DRIVING
THE EXASCALE
TRANSITION

Density Functional Theory and General Notions about First-Principles Codes

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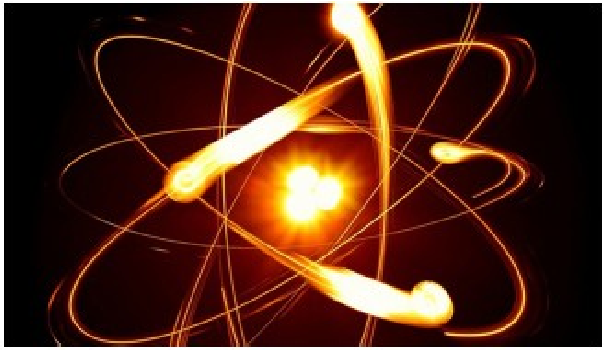
Thanks to Emilio Artacho, Javier Junquera

Patrons:

The physics of low-energy matter



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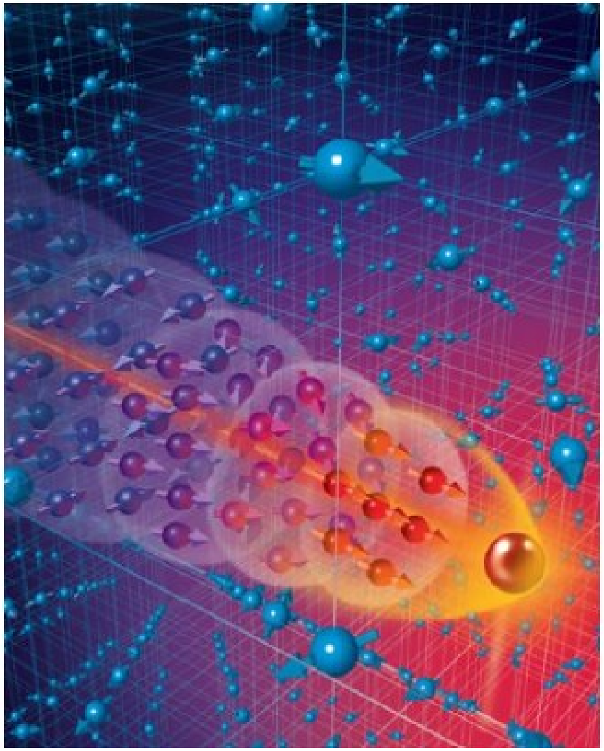
Made of electrons and nuclei
(interacting with photons)

Matter at T up to several million K
(except for nuclear fission and radioactive decay)

- Atomic & molecular physics
- Condensed matter physics (solids, liquids)
- Plasma physics

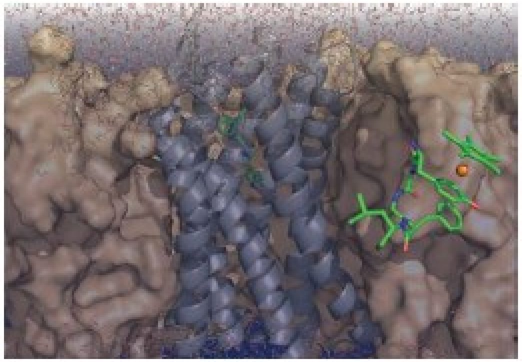
Low energy in the sense of
not probing inner structure of nuclei

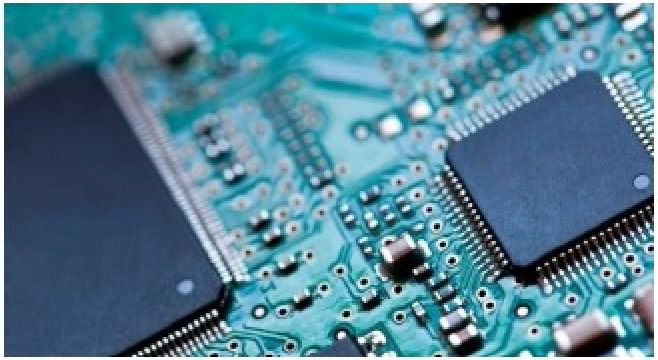


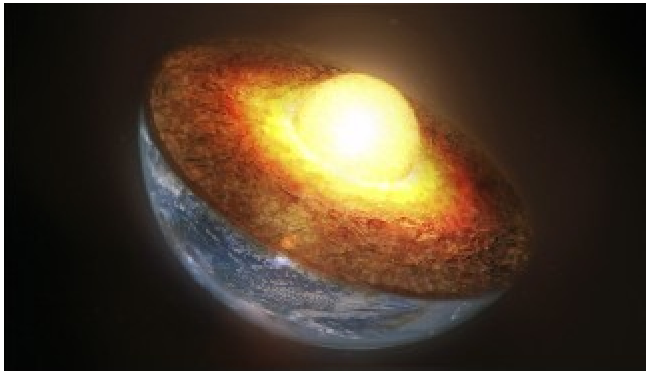
The physics of low-energy matter

Electrons and nuclei are behind properties and processes in

- Chemistry
- Material science
- Biomedicine (biochem, biophys, molecular bio)
- Geo (geophysics, geochemistry)
- Electronics
- Energy research
- Nanoscience and nanotechnology

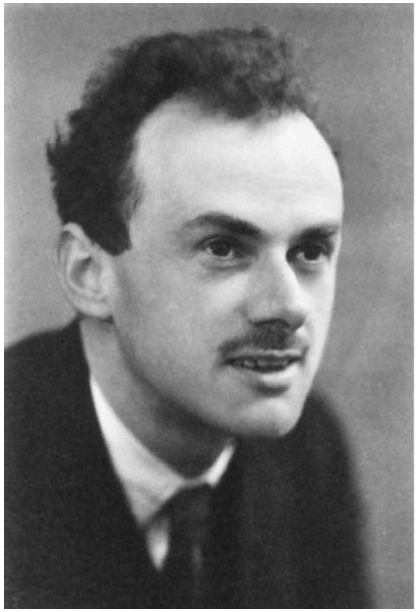






Just electrons and nuclei

"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. It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation."



