Materials modelling with Density Functional Theory

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GDR PULSE 2017 - Atelier Simulations
Université Pierre et Marie Curie, Paris (France)
5 October 2017

Bibliography

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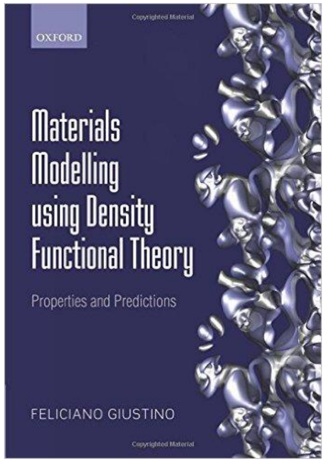
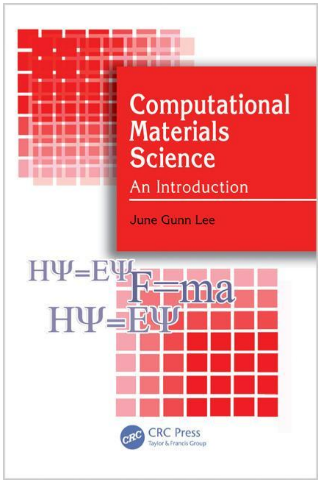


Materials modelling
with Density Functional Theory
(Chapters 1,2,3)
F. Giustino, OXFORD

Computational
Materials Science
(Chapters 4,5,6)
J. Gunn Lee, CRC Press



The ABC of DFT
Kieron Burke and friends,
University of California, Irvine
http://dft.uci.edu/doc/g1.pdf

The ABC of DFT
Kieron Burke and friends
Department of Chemistry, University of California, Irvine, CA 92697
April 10, 2007

Further Bibliography

Further Bibliography

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Outline

- Computational materials modeling from first principles
- Many-body Schrödinger equation
  - Clamped nuclei approximation
  - Independent electrons approximation
  - Mean field approximation
- Density Functional Theory

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- Computational materials modeling from first principles

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- The complexity of such problems require the use of supercomputers

- This is a discipline at the boundary between materials science, physics and chemistry on the one side, and applied mathematics and software engineering

Density Functional Theory (DFT)

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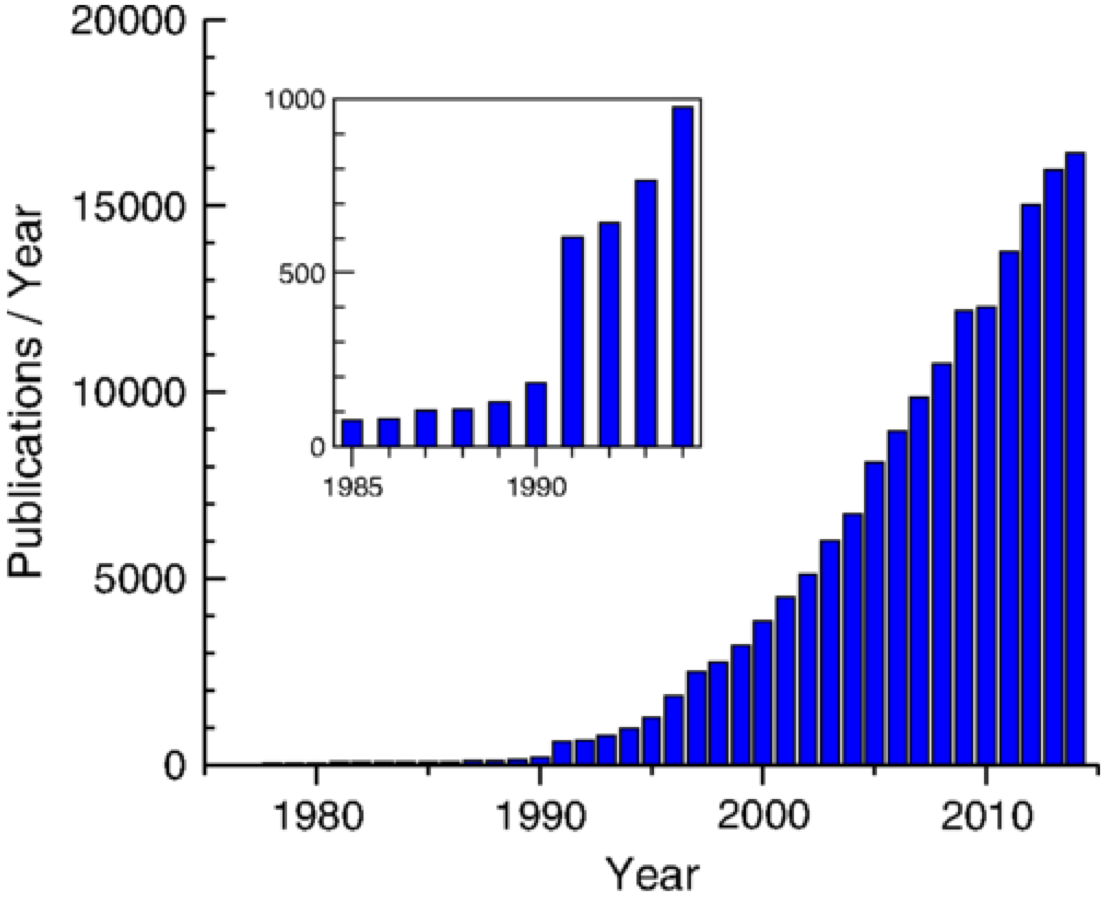

R.O. Jones, Rev. Mod. Phys. 87, 897 (2015)

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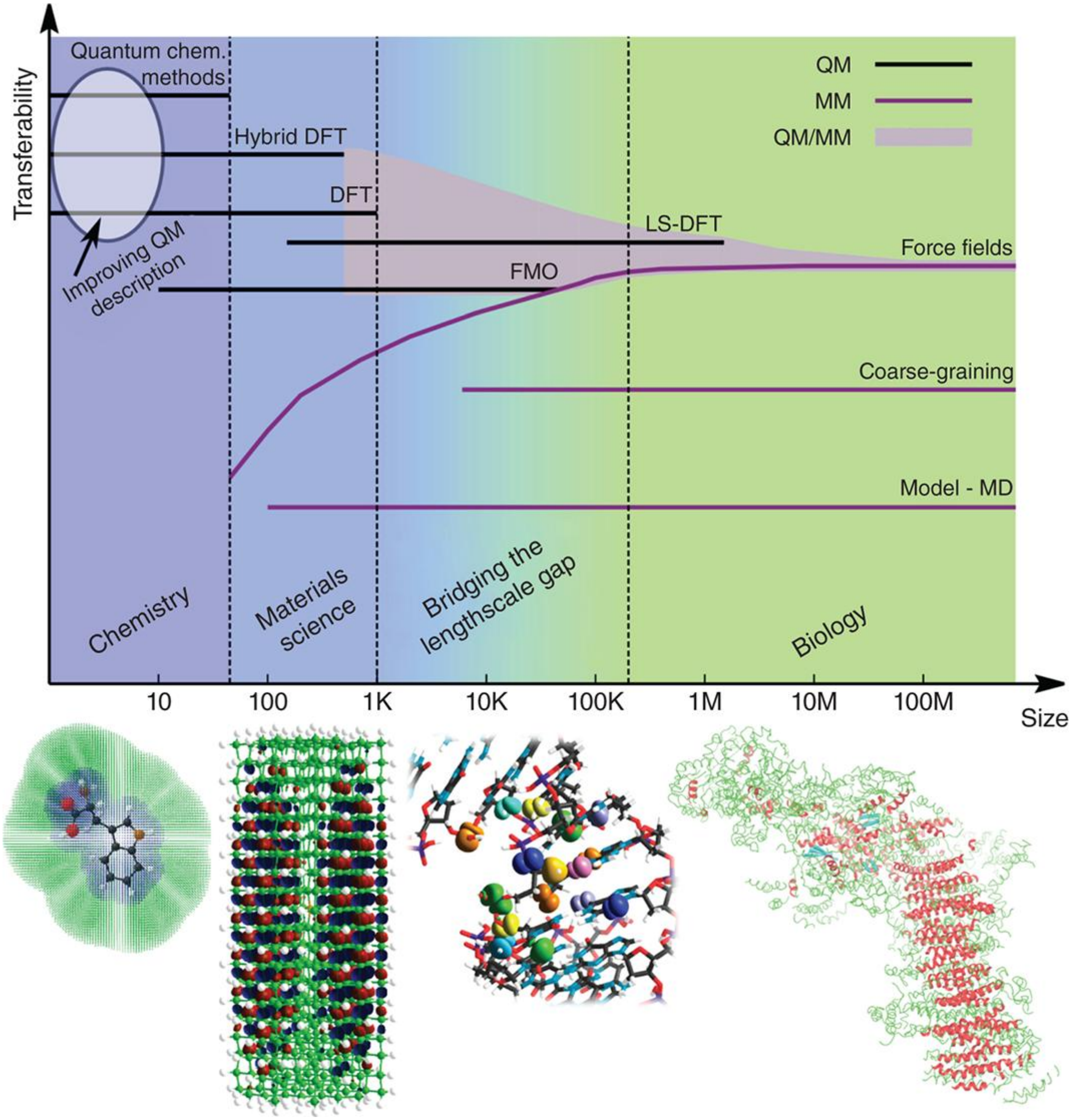

