1st Summer School in Theoretical and Computational Chemistry of Catalonia

July 25–29, 2007

Directors: Feliu Maseras and Pere Alemany

Theoretical and Computational Chemistry
Reference Network

XRQTC

Generalitat de Catalunya
Departament d'Innovació, Universitats i Empresa

MODULE C

“Introduction to electronic structure calculations using SIESTA“

Director: Pablo Ordejón
Institut de Ciéncia de Materials de Barcelona (CSIC)

PROGRAM OF THE MODULE

Theory

- Introduction
- Basic Execution
- Pseudopotentials
- Basis Sets
- Matrix Elements
- Diagonalization
- Order-N Solvers
- Systematic Convergence
- Molecular Dynamics
- Structural Optimizations
- Parallelization
- Analysis and post-processing tools

+ Hands-on Sessions

TEACHERS OF THE MODULE

- Eduardo Anglada
  UAM and NANOTEC, Madrid

- Javier Junquera
  Universidad de Cantabria, Santander

- Andrei Postnikov
  Paul Verlaine University, Metz (France)

- Pablo Ordejón
  ICMAB and CIN2 (CSIC), Barcelona

SUMMARY OF THIS INTRODUCTION

- Computer Simulations
- The 'ab-initio' model for atomistic simulations in condensed matter systems – Approximations!!
- Density Functional Theory in a nutshell
- SIESTA: a tool for large-scale DFT calculations

What is Computer Simulation?

- **"Computer Simulations":** use a computer to "solve" numerically the equations that govern a certain process.

- **Simulation** is present in every branch of science, and even increasingly in everyday life (e.g.: simulations in finances; weather forecast; flght simulators …)

- **Simulation in materials:** Study the way in which the "blocks" that build the material interact with one another and with the environment, and determine the internal structure, the dynamic processes and the response to external factors (pressure, temperature, radiation, etc…).

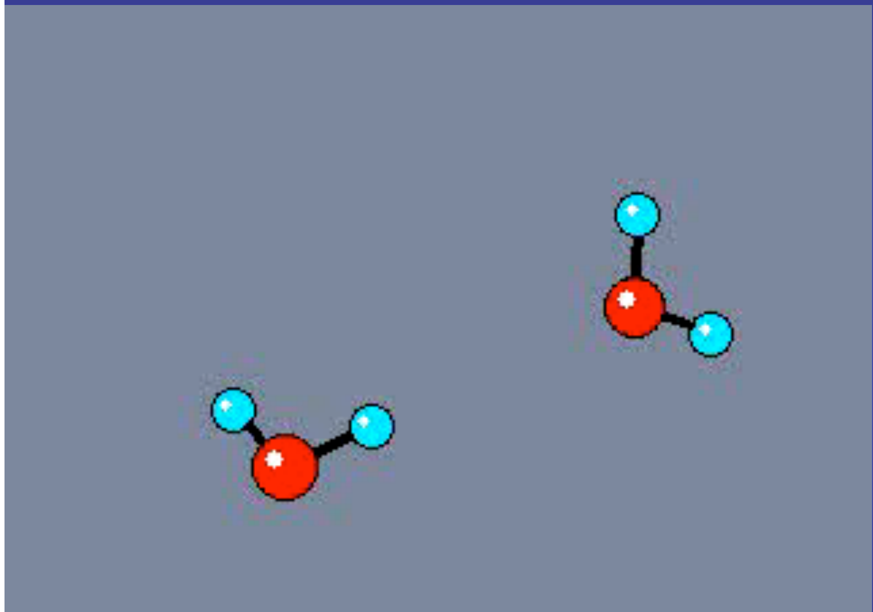
Why are simulations interesting?

- Simulations are the **only general method** to solve **models** describing many particles interacting among themselves.
- **Experiments** are sometimes **limited** (control of conditions, data acquisition, interpretation) and generally expensive.
- Simulations **scale up** with the increase of **computer power** (that roughly doubles every year!!)

Why are simulations interesting?

- Alternative to approximate solutions for models (traditional 'theory')
- Complement and alternative to experimental research
- Increasing scope and power with improving computers and codes

Components of a Simulation



1. A **model of the interactions** between the "blocks" that build the material.

   Here: atomistic models & DFT

2. A **simulation algorithm**: the numerical solution to the equations that describe the model.

3. A set of **tools for the analysis** of the results of the simulation.

Challenges of Simulation of Materials

Physical and mathematical foundations:

- What approximations come in?
  The simulation is only as good as the model being solved
- Systems with many particles and long-time scales are problematical.
  Computer time is limited: few particles for short time.
  - Space-Time is 4d.   2 x L_i → CPU x 16
  - Moore's Law implies lengths and times will double every 4 years if O(N)
- *How do we estimate errors? Statistical and systematic. (bias)*
- How do we manage ever more complex codes?