Paul Dirac (1929)

Underlying physical laws

1) Electromagnetism

2) Quantum Mechanics: Schrödinger equation

$$\hat{H}\,\Psi(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N) = E\,\Psi(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N)$$

This is the fundamental equation to be solved for most systems of electrons and nuclei.
A function defined in a space of 3N dimensions
(N = number of particles) (most = non-relativistic)

Quantum mechanics for many particles

$$\hat{H}\,\Psi(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N) = E\,\Psi(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N)$$

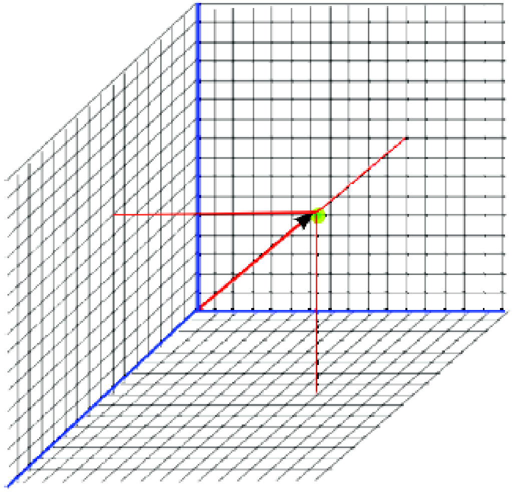
Schrödinger’s equation is exactly solvable for

- Two particles (analytically)
- Very few particles (numerically)

The number of electrons and nuclei in a pebble is $\sim 10^{23}$

Quantum mechanics for many particles

$$\hat{H}\,\Psi(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N) = E\,\Psi(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N)$$



Solving in a computer e.g. discretizing space

A 3D grid in 100 points per side → 100^3 points
Similar grid in 3N space → 100^{3N} points

Computational costs (CPU and memory) scales ~exp(N)

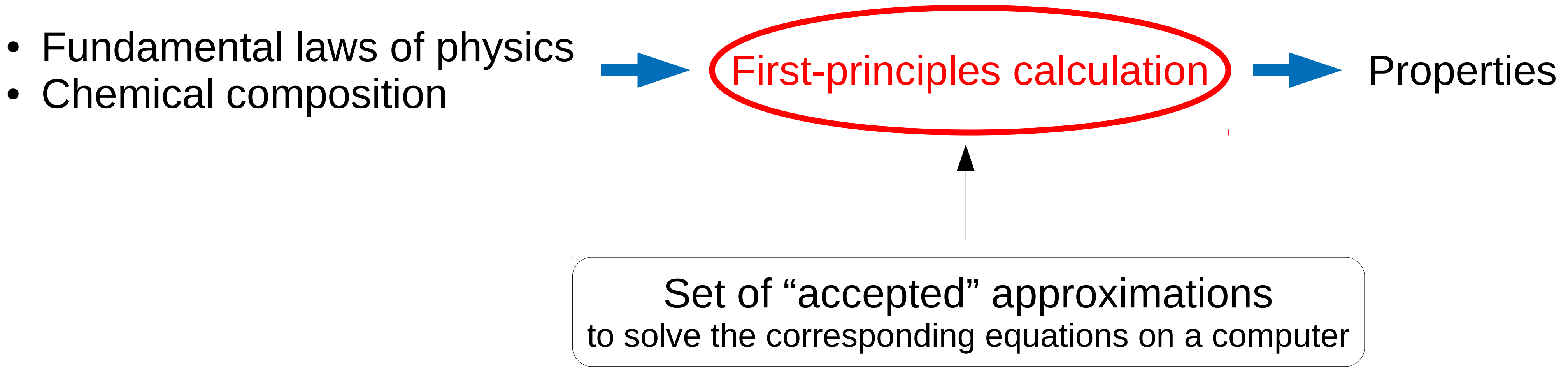
↓

Exponential Complexity

→ We need approximations!

