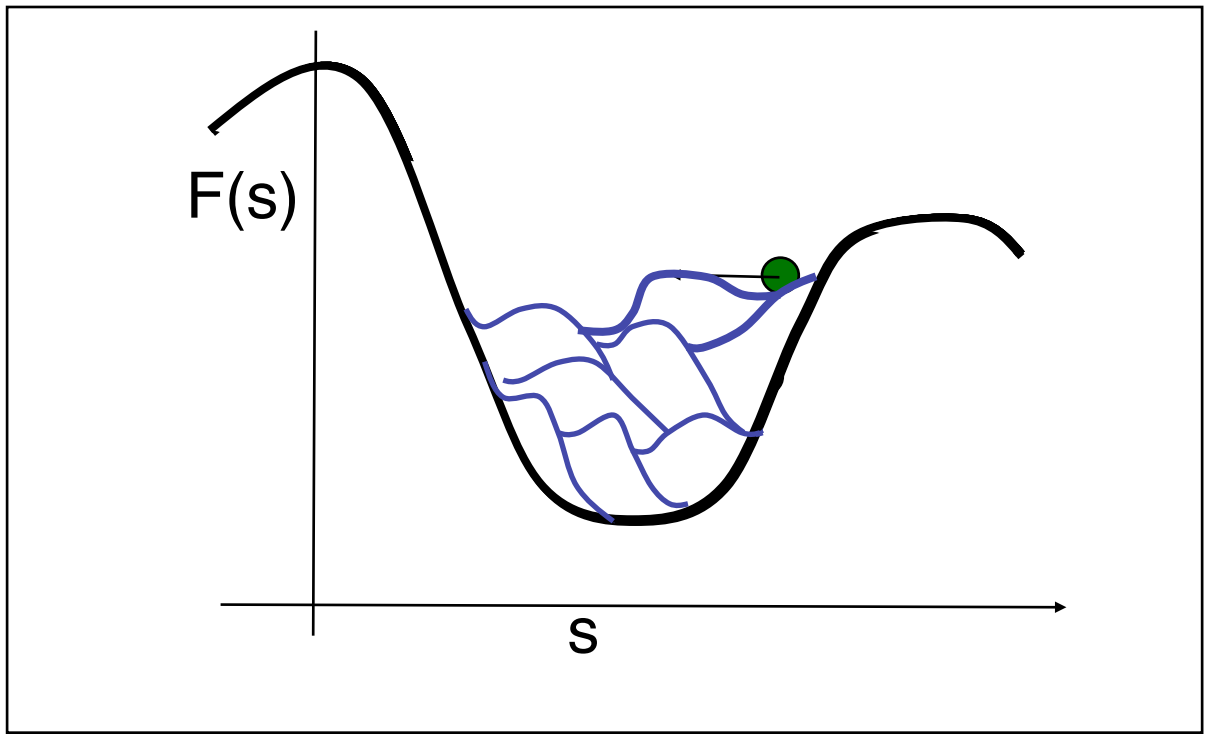



**Metadynamics**

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

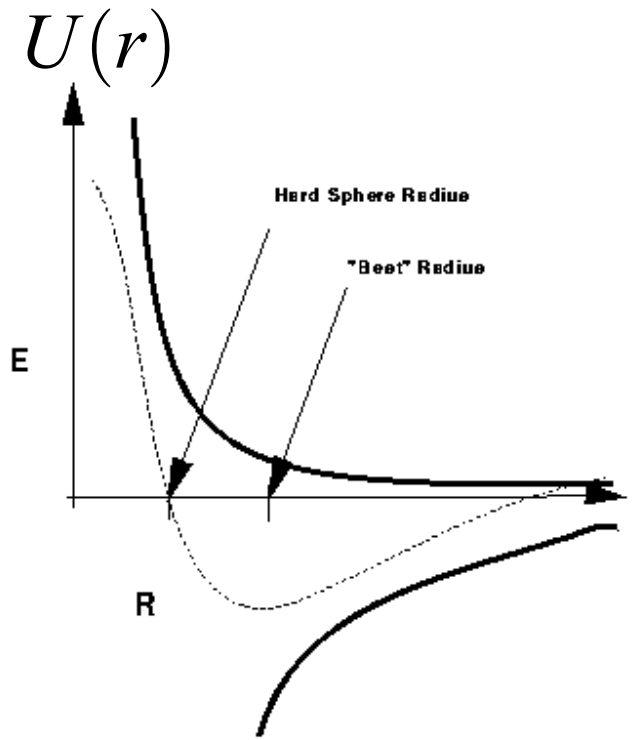
# The Torii Analogy
(Prof. H. Nakamura)

First-principles calculations

Theory  Experiment

Thanks!