L. E. Ratcliff et al., Comput. Mol. Sci. 7, 1759 (2017)

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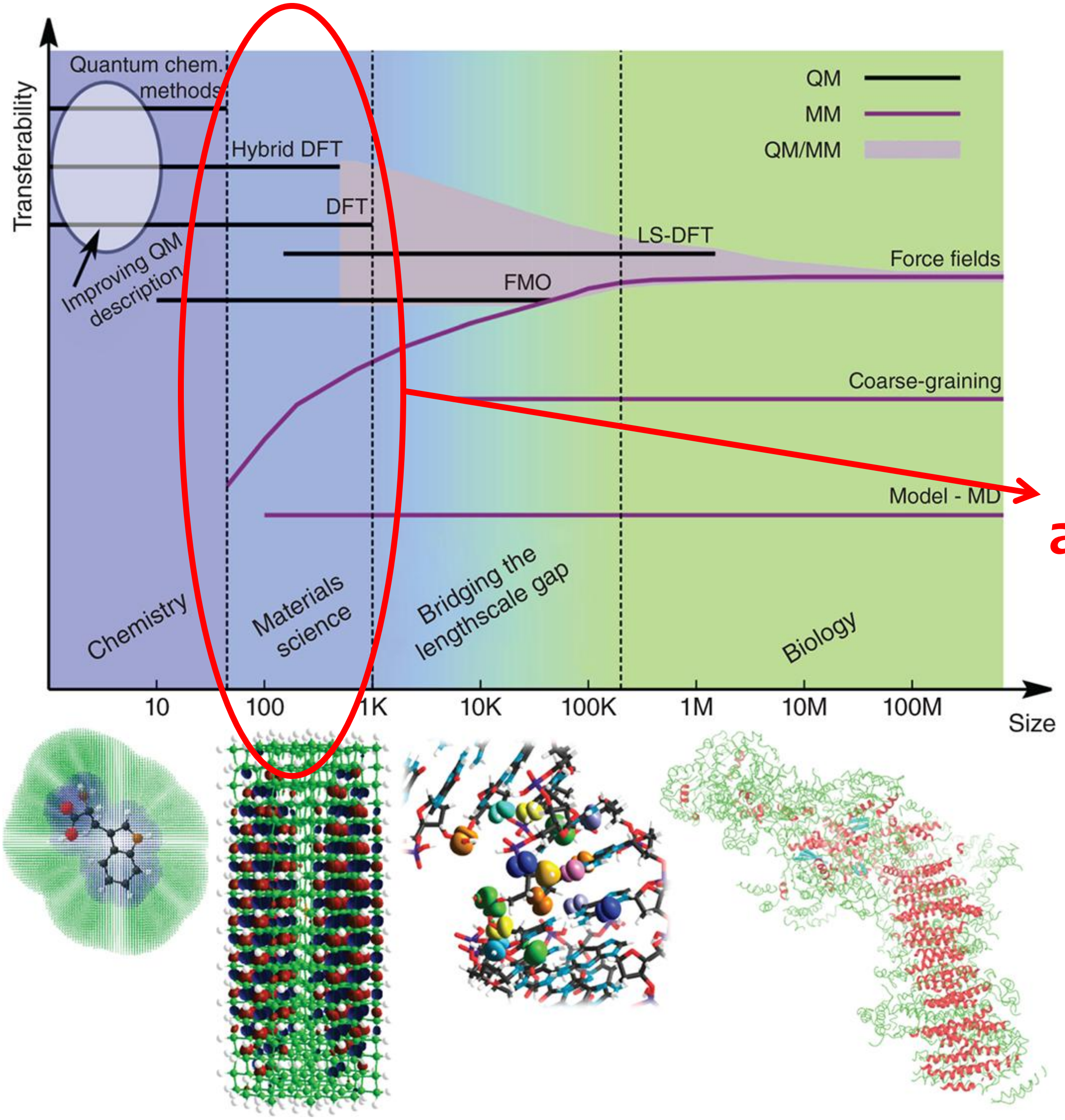

DFT methods are QM based and applicable from few tens to more than 1000 atoms

L. E. Ratcliff et al., Comput. Mol. Sci. 7, 1759 (2017)

Popularity of Density Functional Theory (DFT)

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- **Transferability:** same technique for describing different classes of materials

- **Simplicity:** based on simply and intuitive equations

- **Realiability:** possibility of making direct and quantitative comparison with experiments

- **Software sharing:** online platforms and adoption of open-source software model

- **Reasonable starting point:** even when it fails in describing correctly a property, it respresent an accurate starting point for more accurate theory (more computationally demanding)

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    - Clamped nuclei approximation
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The Coulomb interaction

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Materials = electrons + nuclei

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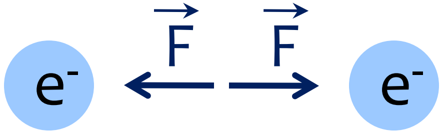
Repulsion between electrons

$$E_{ee} = \frac{e^2}{4\pi\varepsilon_0 d_{ee}}$$



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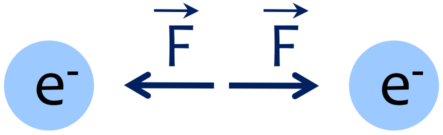
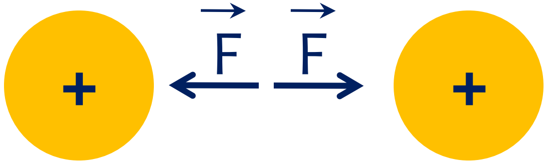


Repulsion between nuclei

$$E_{nn} = \frac{Z^2 e^2}{4\pi\varepsilon_0 d_{nn}}$$



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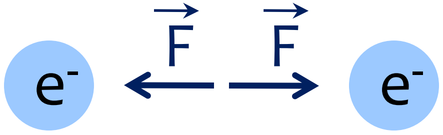

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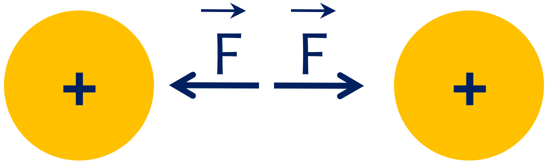
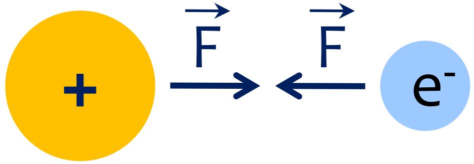


Attraction electrons-nuclei

$$E_{en} = -\frac{Z\cdot e^2}{4\pi\varepsilon_0 d_{en}}$$



Many-body Schrödinger equation

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Knowledge of the wave function

$$r = x\mathbf{u_x} + y\mathbf{u_y} + z\mathbf{u_z} \rightarrow \Psi(r)$$

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Probability of finding a particle in *r*

$$|\Psi(r)|^2$$

Many-body Schrödinger equation

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One electron case

$$\left[\frac{p^2}{2m_e} + V(r)\right] \Psi(r) = E\,\Psi(r)$$

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$$p = -i\hbar\nabla, \quad \nabla = \mathbf{u}_x \frac{\partial}{\partial x} + \mathbf{u}_y \frac{\partial}{\partial y} + \mathbf{u}_z \frac{\partial}{\partial z}$$

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What does happen if we add more electrons?