Walter Kohn, in Nobel Lecture (1998)

First-principles calculations



- Fundamental laws of physics
- Chemical composition

First-principles calculation

Properties

Set of "accepted" approximations
to solve the corresponding equations on a computer

No empirical input or model

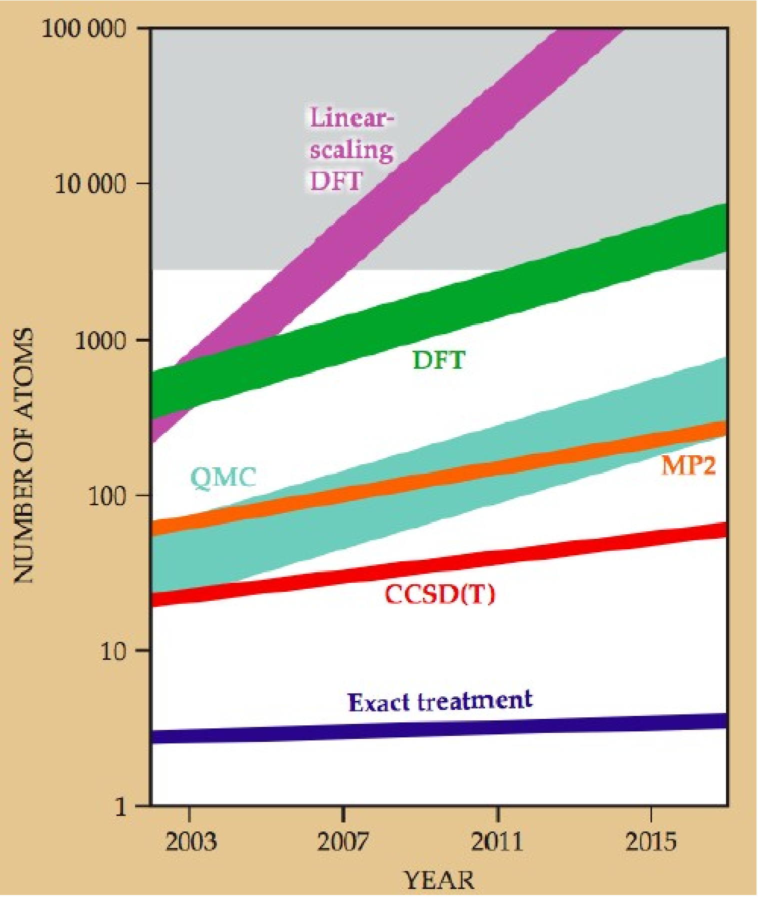
Predictive power!

First-principles calculations

Many-electron problem: old and extremely hard problem

Many different approaches:

- Quantum Chemistry: CI, CCSD(T), MP2…
- Quantum Monte Carlo (QMC)
- Density Functional Theory (DFT)
  Very efficient and general
  Best compromise efficiency/accuracy
  BUT implementations are approximate
  and hard to improve (no systematic improvement)



M. Head-Gordon and E. Artacho

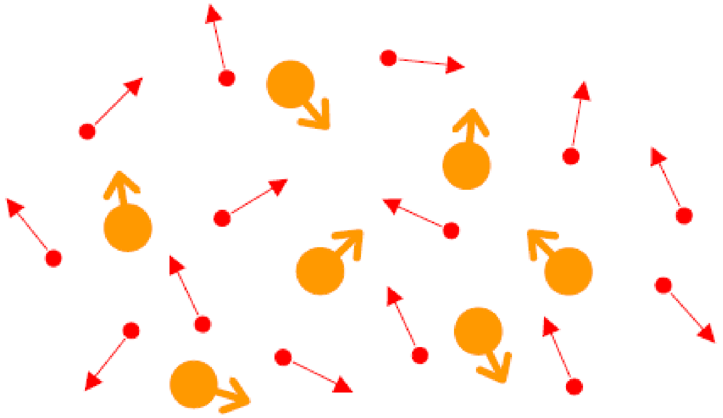
First-principles calculations

A difficult interacting many-body system

$\hat{H} = \sum_i -\frac{\hbar^2}{2m_e}\nabla_i^2$	**Kinetic energy operator for the electrons**
$+ \sum_\alpha -\frac{\hbar^2}{2M_\alpha}\nabla_\alpha^2$	**Kinetic energy operator for the nuclei**
$+ \frac{1}{2}\sum_{i\neq j}\frac{e^2}{\lvert\mathbf{r}_i - \mathbf{r}_j\rvert}$	**Electron-electron interaction**
$- \sum_{i,\alpha}\frac{Z_\alpha e^2}{\lvert\mathbf{r}_i - \mathbf{R}_\alpha\rvert}$	**Potential acting on the electrons due to the nuclei**
$- \frac{1}{2}\sum_{\alpha\neq\beta}\frac{Z_\alpha Z_\beta e^2}{\lvert\mathbf{R}_\alpha - \mathbf{R}_\beta\rvert}$	**Nucleus-nucleus interaction**