Challenges of Simulation of Materials

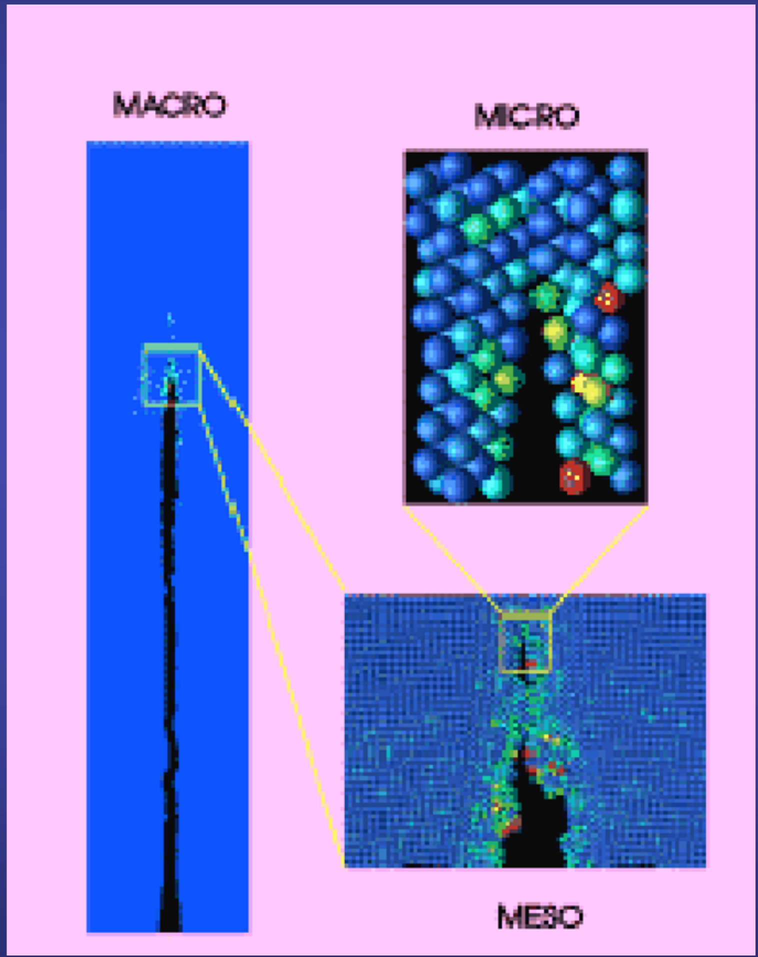
Multiples scales:

lengths

1 cm —— 1 Å (10^{-10} m)

times:

years --- fs (10^{-15} s)



Challenges of Simulation of Materials

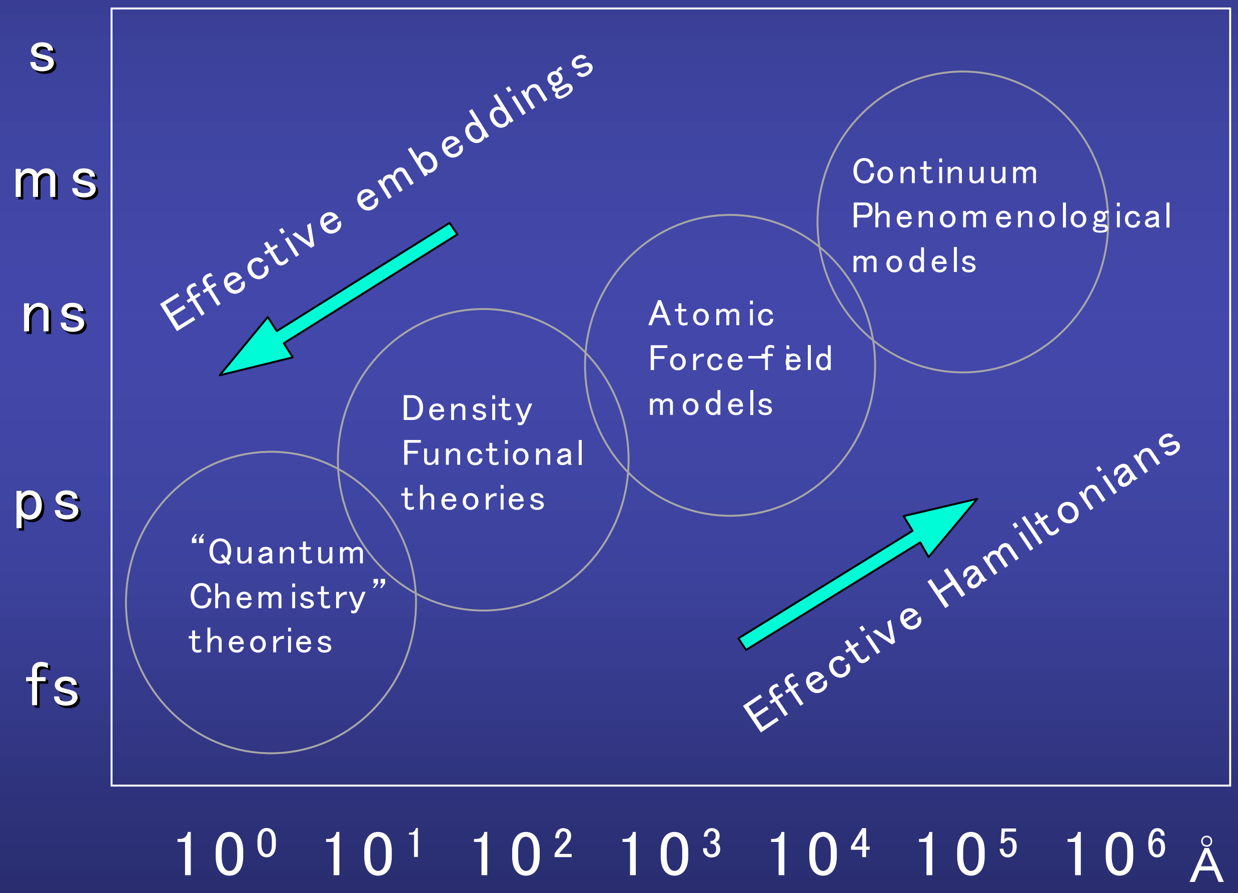
Multiple scales

Macro - and *mesoscopic* phenomena; Thermodynamics

Atomic structure and dynamics

Electronic states Chemical bonds and reactions, excitations …

Taken from: Ceperley/Johnson UIUC



“Complexity” of a Simulation

The relation between computing time T (CPU)

and degrees of freedom N

(number of atoms, electrons, length…)