# Interatomic potentials

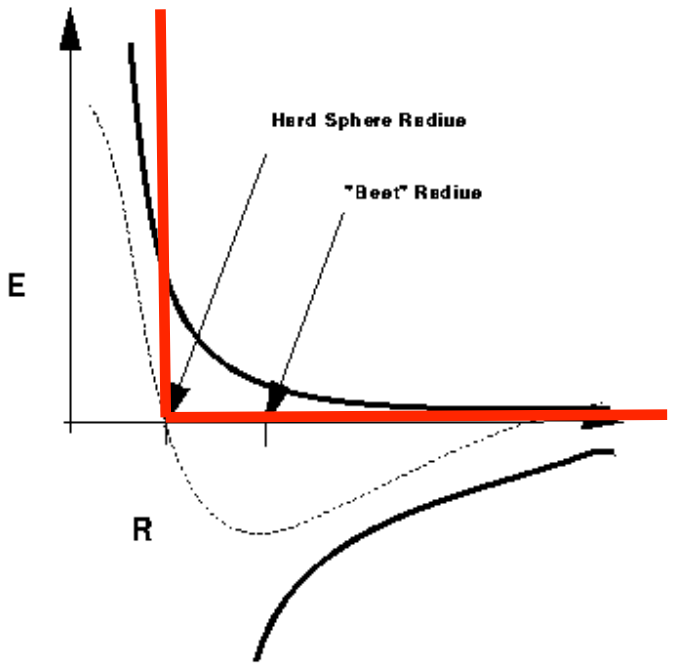



$$U(r) = Ae^{-r/\rho} - Cr^{-6}$$

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

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

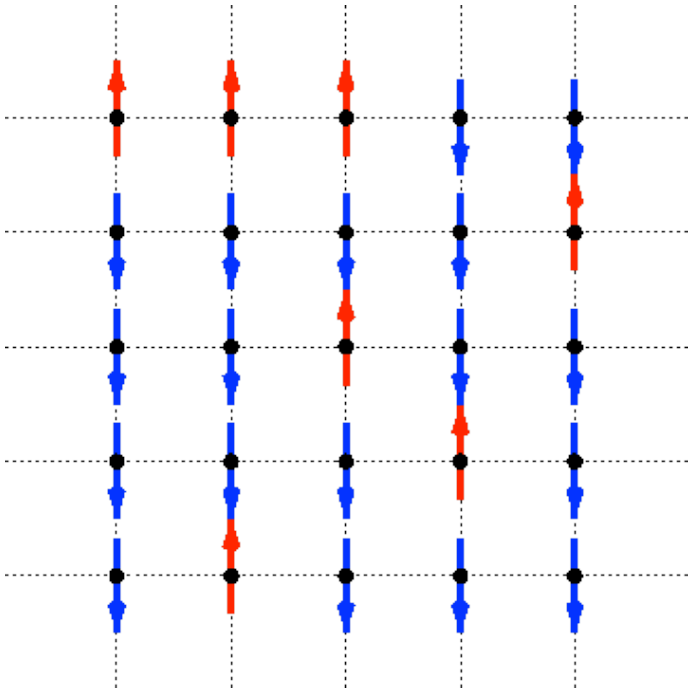
# Molecular dynamics simulation




Alder+Wainwright (1956)
Hard-sphere liquid