First-principles calculations: approximations

Adiabatic or Born-Oppenheimer approximation

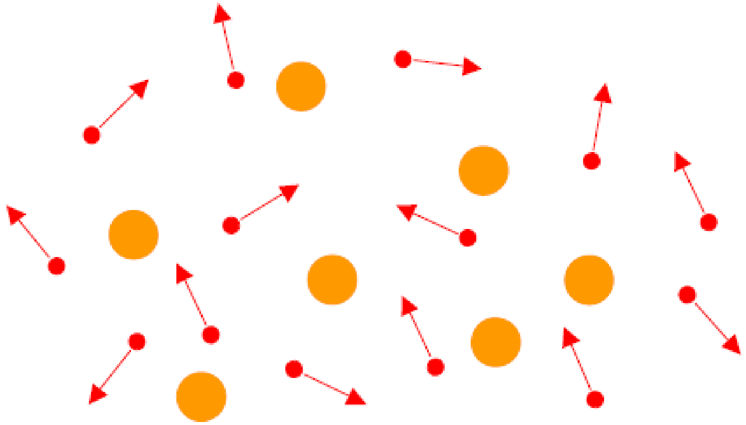


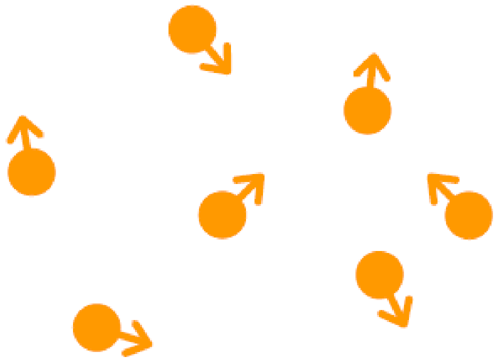
$$\frac{m_n}{m_e} \gg 1$$

→ Nuclei are much slower than electrons

(1) Solve the many-electron problem with fixed positions for the nuclei

(2) Move the nuclei in the potential generated by the electrons





First-principles calculations: approximations

Adiabatic or Born-Oppenheimer approximation

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

Fixed potential "external" to e⁻

Constant

Electrons

For a fixed set of $\{\mathbf{R}_\alpha\}$

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

$$\hat{H}^{\text{el}}_{\{\mathbf{R}_\alpha\}}\Psi^{\text{el}}_{n,\{\mathbf{R}_\alpha\}}(\{\mathbf{r}\}) = E^{\text{el}}_{n,\{\mathbf{R}_\alpha\}}\Psi^{\text{el}}_{n,\{\mathbf{R}_\alpha\}}(\{\mathbf{r}_i\})$$

Nuclei

$$\hat{H} = \sum_\alpha -\frac{\hbar^2}{2M_\alpha}\nabla_\alpha^2 + E^{\text{el}}_{n,\{\mathbf{R}_\alpha\}}$$

Classical dynamics → $\mathbf{F}_\beta = -\dfrac{\delta E^{\text{el}}_{0,\{\mathbf{R}_\alpha\}}}{\delta \mathbf{R}_\beta}$

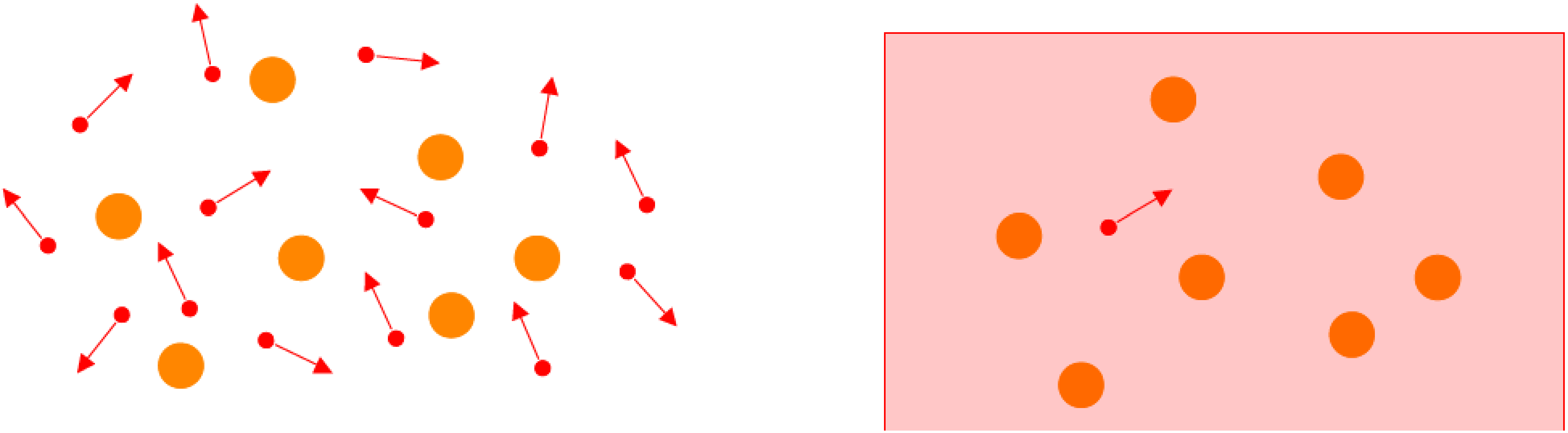
First-principles calculations: approximations

Density functional theory

Many electron wave-function → one electron density

$$\Psi(\{\vec{r}_i\}) \rightarrow n(\vec{r})$$

As if non-interacting electrons in an effective (self-consistent) potential



Density functional theory

Hohenberg-Kohn theorems

Theorem I: For any system of interacting particles in an external potential $V_{\text{ext}}(\mathbf{r})$, the potential $V_{\text{ext}}(\mathbf{r})$ is determined uniquely, except for a constant, by the ground state particle density $n_{GS}(\mathbf{r})$.

→ All properties of the system are completely determined given only $n_{GS}(\mathbf{r})$.

Theorem II: A universal functional for the energy $E[n]$ in terms of the density $n(\mathbf{r})$ can be defined, valid for any external potential $V_{\text{ext}}(\mathbf{r})$. For any particular $V_{\text{ext}}(\mathbf{r})$, the exact ground state energy of the system is the global minimum value of this functional, and the density $n(\mathbf{r})$ that minimizes the functional is the exact ground state density $n_{GS}(\mathbf{r})$.