$T \propto O(N)$ in the best (simplest) cases
(linear scaling)

$T \propto O(N^3)$ quantum mechanics
(Matrix diagonalisation and inversion)

$T \propto e^N$ some models and systems
(Quantum chemistry; multiple minima problems, etc)

Estimate: accessible time and size limits

- Modern Computers: 1 TFlop = 10^{12} Flops — with 3 x 10^7 s/year
  ~ **10^{19} Flops/year**
- With O(N) methods: **#ops = $10^{19} \propto 100 \times N \times n_t$** $\Rightarrow$ $N \times n_t \leq 10^{17}$
  (at least a factor 100 – 10 neighbors x 10 operations, to calculate distances)
- N scales as Volume, which scales as L^3
- Time (n_t) scales as L (for information to propagate along the system) $n_t \sim 10\,L$
- Therefore: $N \times n_t \sim L^3 \times 10L = 10\,L^4 \leq 10^{17} \Rightarrow$

$L \leq 10^4$ atoms/box side

In silicon: 10^4 atoms/box side:

N ~ 10^{12} atoms

L ~ 2 μm!!

$n_t \sim 10^5$ $\delta t \sim 1$ fs $\Rightarrow$ $t \sim 10^{-10}$ s = 0.1 ns

Plan your simulation intelligently !!

Algorithms

Structural Optimization

- minimum energy configurations
- T = 0

- no information on real dynamics
- no temperature
- local minima

Monte Carlo

- T > 0
- thermodynamics: statistical averages
- several ensembles
- long time scales (equilibrium)

- no information on dynamics
- no real time (kMC)
- only at equilibrium

Molecular Dynamics

- T > 0
- thermodynamics: statistical averages
- several ensembles
- información on real dynamics (non-equil)

- large computational cost
- limited time scale (accelerated dyn.)
- ergodicity problems

Structure of a simulation: questions

- what interactions model should I use (level of theory)?

- how do I begin the simulation?
- how many molecules do I need to consider?
- what is the size of my simulation box?
- how do I take the ensemble average in a MC simulation?
- how do I take the time average in a MD simulation?

- how reliable are my simulation results?

MODELS - The ab-initio approach

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

Dirac, 1929

MODELS - The ab-initio approach

Schrödinger´s equation (assuming non-relativistic)

$$\hat{H} = -\frac{\hbar^2}{2m_e}\sum_i \nabla_i^2 + \sum_{i,I}\frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|} + \frac{1}{2}\sum_{i \neq j}\frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_I \frac{\hbar^2}{2M_I}\nabla_I^2 + \frac{1}{2}\sum_{I \neq J}\frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|},$$ [redacted]

[redacted]

[redacted]

[redacted]

What are the main approximations?

Born-Oppenhaimer

Decouple the movement of the electrons and the nuclei.

Density Functional Theory

Treatment of the electron – electron interactions.

Pseudopotentials

Treatment of the (nuclei + core) – valence.

Basis set

To expand the wave functions.

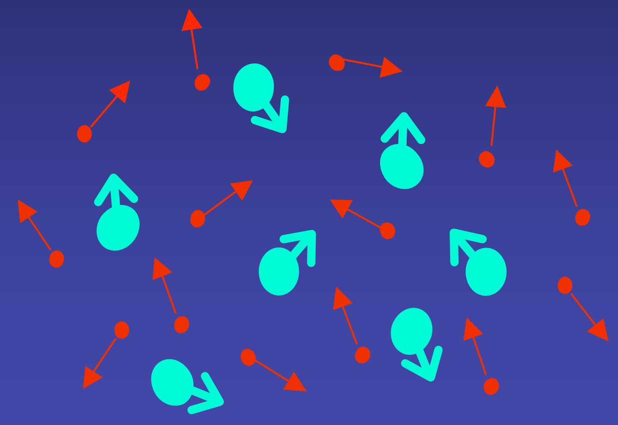
Numerical evaluation of matrix elements

Efficient and self-consistent computations of H and S.

Supercells

To deal with periodic systems

Adiabatic or Born-Oppenheimer approx.



$$\frac{M_\alpha}{m_e} >> 1$$

$\Rightarrow$**Nuclei much slower than the electrons** $\frac{v_{electron}}{v_{nucleus}} >> 1$

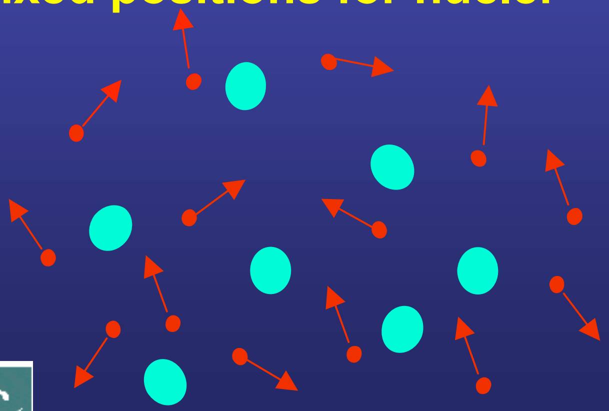
$v_{electron} \approx v_F \approx 10^8 \ \mathrm{cm/s}$ $\qquad v_{nucleus} \approx 10^5 \mathrm{cm/s}$

At any moment the electrons will be in their ground state for that particular instantaneous ionic configuration.