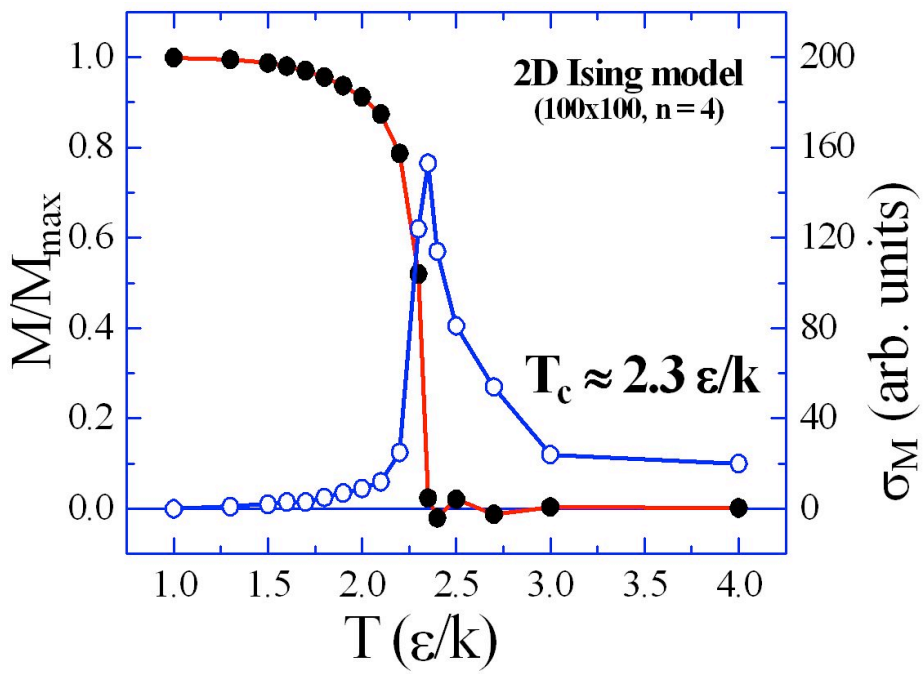
Tremendous growth

Exploration, validation of theories, and checks of interaction potentials



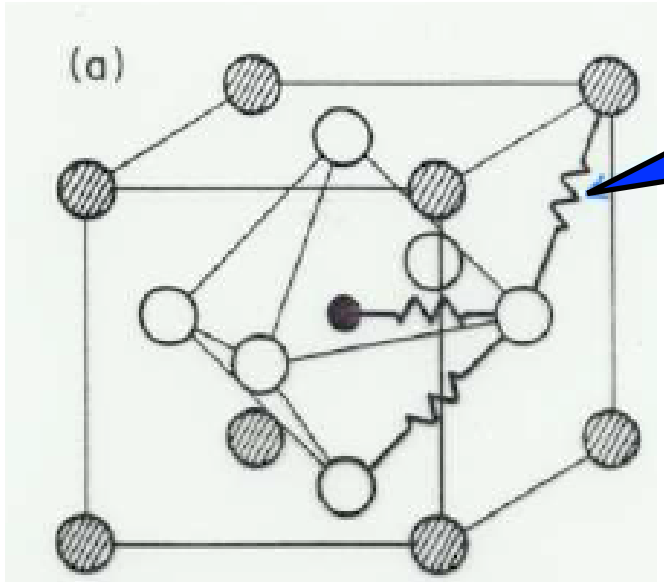
# Ising Model

Monte Carlo Simulation



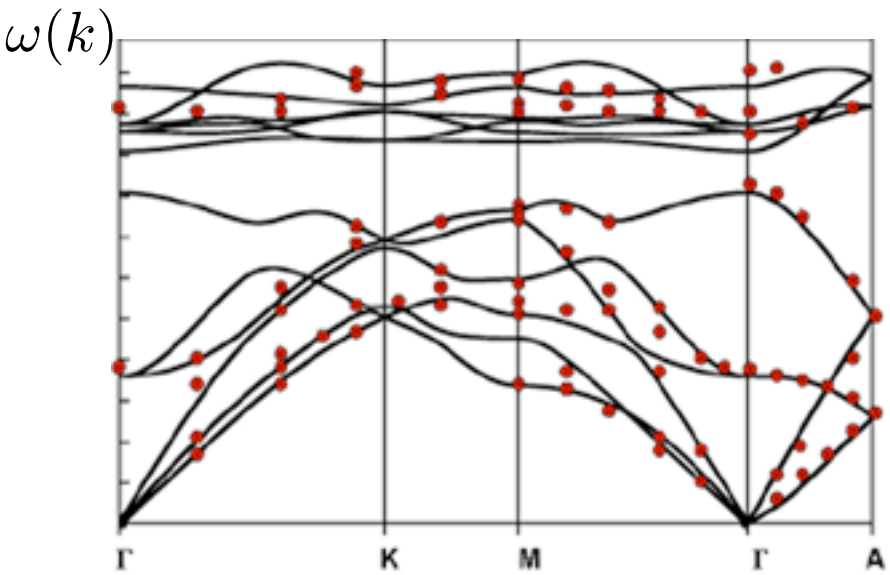
Emergent properties:
Not evident just by looking at the equations