Many-body Schrödinger equation

Many-body Schrödinger equation

In the case of *N* electrons and *M* nuclei:

$$\Psi = \Psi(r_1, r_2, \dots, r_N; R_1, R_2, \dots, R_M)$$

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The probability of finding one electron at *r*:

$$|\Psi(r\ \ , r_2, ..., r_N; R_1, R_2, ..., R_M)|^2$$

The electron density is then:

$$n(r) = \int |\Psi(r, r_2, ..., r_N; R_1, R_2, ..., R_M)|^2 \, dr_2 ... dr_N dR_1 ... dR_M$$

and $$\int n(r) dr = N$$

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Example of Laplace operator for particle 1:

$$\nabla_1^2 = \frac{\partial^2\Psi}{\partial x_1^2} + \frac{\partial^2\Psi}{\partial y_1^2} + \frac{\partial^2\Psi}{\partial z_1^2}$$

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Atomic units

1 Ha	27.2114 eV
1 bohr	0.529177 Å
1 a.u. of mass	$9.109382 \cdot 10^{-31}$ Kg

The many body electronic structure problem

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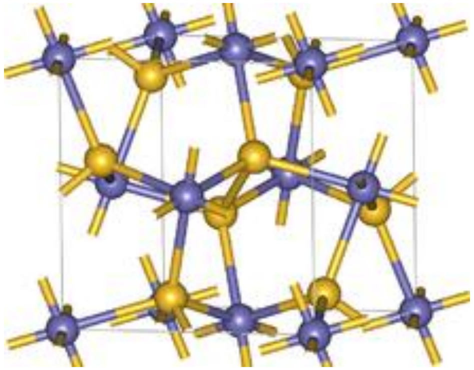

N_e electrons
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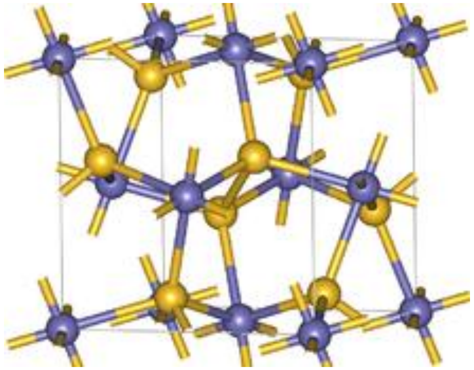

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Schrödinger equation for interacting particles

$$\widehat{H}\Psi(\{R\},\{r\}) = E\Psi(\{R\},\{r\})$$

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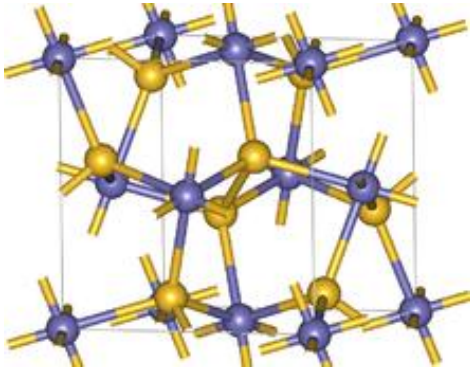

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$$\widehat{H} = \widehat{T}_n(\{R\}) + \widehat{V}_{nn}(\{R\}) + \widehat{T}_e(\{r\}) + \\ + \widehat{V}_{ee}(\{r\}) + \widehat{U}_{en}(\{R\},\{r\})$$

Some comments

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- How to deal with $N \sim 10^{23}$ particles?

- In the case of solids and molecules, we can find some useful approximations

Useful approximations

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$$E = E_{tot} - \frac{1}{2}\sum_{I \neq J} \frac{Z_I Z_J}{|R_I - R_J|}$$

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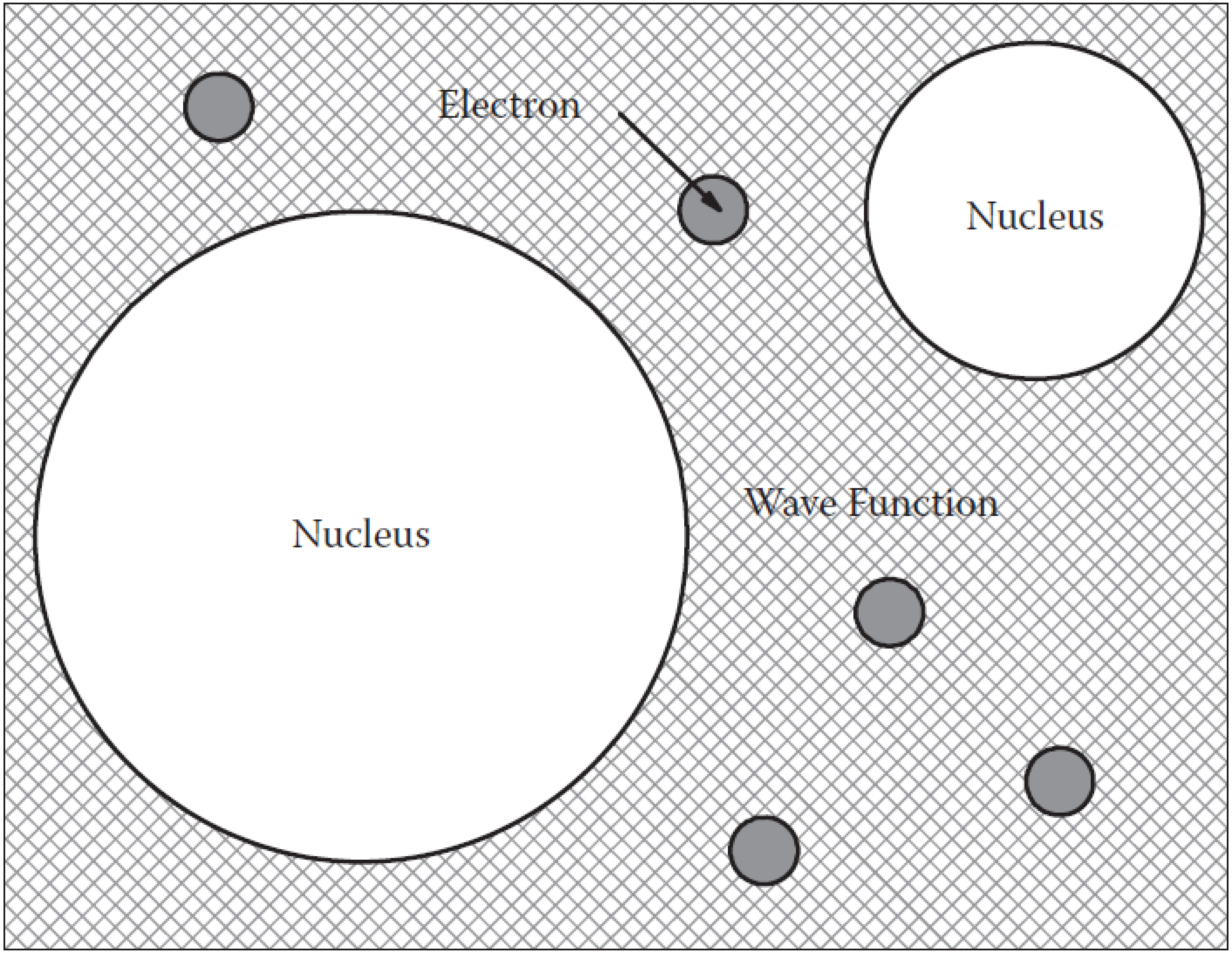

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Fundamental equation of electronic structure theory

$$\left[-\sum_i \frac{1}{2}\nabla_i^2 + \sum_i V_n(r_i) + \frac{1}{2}\sum_{i\neq j} \frac{1}{|r_i - r_j|} \right] \Psi = E\Psi$$

Further simplifications

Further simplifications

Many-electron Hamiltonian

$$\widehat{H}(r_1, \ldots, r_N) = -\sum_i \frac{\nabla_i^2}{2} + \sum_i V_n(r_i) + \frac{1}{2}\sum_{i\neq j}\frac{1}{|r_i - r_j|}$$

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Single-electron Hamiltonian

$$\widehat{H}_0(r) = -\frac{1}{2}\nabla^2 + V_n(r)$$

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Single-electron Hamiltonian

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Many-electron Hamiltonian rewritten:

$$\widehat{H}(r_1, \dots, r_N) = \sum_i \widehat{H}_0(r_i) + \frac{1}{2}\sum_{i \neq j} \frac{1}{|r_i - r_j|}$$

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$$\widehat{H}_0(r)\Phi_i(r) = \epsilon_i\Phi_i(r)$$

$$E = \epsilon_1 + \epsilon_2 + ... + \epsilon_N$$

Some comments

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- The independent electrons approximation carries two important drawbacks

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- It does not obey to the Pauli exclusion principle, which requires that the function changes sign whenever we exchange two electrons, i.e. if we swap r_1 and r_2

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- How can we take into account these effects?