Solve electronic equations assuming fixed positions for nuclei

Move the nuclei as classical particles in the potential generated by the e$^-$

(1)



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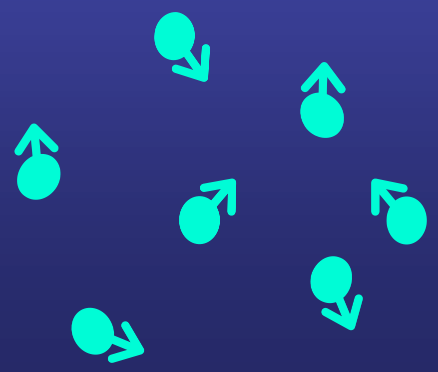


Wave function decoupled, Classical nuclei

$$\hat{H} = \sum_i -\frac{\hbar^2}{2m_e}\nabla_i^2 + \cancel{\sum_\alpha -\frac{\hbar^2}{2M_\alpha}\nabla_\alpha^2} + \frac{1}{2}\sum_{i\neq j}\frac{e^2}{\mid \vec{r}_i - \vec{r}_j \mid} - \sum_{i,\alpha}\frac{Z_\alpha e^2}{\mid \vec{r}_i - \vec{R}_\alpha \mid} + \frac{1}{2}\sum_{\alpha\neq\beta}\frac{Z_\alpha Z_\beta e^2}{\mid \vec{R}_\alpha - \vec{R}_\beta \mid}$$

Fixed potential “external” to e⁻

Constant (scalar)

Electrons

$$\hat{H}^{el}_{\{\vec{R}_\alpha\}} = \sum_i -\frac{\hbar^2}{2m_e}\nabla_i^2 + \frac{1}{2}\sum_{i\neq j}\frac{e^2}{|\vec{r}_i - \vec{r}_j|} + V^{ext}_{\{\vec{R}_\alpha\}}\left(\{\vec{r}_i\}\right)$$

$$\hat{H}^{el}_{\{\vec{R}_\alpha\}}\Psi^{el}_{n,\{\vec{R}_\alpha\}}\left(\{\vec{r}_i\}\right) = E^{el}_n \Psi^{el}_{n,\{\vec{R}_\alpha\}}\left(\{\vec{r}_i\}\right)$$

Nuclei

$$\hat{H} = \sum_\alpha -\frac{\hbar^2}{2M_\alpha}\nabla_\alpha^2 + E^{el}_n\left(\{\vec{R}_\alpha\}\right)$$

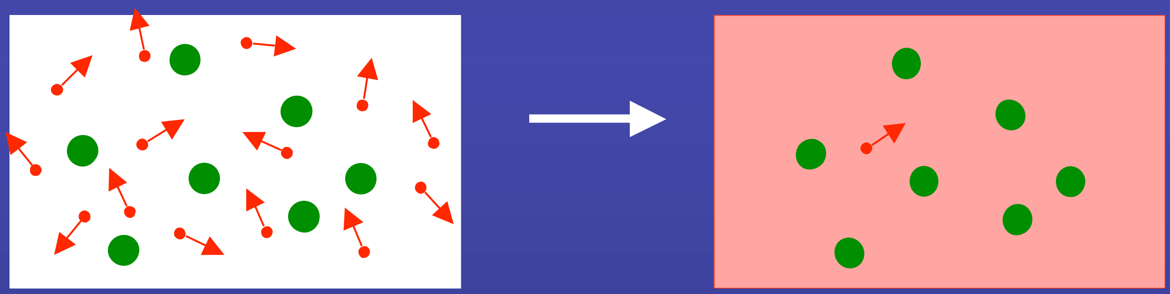
Classical dynamics

$$\vec{F}_\alpha = -\frac{\partial E^{el}_0\left(\{\vec{R}_\mu\}\right)}{\partial \vec{R}_\alpha}$$

Density Functional Theory... in a nutshell

1. [illegible] *particle density* (Hohenberg-Kohn Theorems)

2. Interacting electrons: As if *non-interacting* electrons in an *effective potential* (Kohn-Sham Ansatz)



[illegible]

3. **Approximation**: the effective XC potential – Local and Quasilocal, Hybrids

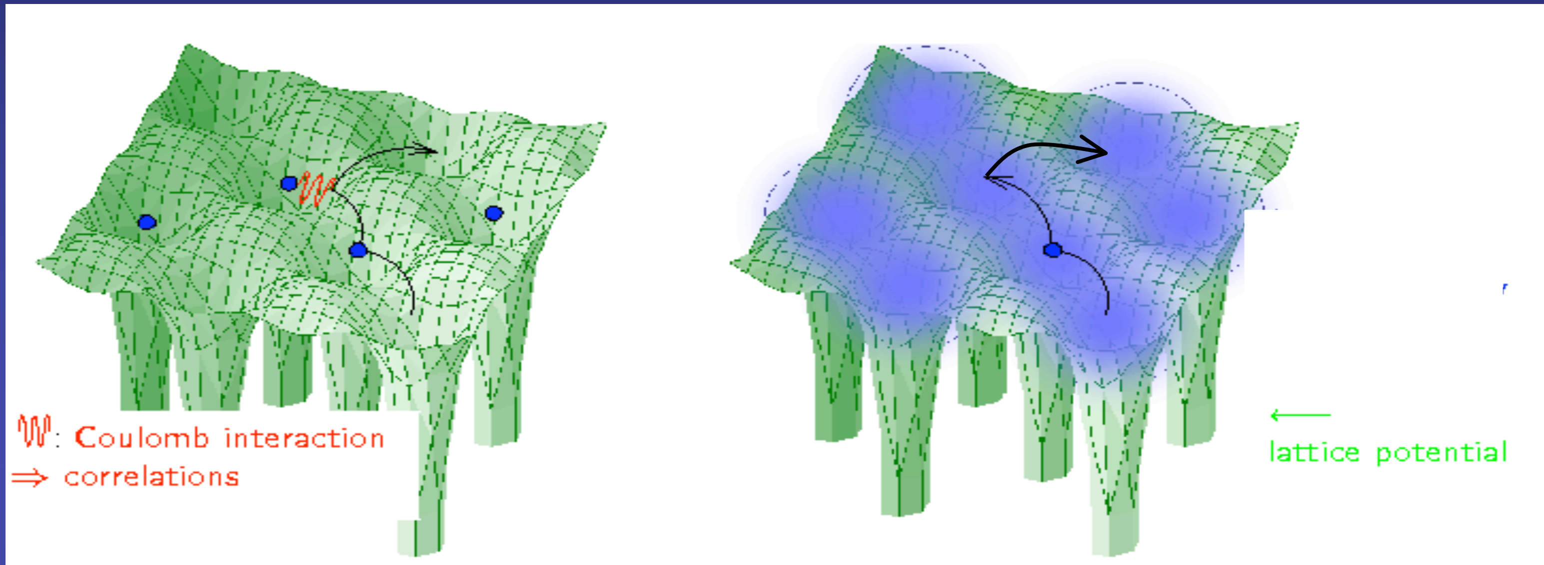
$$V_{XC}(\vec{r}) = V_{XC}(\rho(\vec{r}))$$

