Key concepts in Density Functional Theory (I)
From the many body problem to the Kohn-Sham scheme

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Outline

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1 **The many-body problem**

2 A solution: density functional theory

3 Hohenberg-Kohn theorems

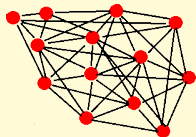4 Practical implementations: the Kohn-Sham scheme

5 Summary

The many-body problem

Schrödinger equation for a quantum system of N interacting particles:

N_e electrons
N_n nuclei

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

$$\hat{H}\Psi\left(\{\mathbf{R}\},\{\mathbf{r}\}\right) = E\Psi\left(\{\mathbf{R}\},\{\mathbf{r}\}\right)$$

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

The many-body Hamiltonian

$$\hat{H} = \hat{T}_{\mathrm{n}}\left(\{\mathbf{R}\}\right) + \hat{V}_{\mathrm{nn}}\left(\{\mathbf{R}\}\right) + \hat{T}_{\mathrm{e}}\left(\{\mathbf{r}\}\right) + \hat{V}_{\mathrm{ee}}\left(\{\mathbf{r}\}\right) + \hat{U}_{\mathrm{en}}\left(\{\mathbf{R}\},\{\mathbf{r}\}\right)$$

$$\hat{T}_{\mathrm{n}} = \sum_{I=1}^{N_{\mathrm{n}}} -\frac{\nabla_I^2}{2M_I}, \ \hat{T}_{\mathrm{e}} = \sum_{i=1}^{N_{\mathrm{e}}} -\frac{\nabla_i^2}{2m},$$

$$\hat{V}_{\mathrm{nn}} = \frac{1}{2}\sum_{I,J,I\neq J}^{N_{\mathrm{n}}} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|}, \ \hat{V}_{\mathrm{ee}} = \frac{1}{2}\sum_{i,j,i\neq j}^{N_{\mathrm{e}}} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|},$$
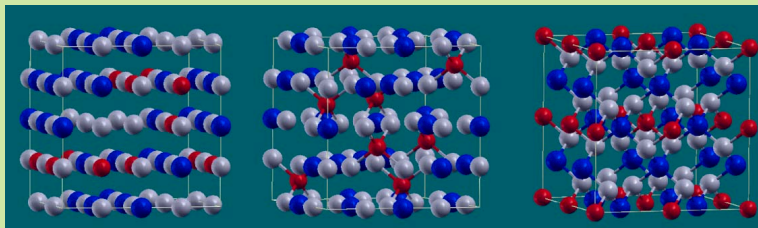
$$\hat{U}_{\mathrm{en}} = -\sum_{j,J}^{N_{\mathrm{e}},N_{\mathrm{n}}} \frac{Z_J}{|\mathbf{R}_J - \mathbf{r}_j|}$$

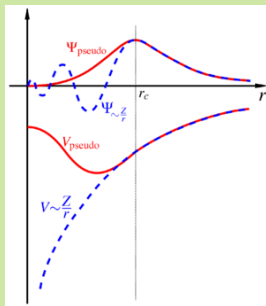# Starting approximations

Born-Oppenheimer separation

In the adiabatic approximation the nuclei are frozen in their equilibrium positions.

Example of equilibrium geometries

Starting approximations

Pseudopotential and pseudowavefunction

Concept of pseudopotentials

The chemically *inert* core electrons are frozen in their atomic configuration and their effect on chemically *active* valence electrons is incorporated in an effective potential.

Pseudopotentials: generation criteria

A pseudopotential is not unique, several methods of generation also exist.

1. The pseudo-electron eigenvalues must be the same as the valence eigenvalues obtained from the atomic wavefunctions.

2. Pseudo-wavefunctions must match the all-electron wavefunctions outside the core (plus continuity conditions).

3. The core charge produced by the pseudo-wavefunctions must be the same as that produced by the atomic wavefunctions (for norm-conserving pseudopotentials).

4. The logaritmic derivatives and their first derivatives with respect to the energy must match outside the core radius (scattering properties).