The use of the computer is essential
for exploration of models

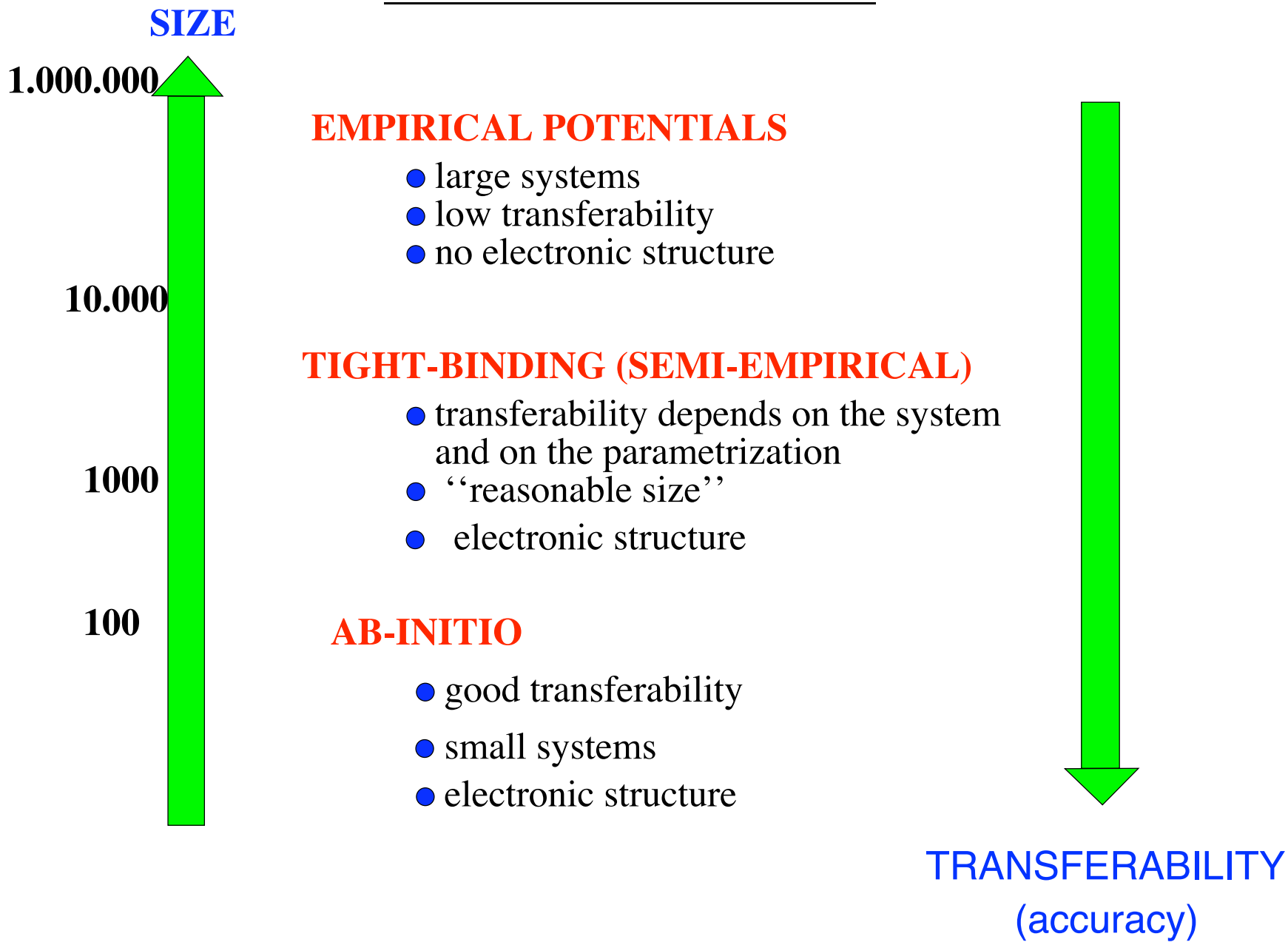



Spring constant

Basic idea: Vibrations around an equilibrium point




Parameters can be fitted to experiment


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)