LDA

$$V_{XC}(\vec{r}) = V_{XC}(\rho(\vec{r}), \nabla\rho(\vec{r}))$$

GGA

Density Functional Theory... in a nutshell



Ground State (HK) [redacted]

[redacted] One electron (KS)

[redacted]

Kohn-Sham Eqs.: Self-consistency

Initial guess

$$n^{\uparrow}(\vec{r}), n^{\downarrow}(\vec{r})$$

Calculate effective potential

$$V_{eff}^{\sigma}(\vec{r}) = V_{ext}(\vec{r}) + V_{Hartree}[n] + V_{xc}^{\sigma}[n^{\uparrow}, n^{\downarrow}]$$

Solve the KS equation

$$\left[-\frac{1}{2}\nabla^2 + V_{eff}^{\sigma}(\vec{r})\right]\psi_i^{\sigma}(\vec{r}) = \varepsilon_i^{\sigma}\psi_i^{\sigma}(\vec{r})$$

Compute electron density

$$n^{\sigma}(\vec{r}) = \sum_i f_i^{\sigma} \left|\psi_i^{\sigma}(\vec{r})\right|^2$$

Self-consistent?

No → back to "Calculate effective potential"

Yes → **Output quantities**

Energy, forces, stresses …

Density Functional Theory

LDA and GGA:

Practical scheme for up to ~1000 atoms

Predictive Power:

- Accuracy in geometries: better than 0.1 Å
- Accuracy in (relative) energies: better than 0.2 eV (often much better — 0.01 eV)

Caveats (many!):

- Problems describing weak interactions (Van der Waals)
- Problems describing strongly correlated systems
- Excited electronic states

Typical Accuracy of the xc functionals

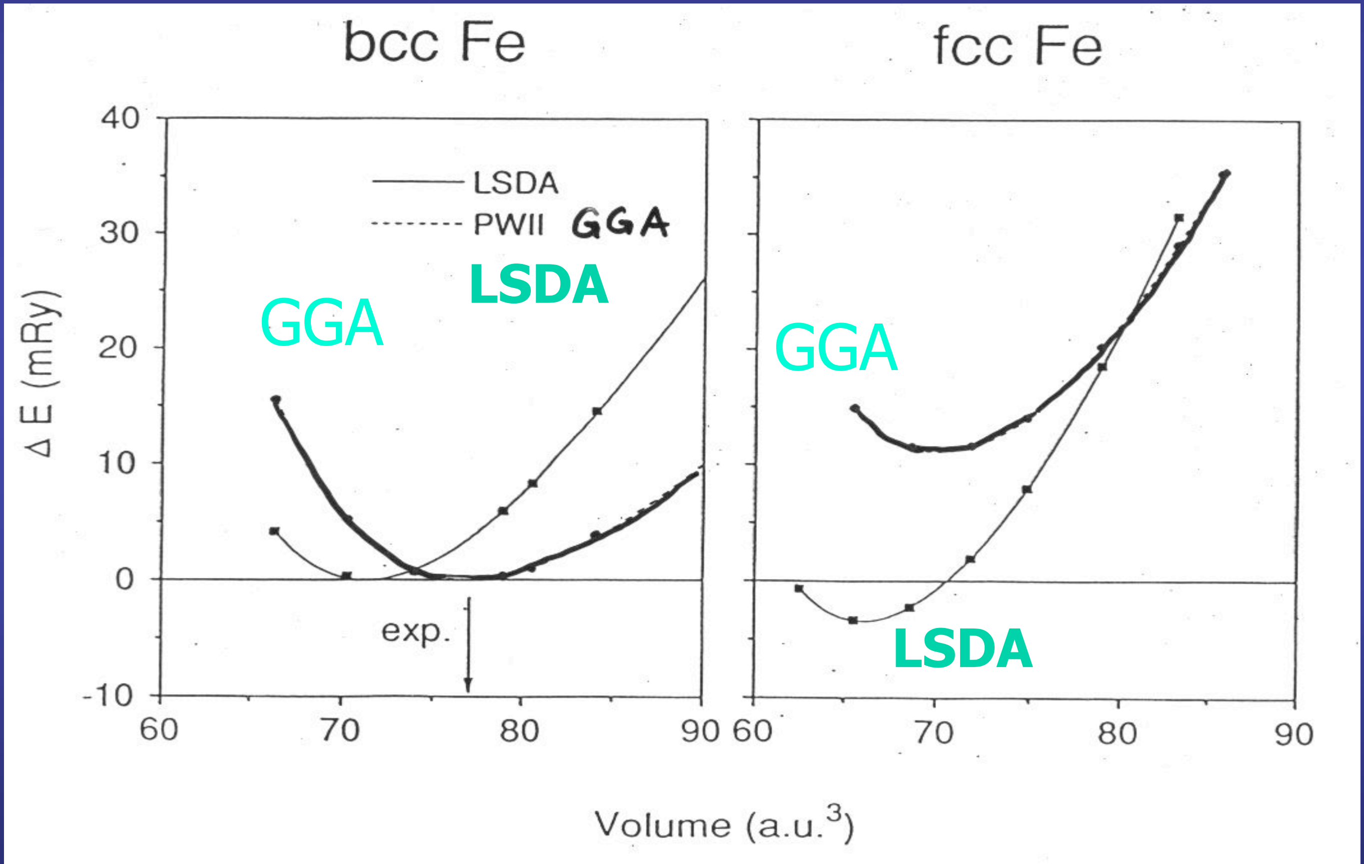
	LDA	GGA
a	-1% , -3%	+1%
B	+10, +40%	-20%, +10%
E_c	+15%	-5%
E_{gap}	-50%	-50%