→ The functional $E[n]$ alone is sufficient to determine the exact ground state energy and density. Excited states must be determined by other means.

Density functional theory

Hohenberg-Kohn theorems

$$\hat{H} = -\frac{\hbar^2}{2m_e}\sum_i \nabla_i^2 + \frac{1}{2}\sum_{i\neq j}\frac{e^2}{|\mathbf{r_i}-\mathbf{r_j}|} + \sum_i V_{ext}(\mathbf{r_i}) = T + V_{ee} + \sum_i V_{ext}(\mathbf{r_i})$$

$$E_{\mathrm{HK}}[n] = \underbrace{T[n] + E_{\mathrm{int}}[n]}_{\big\downarrow} + \int d^3r\, V_{\mathrm{ext}}(\mathbf{r})n(\mathbf{r}) + E_{\mathrm{II}}$$

$$1.\ E_{\mathrm{HK}}[n] \equiv F_{\mathrm{HK}}[n] + \int d^3r\, V_{\mathrm{ext}}(\mathbf{r})n(\mathbf{r}) + E_{II} \geq E_{\mathrm{GS}}$$

$$2.\ E[n_{\mathrm{GS}}(\mathbf{r})] = E_{\mathrm{GS}}$$

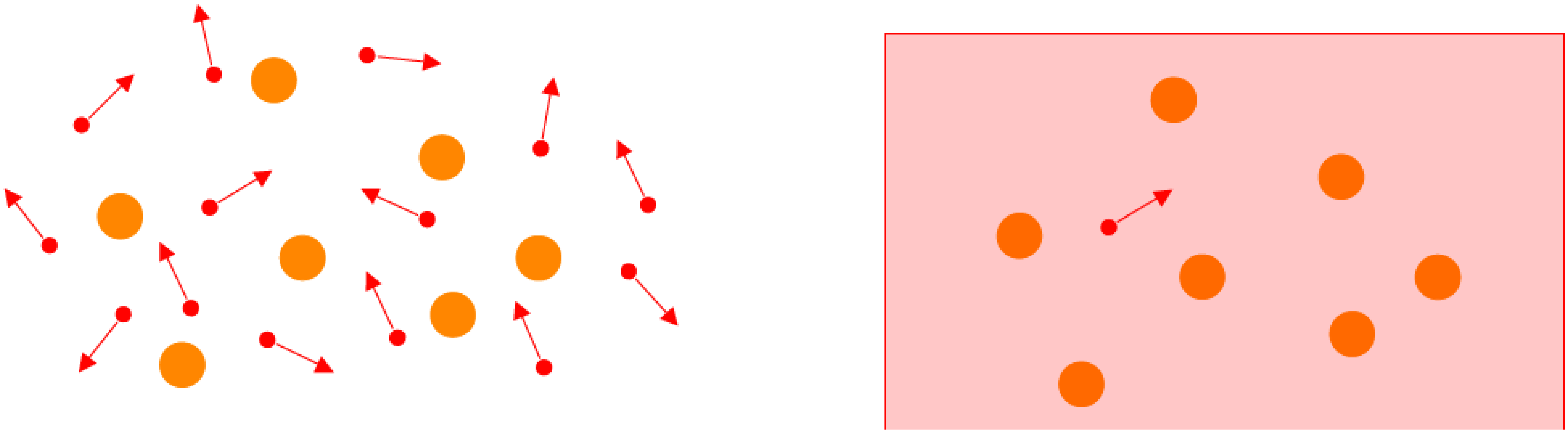
If $F_{\mathrm{HK}}[n]$ was known, by minimizing E_{HK} with respect to variations in $n(\mathbf{r})$, one would find the exact ground state density and energy.

PROBLEM: Functional $F_{HK}[n]$ is unknown

Density functional theory

Kohn-Sham ansatz

The exact ground state density can be represented by the ground state density of an auxiliary system of non-interacting particles.



Actual calculations are performed on the auxiliary independent-particle system defined by the auxiliary Hamiltonian:

$$\hat{H}^{\sigma}_{\text{aux}} = -\frac{1}{2}\nabla^2 + V^{\sigma}_{\text{eff}}(\mathbf{r})$$

Density functional theory

Kohn-Sham ansatz

Finally they rewrote the functional as:

$$\mathrm{E}_{\mathrm{KS}}[n] = T_0[n] + \int d^3r\, V_{\mathrm{ext}}(\mathbf{r})n(\mathbf{r}) + E_{\mathrm{Hartree}}[n] + E_{\mathrm{II}} + E_{\mathrm{xc}}[n]$$

Kinetic energy of the system
of independent particles

$$\frac{1}{2}\int d^3r d^3r' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

All the rest:
exchange-correlation

Equivalent to independent particles under the potential:

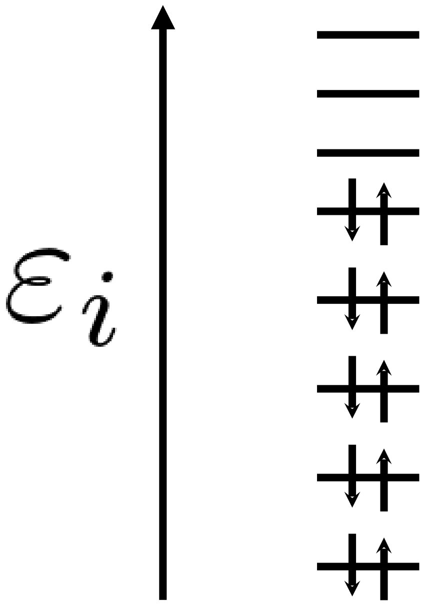
$$V_{\mathrm{KS}}^{\sigma} = V_{\mathrm{ext}}(\mathbf{r}) + V_{\mathrm{Hartree}}(\mathbf{r}) + V_{\mathrm{xc}}^{\sigma}(\mathbf{r})$$

The problem is now to determine the exchange-correlation functional

Density functional theory

$$\hat{h}_{\mathrm{KS}} = -\frac{1}{2}\nabla^2 + V_{\mathrm{KS}}(\mathbf{r})$$

$$\hat{h}_{\mathrm{KS}}\psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r})$$

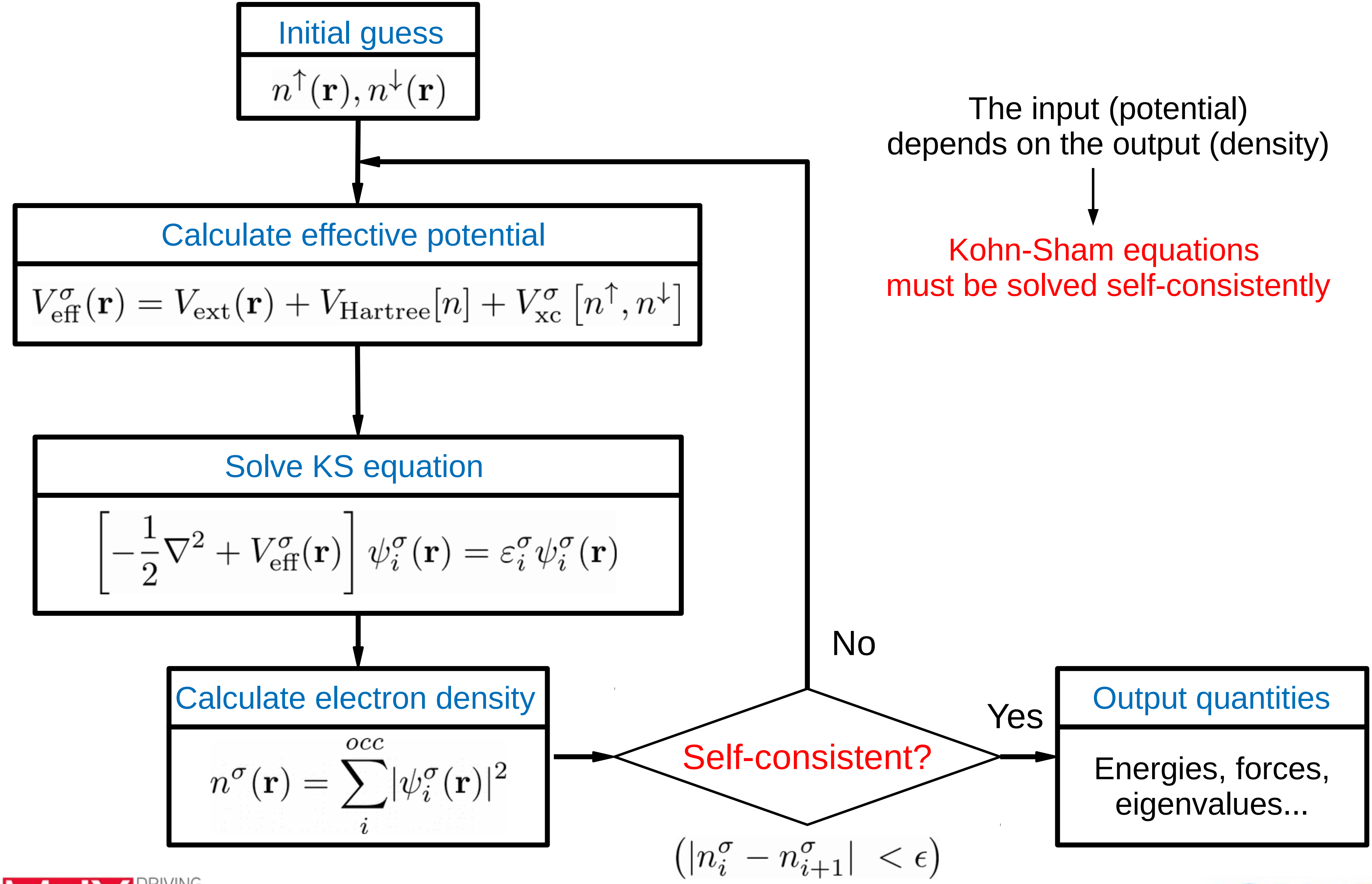


The one-particle eigenstates are filled from lower to higher energies

$$n(\mathbf{r}) = \sum_i^{\mathrm{occ}} |\psi_i(\mathbf{r})|^2$$

Careful: Kohn-Sham eigenvalues correspond to “Kohn-Sham electrons”, not to the real electrons from the interacting many-body system.