Exclusion Principle

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For *N* electrons we have: $n(r) = \sum_i |\Phi_i(r)|^2$

Outline

- Computational materials modeling from first principles

- Many-body Schrödinger equation
  - Clamped nuclei approximation
  - Independent electrons approximation
  - Mean field approximation

- Density Functional Theory

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Hartree Potential

$$V_H(r) = \int dr' \frac{n(r')}{|r - r'|}$$

Mean-field approximation

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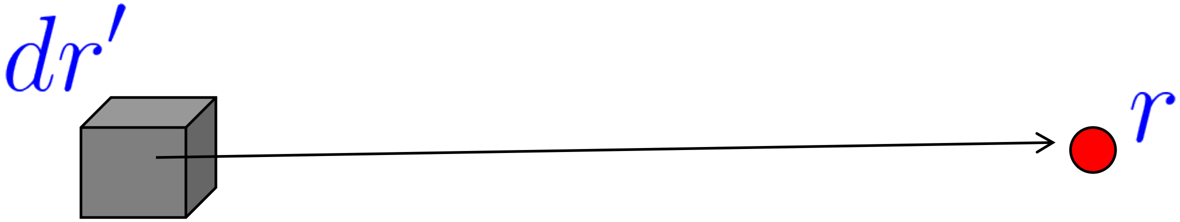

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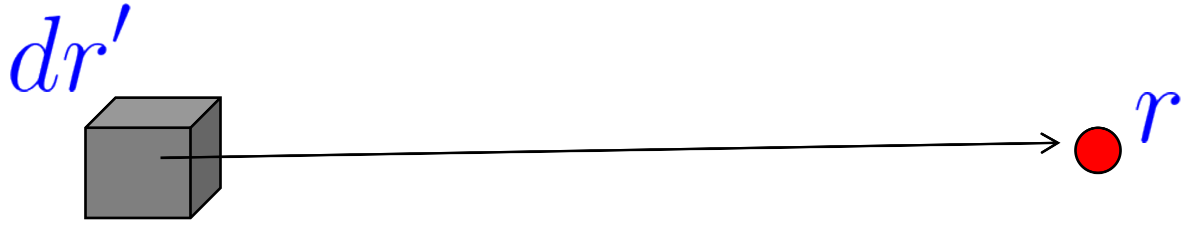

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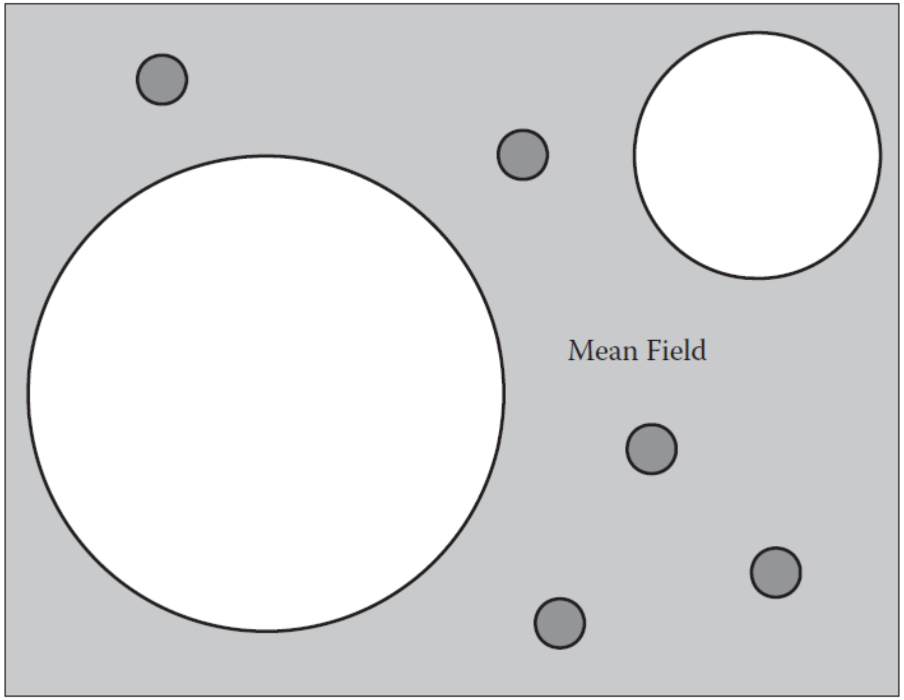

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V_H is the average potential experienced by each electron

This approach is a ‘self consistent method’

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- This approach has to done numerically, but it is feasible in terms of computer memory

- The mean-field approximation would be very good if the electrons were classical particles

- This approach is still not very accurate for the study of materials at the atomic scale

Introduction to Hartree-Fock equations

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To find the answer we have to apply
the variational principle to our system

$$E = \int dr_1 ... dr_N \Psi^* \widehat{H} \Psi$$

$$E = < \Psi \mid \widehat{H} \mid \Psi >$$

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$$\frac{\delta E}{\delta \phi_i^*} = 0$$

$$\int dr \phi_i^*(r)\phi_j(r) = \delta_{ij}$$

Hartree-Fock equations

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Fock exchange potential

$$V_x(r,r') = -\sum_j \frac{\phi_j^*(r')\phi_j(r)}{|r-r'|}$$

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- This refinement introduces the *non-local* potential $V_x(r,r')$ in the single particle equations. This complicates enormously the practical solution

- The potential V_x derives from Pauli’s exclusion principle and prevents two electrons from occupying the same quantum state

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- The only remaining element left out of the picture is the correlation between electrons

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- To take into account also this effect, we can add another component to the single-particle potential $V_n+V_H+V_x$
- We will call this additional term V_c

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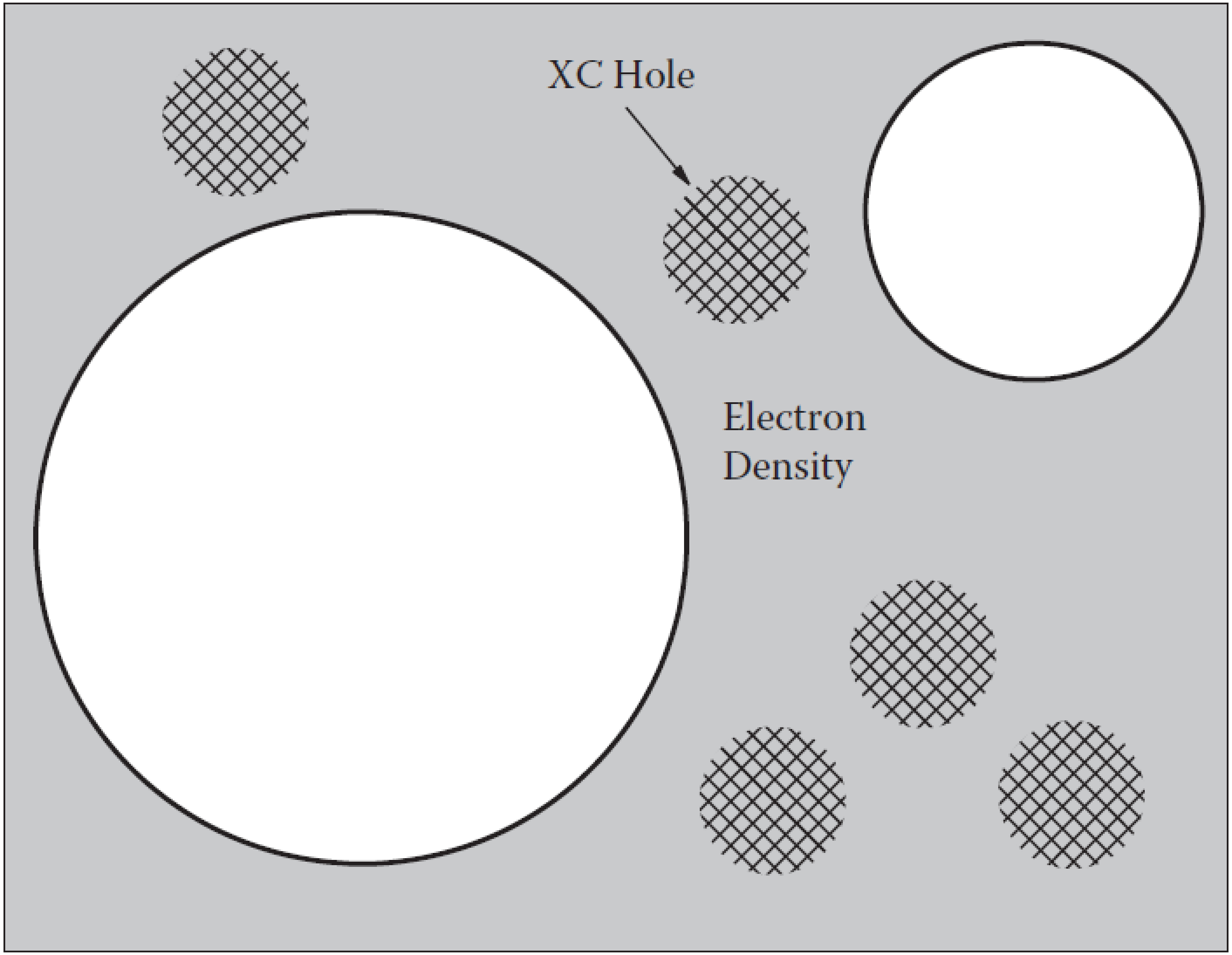