LDA: **crude aproximation but sometimes is accurate enough (structural properties, …).**

GGA: **usually tends to overcompensate LDA results, not always better than LDA.**

In many cases, GGA is a must:

Ground state of Iron



LSDA

- NM
- fcc
- in contrast to experiment

GGA

- FM
- bcc
- Correct lattice constant

Experiment

- FM
- bcc

Results obtained with Wien2k.

Courtesy of Karl H. Schwartz

Treatment of the boundary conditions

Isolated objects (atoms, molecules, clusters)

open boundary conditions

(defined at infinity)

3D periodic objects (crystals)

periodic boundary conditions

(might be considered as the repetition of a building block, the unit cell)

Mixed boundary conditions

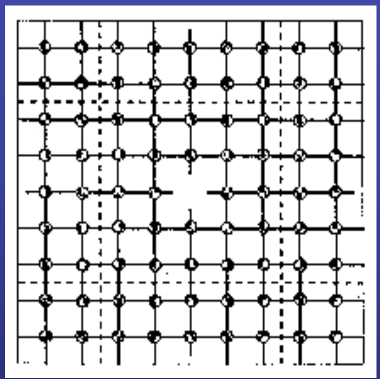
1D periodic (chains)

2D periodic (slabs and interfaces)

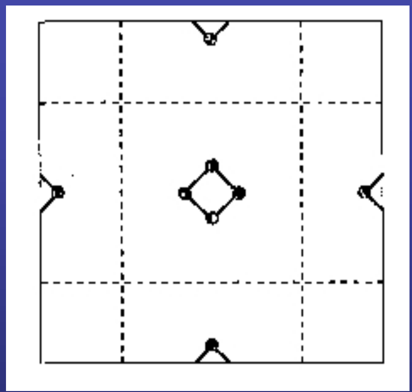
Supercells

Systems with open and mixed periodic boundary conditions are made artificially periodic

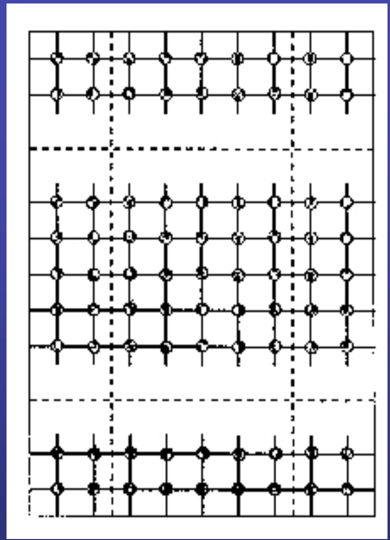
Defects



Molecules

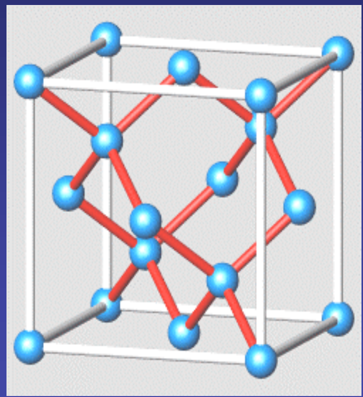


Surfaces



M. C. Payne *et al.*, Rev. Mod. Phys., 64, 1045 (1992)

A periodic potential: Bloch’s theorem



$$V(\vec{r}) = V(\vec{r} + \vec{R})$$

Bloch Theorem: **The eigenstates of the one-electron Hamiltonian in a periodic potential can be chosen to have the form of a plane wave times a function with the periodicity of the Bravais lattice.**

$$\psi_{n,\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} u_{n,\vec{k}}(\vec{r})$$

$$u_{n,\vec{k}}(\vec{r} + \vec{R}) = u_{n,\vec{k}}(\vec{r})$$

Periodicity in reciprocal space

$$\begin{cases} \psi_{n\ \vec{k}+\vec{K}'}(\vec{r}) & = \psi_{n\vec{k}}(\vec{r}) \\ \varepsilon_{n\ \vec{k}+\vec{K}'} & = \varepsilon_{n\ \vec{k}} \end{cases}$$

k-points Sampling

Instead of computing an **infinite** number of electronic **wave functions**

Finite number of **wave functions (bands)** at an infinite number of k-points.

$$\rho(\vec{r}) = \sum_i \int_{BZ} d\vec{k}\, n(\vec{k}) \left|\psi_i(\vec{k})\right|^2$$