Density functional theory



Initial guess

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

Calculate effective potential

$$V^{\sigma}_{\text{eff}}(\mathbf{r}) = V_{\text{ext}}(\mathbf{r}) + V_{\text{Hartree}}[n] + V^{\sigma}_{\text{xc}}\left[n^{\uparrow}, n^{\downarrow}\right]$$

Solve KS equation

$$\left[-\frac{1}{2}\nabla^2 + V^{\sigma}_{\text{eff}}(\mathbf{r})\right]\psi^{\sigma}_i(\mathbf{r}) = \varepsilon^{\sigma}_i\psi^{\sigma}_i(\mathbf{r})$$

Calculate electron density

$$n^{\sigma}(\mathbf{r}) = \sum_i^{occ}|\psi^{\sigma}_i(\mathbf{r})|^2$$

Self-consistent?

$$\left(|n^{\sigma}_i - n^{\sigma}_{i+1}| < \epsilon\right)$$

No

Yes

Output quantities

Energies, forces, eigenvalues...

The input (potential)
depends on the output (density)

↓

Kohn-Sham equations
must be solved self-consistently

Density functional theory

Exchange and correlation functionals

$$E_{\mathrm{xc}}, V_{\mathrm{xc}} \equiv \frac{\delta E_{\mathrm{xc}}[n]}{\delta n(\mathbf{r})}$$

Local density approximation (LDA)

Solids can be often be considered as close to the limit of the homogeneous electron gas.
In this limit the effects of exchange and correlation are *local* in character.

$$V_{\mathrm{xc}}[n] \approx V_{\mathrm{xc}}(n(r))$$

Exchange-correlation energy of the homogeneous electron gas
as a function of a given density

Exchange

$$E_{\mathrm{x}}^{\mathrm{LDA}}[n] = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{\frac{1}{3}} \int n(\mathbf{r})^{\frac{4}{3}} d^3\mathbf{r}$$

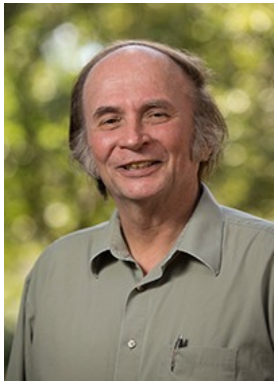
Correlation

E_c calculated from Quantum Monte Carlo

Density functional theory

Exchange and correlation functionals

John Perdew's Jacob's ladder



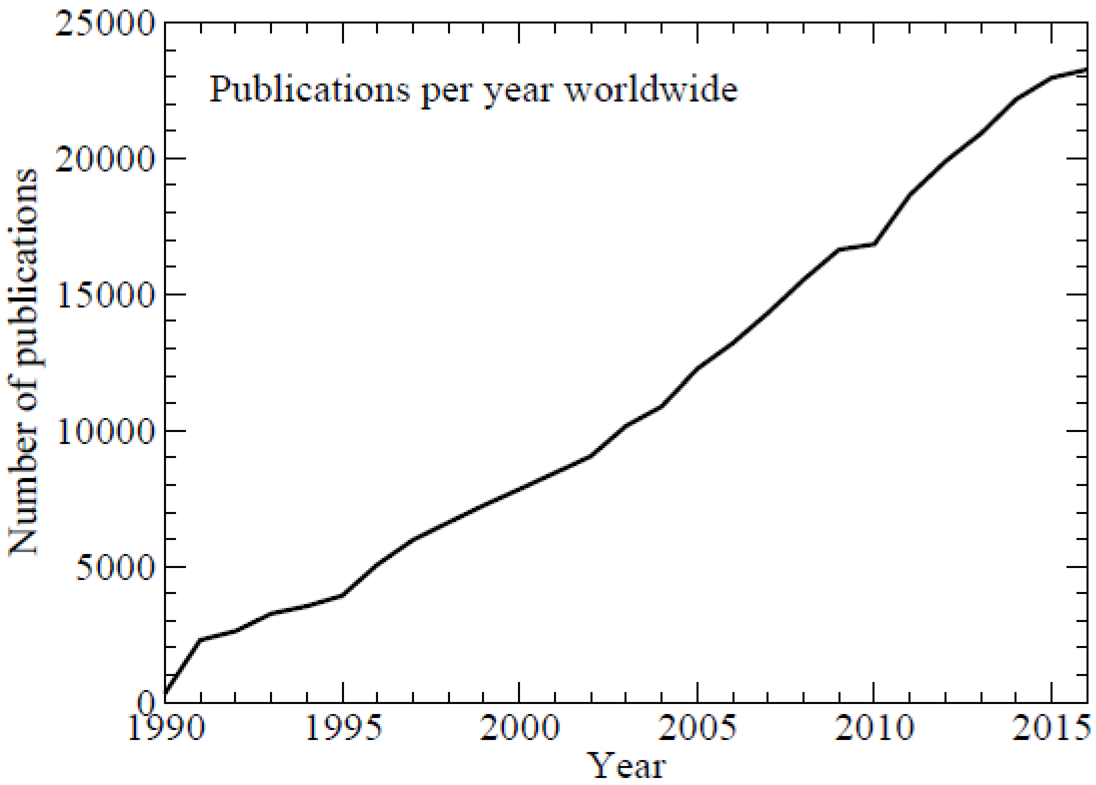
increased accuracy ↑

Ingredients	***XC families***	***Examples***
$\text{unoccupied } \{\phi_i\}$	generalized RPA	*so far not practical*
$n, \nabla n, (\tau,)\, \varepsilon_x$	hyper-GGA	B3LYP, B3PW91, PBE0...
$n, \nabla n, \tau \text{ and/or } \nabla^2 n$	meta-GGA	TPSS, M06L, tHCTH...
$n, \nabla n$	GGA	PBE, PW91, AM05, BLYP...
n	LDA	PW, CA(PZ), VWN...