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- We have introduced V$_c$

- We have simplified V$_x$, making it to depend only on *r*

- We still do not know the exact form of V$_x$ and V$_c$, but convenient and accurate approximations have been done

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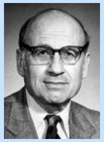
Density Functional Theory (DFT)



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Nobel Prize in
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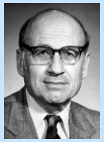

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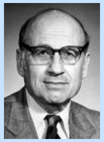

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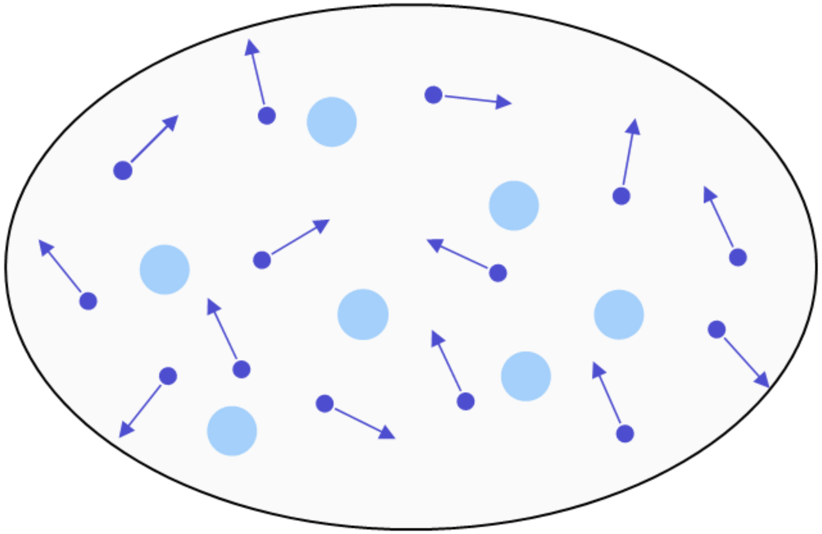

interacting particles in a
real external potential

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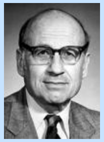

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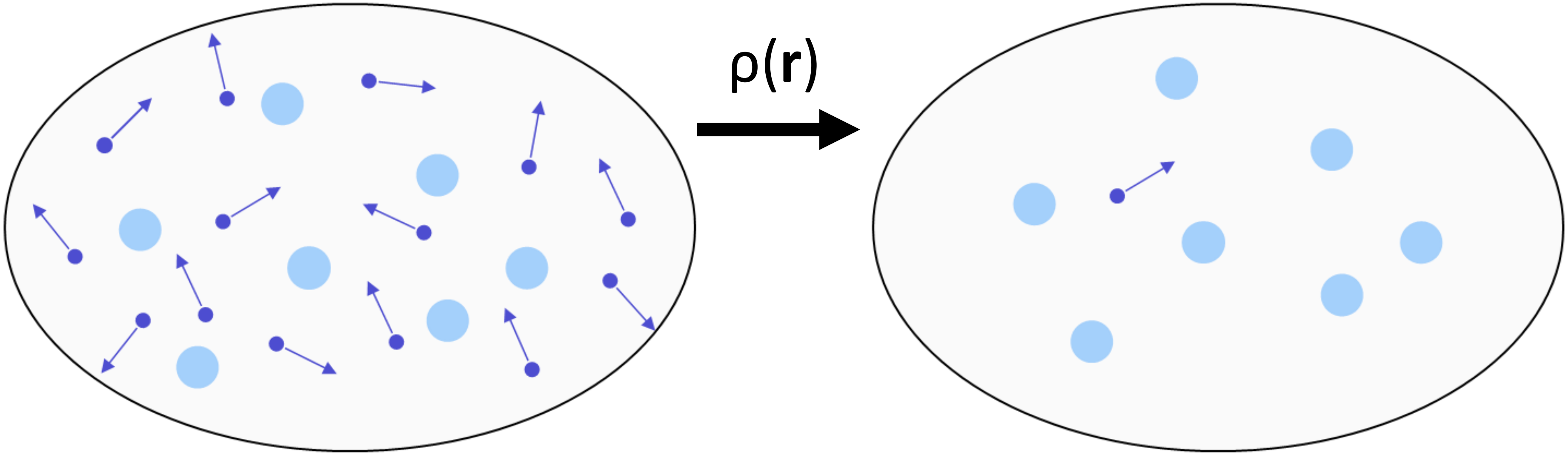

interacting particles in a real external potential

a set of non-interacting electrons (with the same density as the interacting system) in some effective potential

Total energy of the electronic ground state

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$$E =< \Psi \mid \widehat{H} \mid \Psi > = \int dr_1 ... dr_N \Psi^*(r_1, ..., r_N) \widehat{H} \Psi(r_1, ..., r_N)$$

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The structure of the Hamiltonian does not depend on the particular material under consideration

Any change in E is associated to a change in the wave function ψ

It is possible to say that E is a functional of ψ:

$$E = F[\Psi]$$

Density Functional Theory concept

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- The core concept of DFT is the observation that, if *E* is the lowest possible energy of the system, i.e. the energy of the ground state, then ***E*** **is a functional of the electron density only:**

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- All we need for calculating the energy of the system is the electron density *n*

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This indicates that the total energy must be a functional of the density:

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Density Functional
Exact form still unknown

$$E = F[n]$$

$$F[n] = \int dr\, n(r) V_n(r) + < \Psi[n] \mid \widehat{T} + \widehat{W} \mid \Psi[n] >$$

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- The idea of Kohn and Sham was to split these implicit terms into the kinetic and Coulomb energy of independent electrons plus an extra term which account for the difference:

$$E = F[n] = \overbrace{\underbrace{\int dr\, n(r)V_n(r)}_{\text{External Potential}} - \underbrace{\sum_i \int dr\, \phi_i^*(r)\frac{\nabla^2}{2}\phi_i(r)}_{\text{Kinetic Energy}} + \underbrace{\frac{1}{2}\iint dr\, dr' \frac{n(r)n(r')}{|r-r'|}}_{\text{Hartree Energy}}}^{\text{Total energy in the independent electrons approximation}} + \underbrace{E_{xc}[n]}_{\text{XC Energy}}$$