In practice: electronic wave functions at k-points that are very close together will be almost identical $\Rightarrow$

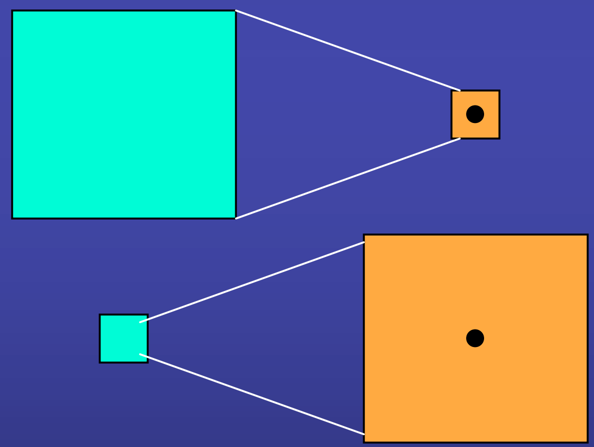
k-point Sampling

$$\int d\vec{k} \longrightarrow \sum_{\vec{k}} \Delta\vec{k}$$

k-points Sampling

Essential for:

Small cells



Real space ↔ Reciprocal space

Metals Magnetic systems

Good description of the Bloch states at the Fermi level

Large cells: Γ point

k = (0,0,0)

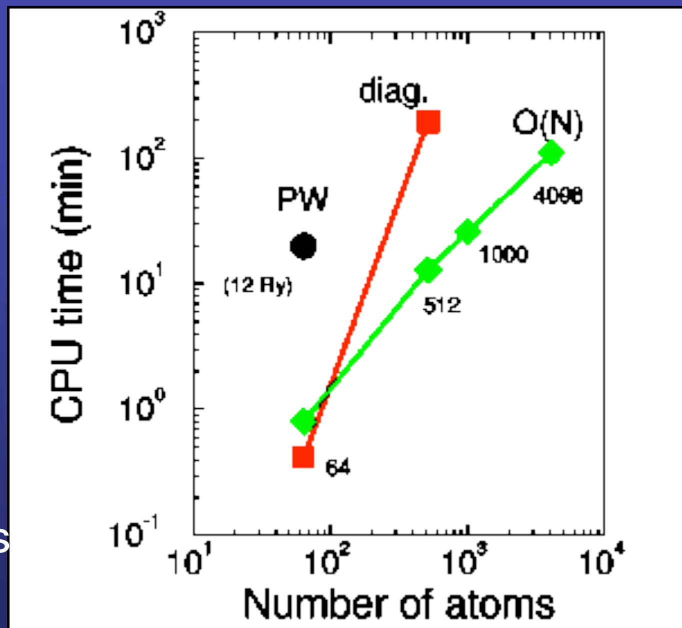
A code for DFT simuls. in large systems

Spanish Initiative for Electronic Simulations with Thousands of Atoms

Soler, Artacho, Gale, García, Junquera, Ordejón and Sánchez-Por
J. Phys.: Cond. Matt **14**, 2745 (2002)

- Numerical atomic orbitals

- O(N) methodology
- Very efficient
- Parallelized (132.000 atoms in 64 nodes



The SIESTA code

http://www.uam.es/siesta

- Linear-scaling DFT
- Numerical atomic orbitals, with quality control.
- Forces and stresses for geometry optimization.
- Diverse Molecular Dynamics options.
- Capable of treating large systems with modest hardware.
- Parallelized.

The SIESTA Team

- Emilio Artacho *(Cambridge University)*
- Julian Gale *(Curtin Inst. of Tech., Perth)*
- Alberto García *(ICMAB, Barcelona)*
- Javier Junquera *(U. Cantabria, Santander)*
- Richard Martin *(U. Illinois, Urbana)*
- Pablo Ordejón *(ICMAB, Barcelona)*
- Daniel Sánchez-Portal *(UPV, San Sebastián)*
- José M. Soler *(UAM, Madrid)*

The SIESTA Manager

- Eduardo Anglada *(UAM and Nanotec, Madrid)*

Main SIESTA Reference

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **14** (2002) 2745–2779 PII: S0953-8984(02)30737-9

The SIESTA method for *ab initio* order-*N* materials simulation

José M Soler[1], Emilio Artacho[2], Julian D Gale[3], Alberto García[4], Javier Junquera[1,5], Pablo Ordejón[6] and Daniel Sánchez-Portal[7]

BASIC REFERENCE:

J. Soler *et al*, J. Phys: Condens. Matter, **14**, 2745 (2002)

350 citations (Dec 2005)
> 700 (June 2007)

More than 1000 registered users
(SIESTA is free for academic use)