In addition, dispersion corrected (vdW) functionals (Dion, Langreth...), LDA+U

http://octopus-code.org/wiki/Libxc_functionals

Density functional theory



Mavropoulos and Dederichs, *Psi-k highlight*, April 2017

Density functional theory using the Kohn-Sham approach is the most widely used method for electronic structure calculations.

Nobel Prize in Chemistry 1998 to Walter Kohn.

Density functional theory

Practical considerations

- **Basis sets:** how we expand the wave-function?
- **Pseudopotentials:** do we treat all electrons on an equal footing?
- **Boundary conditions:** are we considering periodic or non-periodic systems?
- **Other issues:** numerical algorithms, license...

Different choices lead to different implementations:
Many different codes

Density functional theory

Basis sets

Expand the wave-function in terms of a finite set of basis functions:

$$\{\phi_\mu(\mathbf{r})\} : \qquad \psi_n(\mathbf{r}) \approx \sum_\mu \phi_\mu(\mathbf{r}) c_{\mu,n}$$

$$\hat{h}\psi_n(\mathbf{r}) = \varepsilon_n \psi_n(\mathbf{r}) \quad \Longrightarrow \quad \sum_\mu \left[\hat{h}\phi_\mu(\mathbf{r})\right] c_{\mu,n} = \varepsilon_n \sum_\mu \phi_\mu(\mathbf{r}) c_{\mu,n} \quad \Longrightarrow$$

$$\sum_\mu h_{\nu\mu} c_{\mu,n} = \varepsilon_n \sum_\mu S_{\nu\mu} c_{\mu,n}$$

with

$$h_{\nu\mu} \equiv \int d^3\mathbf{r}\, \phi_\nu^*(\mathbf{r}) \hat{h} \phi_\mu(\mathbf{r})$$

$$S_{\nu\mu} \equiv \int d^3\mathbf{r}\, \phi_\nu^*(\mathbf{r}) \phi_\mu(\mathbf{r})$$

Density functional theory

Different basis sets

Richard Martin's classification

1) **Plane waves and grids:**

Pros: Expansion in plane waves is conceptually simple and easy to implement
Systematic way of improving the calculation, no dependence on atomic positions

Cons: Large number of plane waves → memory requirements
Vacuum as expensive as matter

Codes: Quantum Espresso, VASP, Abinit, CASTEP...

2) **Localized atomic-like orbitals:** *gaussians, slater type, numerical atomic orbitals...*

Pros: Very efficient, straightforward physical interpretation, no cost for vacuum

Cons: Harder to reach convergence, greater care in the election of the basis, Pulay terms

Codes: **SIESTA**, Gaussian, CRYSTAL, OpenMX, ADF...

3) **Atomic sphere methods:** *FP-LAPW, LMTO, KKR...*

Atomic-like features near the nucleus, smooth functions between atoms

Pros: Very precise, best of both worlds

Cons: Computationally expensive, more difficult to implement

Codes: FLEUR, Wien2k, Elk, RSPt...

If applied carefully, all of them agree after convergence

Density functional theory

Pseudopotentials

Do we treat all electrons on an equal footing?

- **YES:** all-electron methods
  No approximation, but more expensive. Difficult for plane-waves basis sets.
  CODES: FLEUR, Wien2k, RSPt, FHI-AIMS, CRYSTAL, Gaussian...

- **NO:** pseudopotentials (ECP's)
  The core electrons are substituted by an effective ionic potential acting on the valence e^-
  More efficient
  CODES: **SIESTA**, Quantum Espresso, VASP, Abinit, Gaussian...

  PAW: “all-electron frozen core”, between both worlds
  CODES: Quantum Espresso, VASP, Abinit...

Density functional theory

Boundary conditions

- **Periodic boundary conditions:** 3D periodic objects, crystals
  A unit cell is repeated filling all the space
  Makes use of Bloch theorem
  Surfaces, molecules can be treated by the inclusion of vacuum (supercells)
  CODES: **SIESTA**, Quantum Espresso, FLEUR...

- **Open boundary conditions:** atoms, molecules, clusters
  CODES: Gaussian, NRLMOL, deMon, TURBOMOLE...

- **Mixed boundary conditions:** 1D and 2D periodic objects (chains, slabs)
  CODES: FLEUR, KKR-GF...

Density functional theory

SIESTA

Spanish Initiative for Electronic Simulations with Thousands of Atoms

- Kohn-Sham Density Functional Theory
- Exchange-correlation: LDA, GGA, vdW-DF, LDA+U
- Numerical atomic orbitals as basis sets
- Norm-conserving pseudopotentials
- Periodic boundary conditions
- Technical details → *see next: SIESTA internals*
- GPL license

References

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  R.O. Jones and O. Gunnarsson, *“The density functional formalism, its applications and prospects”.* Rev. Mod. Phys. **61**, 689 (1989)
  R.O. Jones, *“Density functional theory: Its origins, rise to prominence, and future”.* Reviews of Modern Physics **87**, 897 (2015)

- **Many, many more**