The Kohn-Sham idea: energy decomposition

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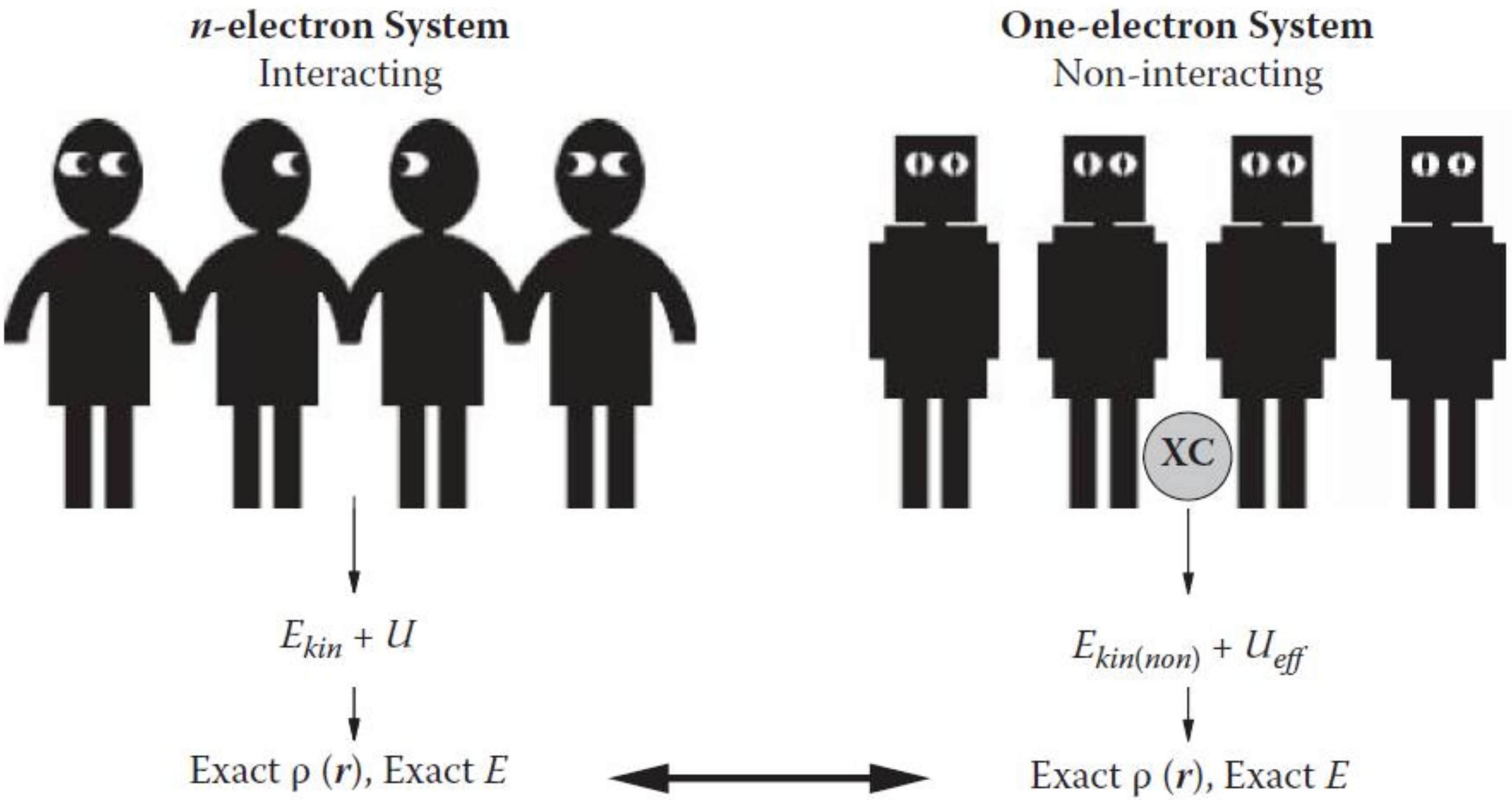

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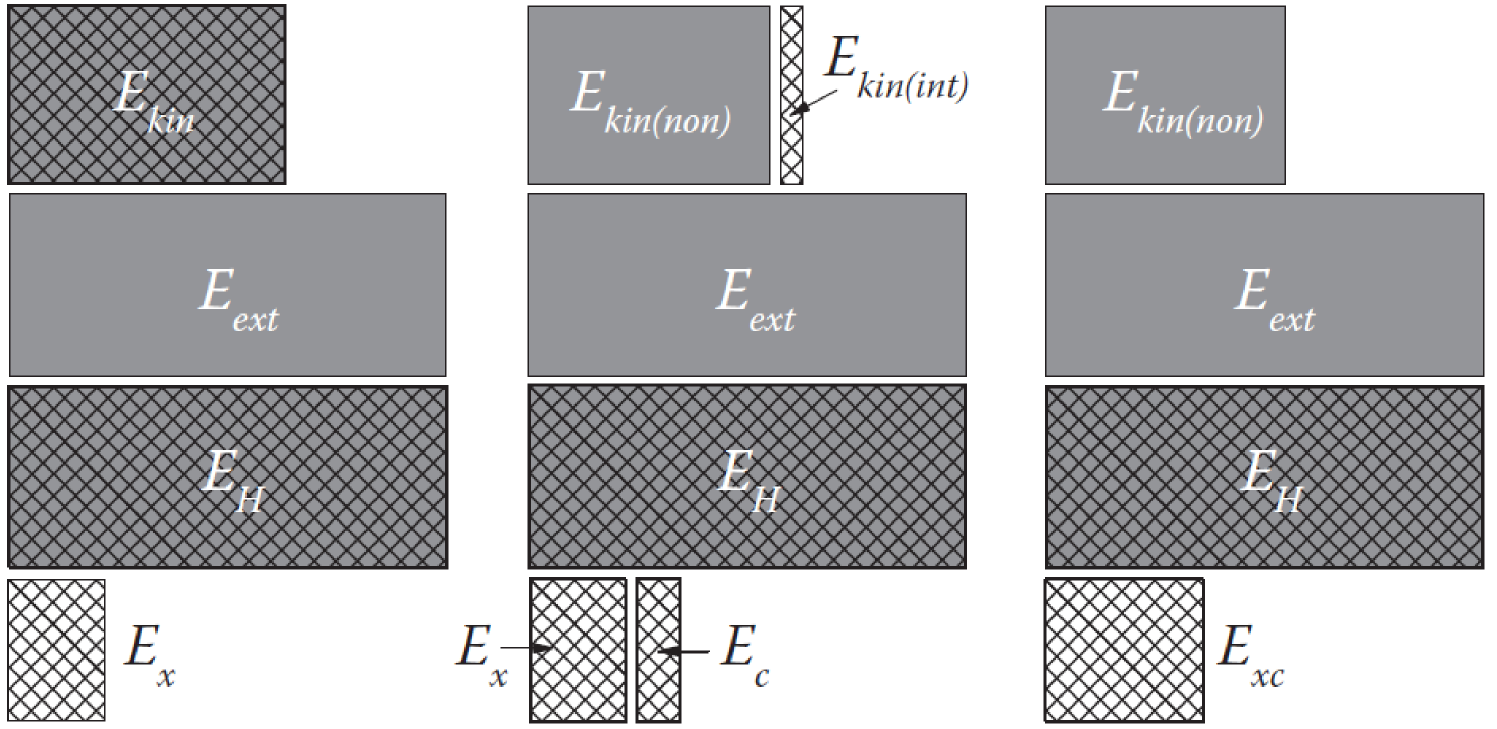
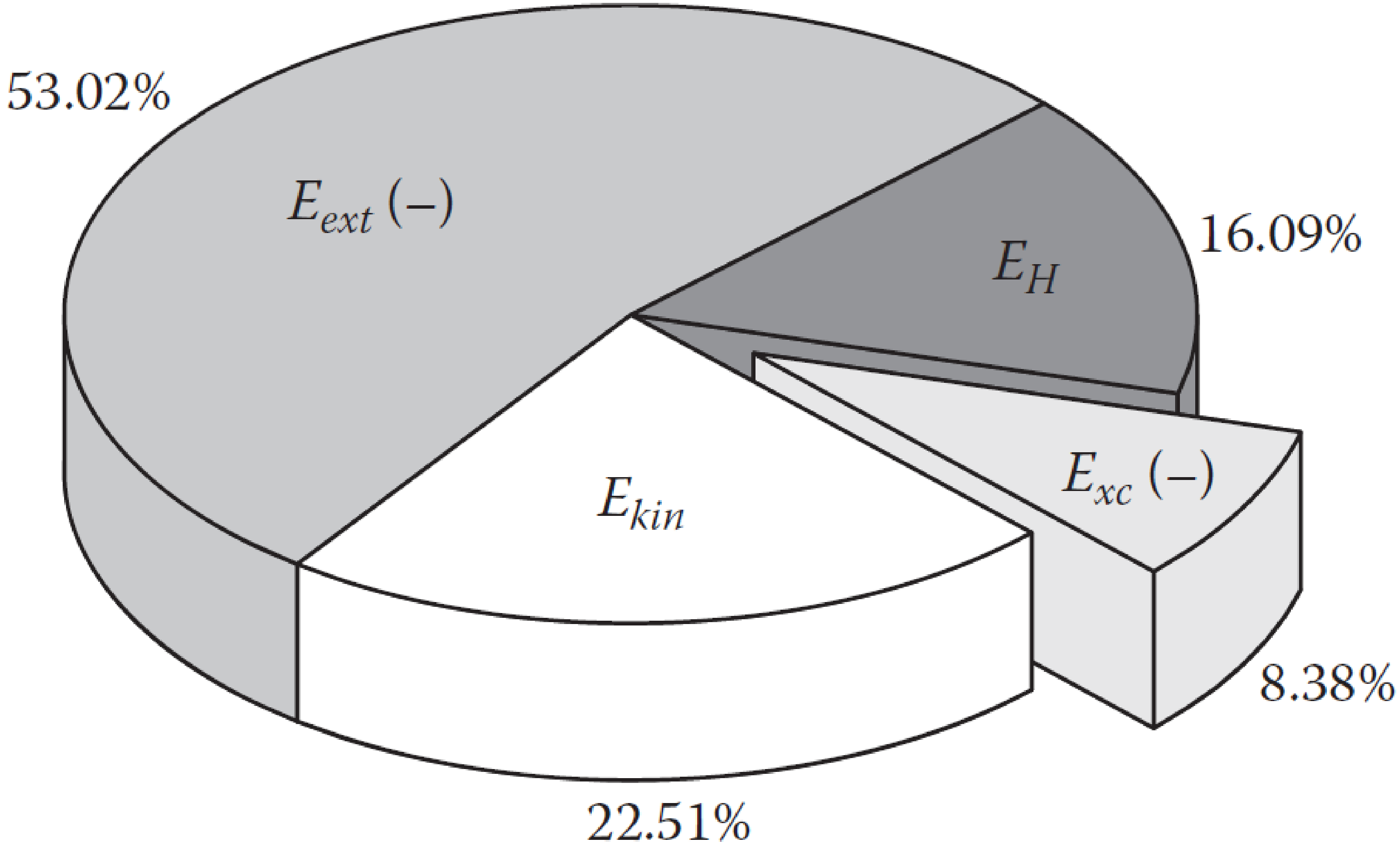