More than 450 published papers
have used the program

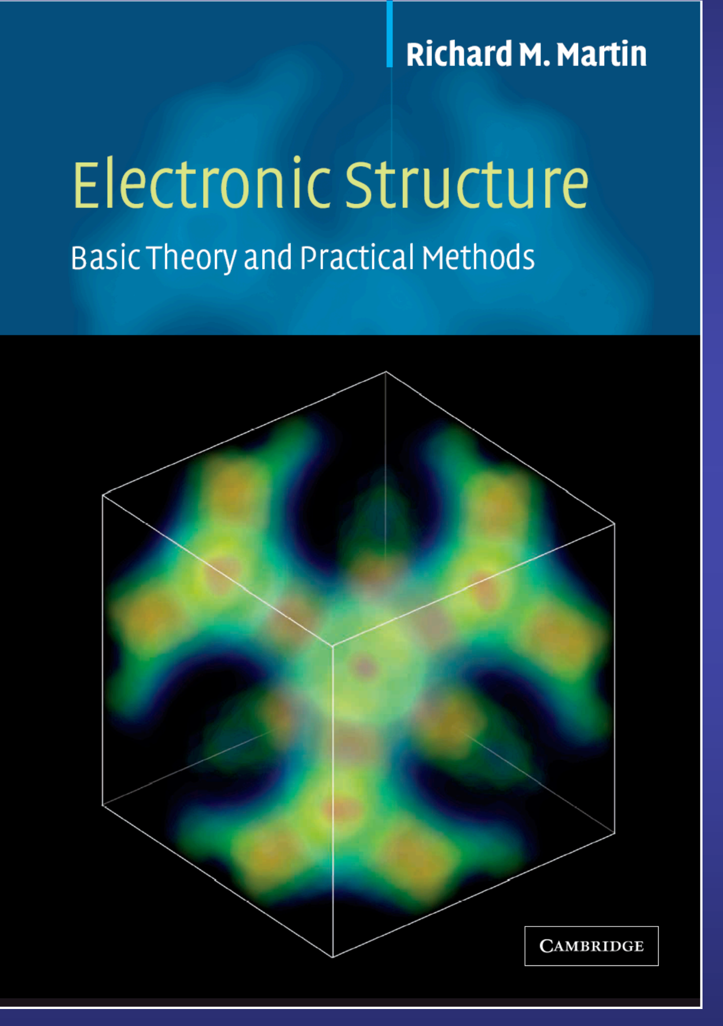
Siesta resources (I)

- Web page: http://www.uam.es/siesta
- Pseudos and basis database
- Mailing list
- Usage manual
- Soon: http://cygni.fmc.uam.es/mediawiki
- Issue tracker (for bugs, etc)
- Mailing list archives
- Wiki

Siesta resources (2)

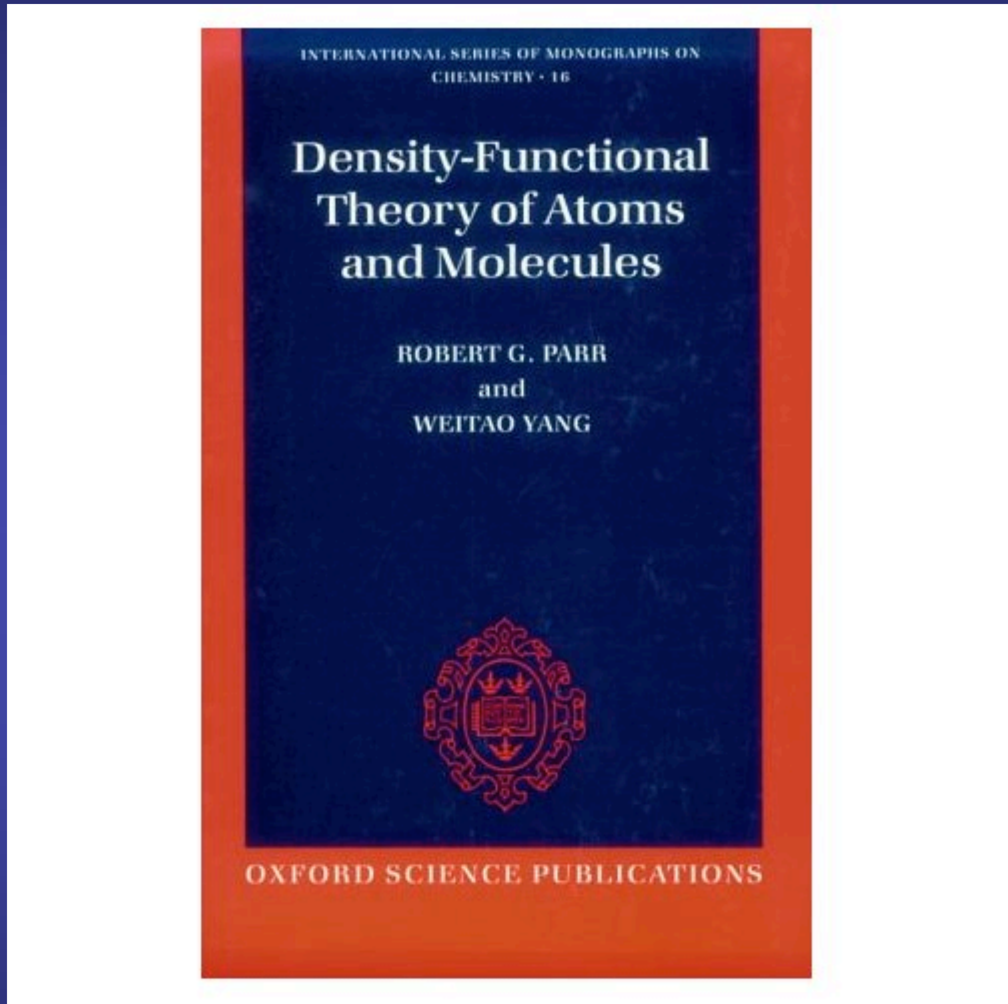
- Andrei Postnikov Siesta utils page:
  http://www.home.uni-osnabrueck.de/apostnik/download.html
- Lev Kantorovich Siesta utils page:
  http://www.cmmp.ucl.ac.uk/~lev/codes/lev00/index.html

Basics of Electronic Structure Methods



comprehensive review of DFT,
including most relevant references and exercises

Basics of DFT



Rigorous and unified account of the *fundamental principles* of DFT

OUTLOOK FOR THE COURSE

- Tutorial: Theory & Practical Sessions
- Basic Understanding of concepts involved in the calculations
- Practical know-how
- Meaningful (not blind) Simulations!!
- DO ASK WHAT YOU DO NOT UNDERSTAND!!