(a) *n*-electron HF System → (b) Energy Decomposition → (c) Fictitious one-electron System

The Kohn-Sham idea: the He atom

The Kohn-Sham idea: the He atom



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$$V_{xc}(r) = \frac{\delta E_{xc}[n]}{\delta n}\Big|_{n(r)}$$

Exchange correlation potential (unknown)

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- We do not know what this functional is, **but we can build some accurate approximations**

- One of the simplest one is the local density approximation (LDA)

Putting DFT theory in practice: self consistency

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$$\left[-\frac{1}{2}\nabla^2 + V_{tot}(r)\right]\phi_i(r) = \epsilon_i\phi_i(r)$$

$$V_{tot}(r) = V_n(r) + V_H(r) + V_{xc}(r)$$

$$V_n(r) = -\sum_I \frac{Z_I}{|r - R_I|}$$

$$\nabla^2 V_H(r) = -4\pi n(r)$$

$$V_{xc}(r) = \frac{\delta E_{xc}[n]}{\delta n}(r)$$

$$n(r) = \sum_i |\Phi_i(r)|^2$$

Putting DFT theory in practice: self consistency

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Initial guess for electron density

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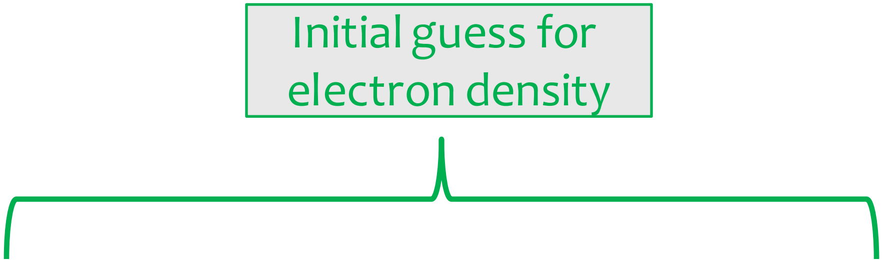

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Putting DFT theory in practice: self consistency

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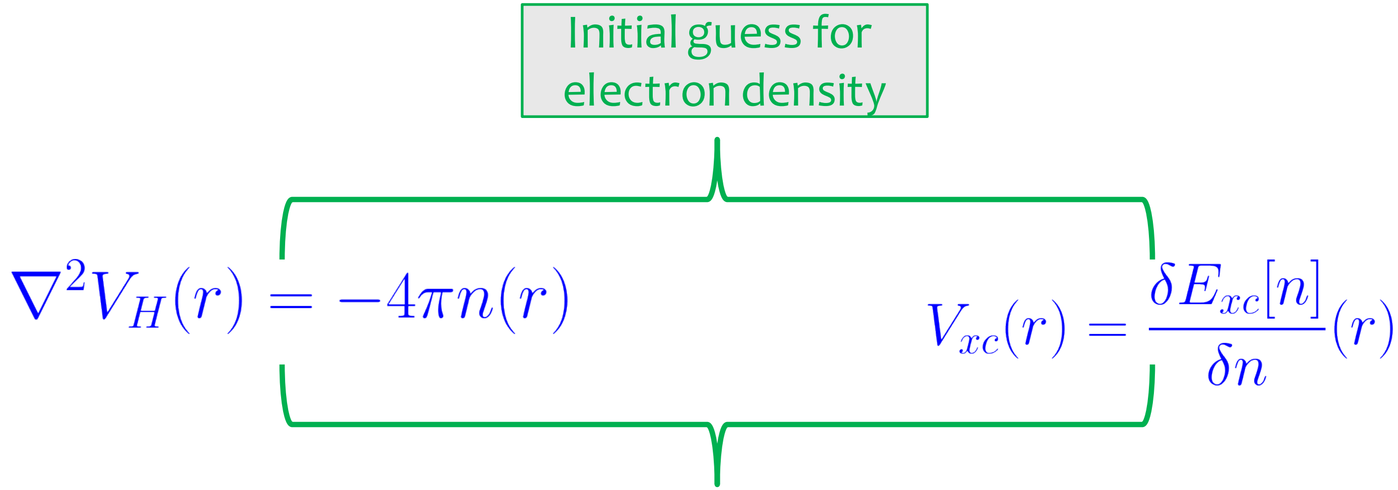

Initial guess for electron density

$$\nabla^2 V_H(r) = -4\pi n(r)$$

$$V_{xc}(r) = \frac{\delta E_{xc}[n]}{\delta n}(r)$$

$$V_{tot}(r) = V_n(r) + V_H(r) + V_{xc}(r)$$

Putting DFT theory in practice: self consistency

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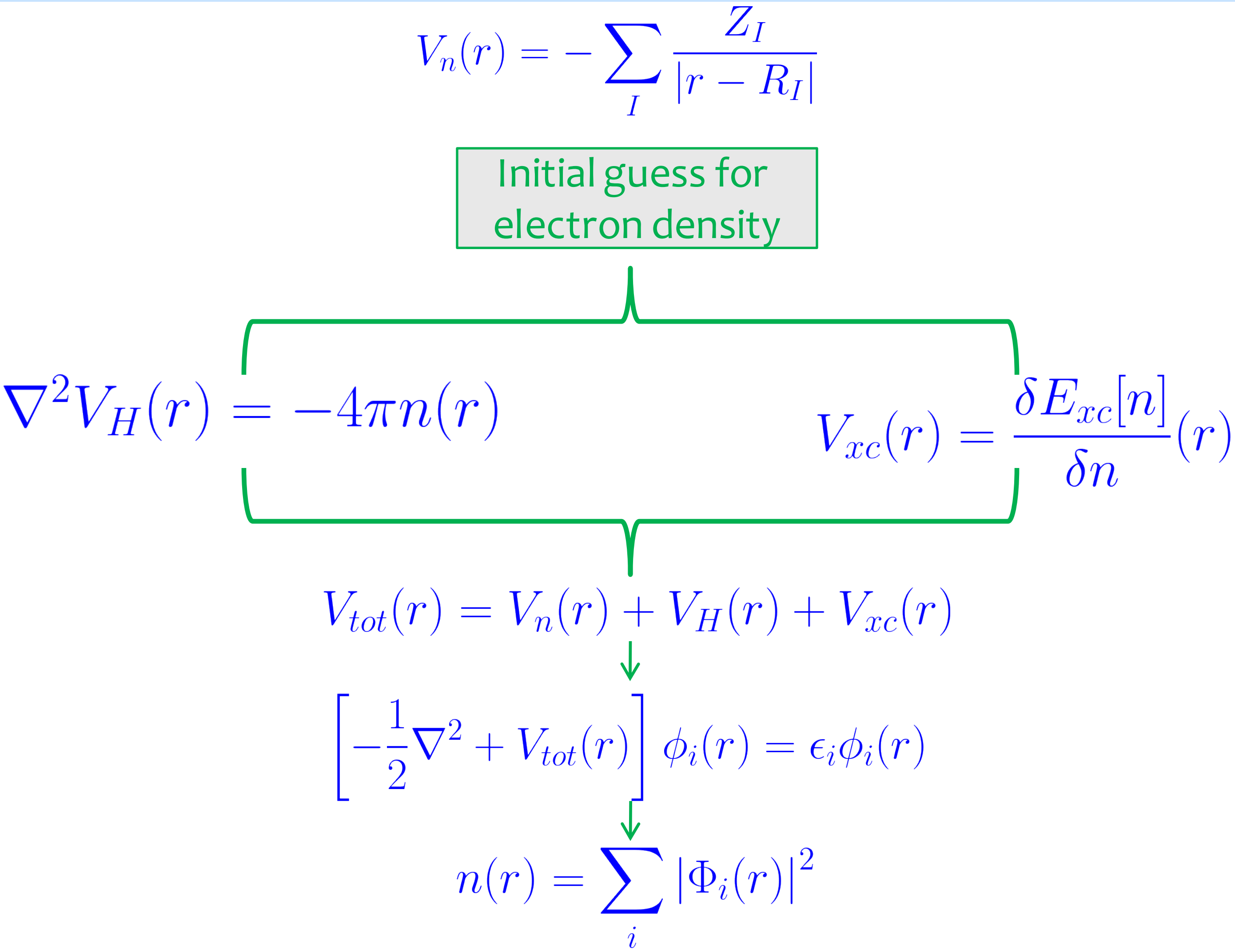
$$\downarrow$$

$$\left[-\frac{1}{2}\nabla^2 + V_{tot}(r)\right]\phi_i(r) = \epsilon_i \phi_i(r)$$

Putting DFT theory in practice: self consistency



$$V_n(r) = -\sum_I \frac{Z_I}{|r - R_I|}$$

Initial guess for electron density

$$\nabla^2 V_H(r) = -4\pi n(r) \qquad V_{xc}(r) = \frac{\delta E_{xc}[n]}{\delta n}(r)$$

$$V_{tot}(r) = V_n(r) + V_H(r) + V_{xc}(r)$$

$$\left[-\frac{1}{2}\nabla^2 + V_{tot}(r)\right]\phi_i(r) = \epsilon_i \phi_i(r)$$

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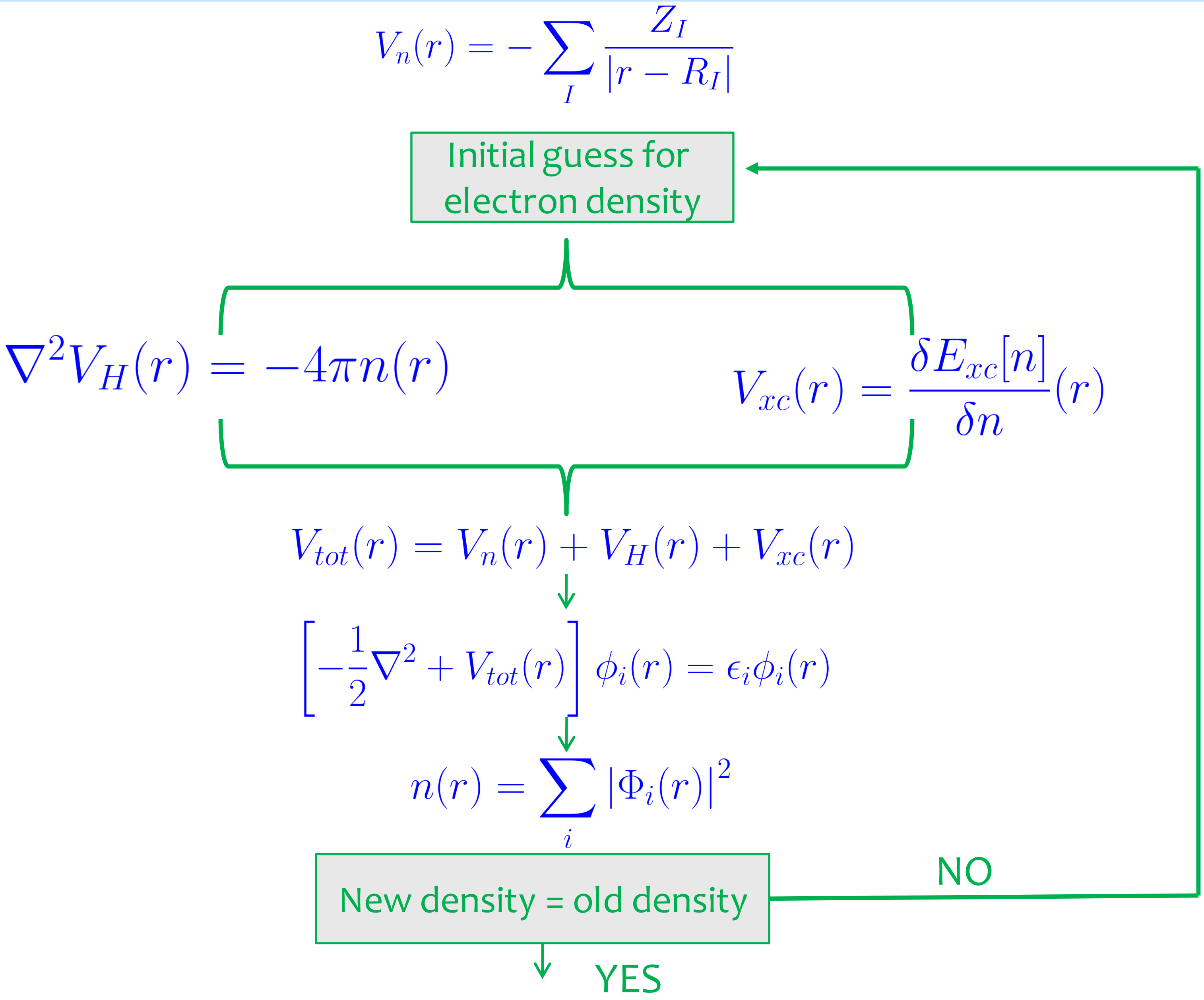
Putting DFT theory in practice: self consistency



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Initial guess for electron density

$$\nabla^2 V_H(r) = -4\pi n(r)$$

$$V_{xc}(r) = \frac{\delta E_{xc}[n]}{\delta n}(r)$$

$$V_{tot}(r) = V_n(r) + V_H(r) + V_{xc}(r)$$

$$\left[-\frac{1}{2}\nabla^2 + V_{tot}(r)\right]\phi_i(r) = \epsilon_i \phi_i(r)$$

$$n(r) = \sum_i |\Phi_i(r)|^2$$

New density = old density

NO

YES

Calculations of materials properties with DFT

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Good accuracy

- Equilibrium structures
- Vibrational properties and vibrational spectra
- Binding energies of molecules and cohesive energies of solids
- Ionization potential and electron affinity of molecules
- Band structures of metals and semiconductors

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Failures

- Electronic band gaps of semiconductors and insulators
- Magnetic properties of Mott-Hubbard insulators (systems with localized d and f orbitals)
- Systems where van der Waals forces are important, e.g. proteins

DFT software packages

DFT software packages

SIESTA code

http://icmab.es/siesta

VASP code

http://www.vasp.at

Quantum espresso code

www.quantum-espresso.org