5. Additional criteria for different recipes.

Pseudopotentials: quality assessment

It is important to find a compromise between

1. Transferability: ability to describe the valence electrons in different environments.

2. Efficiency: softness – few plane waves basis functions.

Moreover:
Which states should be included in the valence and which states in the core? Problem of semicore states.

The many-body Hamiltonian
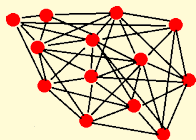
Applying the Born-Oppenheimer separation...

$$0 = \hat{T}_{\mathrm{n}} = \sum_{I=1}^{N_{\mathrm{n}}} -\frac{\nabla_I^2}{2M_I}, \ \hat{T}_{\mathrm{e}} = \sum_{i=1}^{N_{\mathrm{e}}} -\frac{\nabla_i^2}{2m},$$

$$\text{constant} \rightarrow \hat{V}_{\mathrm{nn}} = \frac{1}{2} \sum_{I,J,I\neq J}^{N_{\mathrm{n}}} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|}, \ \hat{V}_{\mathrm{ee}} = \frac{1}{2} \sum_{i,j,i\neq j}^{N_{\mathrm{e}}} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|},$$

$$\hat{U}_{\mathrm{en}} = - \sum_{j,J}^{N_{\mathrm{e}},N_{\mathrm{n}}} \frac{Z_J}{|\mathbf{R}_J - \mathbf{r}_j|} = \sum_{j}^{N_{\mathrm{e}}} v(\mathbf{r}_j)$$

The many-body problem

Schrödinger Equation for a quantum-system of N_e interacting electrons:

N_e electrons

Still, how to deal with $N_e \approx 10^{23}$ particles?

$$\hat{H}\Psi\left(\{\mathbf{r}\}\right) = E_e\Psi\left(\{\mathbf{r}\}\right)$$

$$\hat{H} = \sum_{i=1}^{N_e}\left[-\frac{\nabla_i^2}{2m} + v\left(\mathbf{r}_i\right)\right] + \frac{1}{2}\sum_{i,j,i\neq j}^{N_e}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

Why we don't like the electronic wavefunction

How many DVDs are necessary to store a wavefunction?

Classical example: Oxygen atom (8 electrons)

$\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_8)$ depends on 24 coordinates

Rough table of the wavefunction:

|		
10 entries per coordinate:	$\implies$	10^{24} entries
1 byte per entry :	$\implies$	10^{24} bytes
5×10^9 bytes per DVD:	$\implies$	2×10^{14} DVDs
10 g per DVD:	$\implies$	2×10^{15} g DVDs
	$=$	$\times 10^9$ t DVDs

Outline

1. The many-body problem

2. **A solution: density functional theory**

3. Hohenberg-Kohn theorems

4. Practical implementations: the Kohn-Sham scheme

5. Summary

Ground state densities vs potentials

Question at the heart of DFT

Is there a 1-to-1 mapping between different external potentials $v(\mathbf{r})$ and their corresponding ground state densities $\rho(\mathbf{r})$?
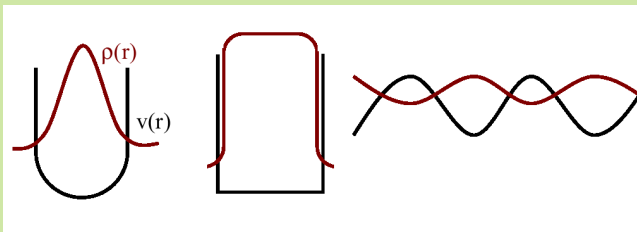
Density functional theory (DFT): the essence

If we can give a positive answer, then it can be proved that

(i) all observable quantities of a quantum system are completely determined by the density.

(ii) which means that the basic variable is no more the many-body wavefunction $\Psi(\{\mathbf{r}\})$ but the electron density $\rho(\mathbf{r})$.

📄 P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).

📄 You can find all details in R. M. Dreizler and E.K.U. Gross, *Density Functional Theory*, Springer (Berlin, 1990).

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Density functional theory (DFT)

Hohenberg-Kohn (HK) theorem – I

The expectation value of any physical observable of a many-electron system is a unique functional of the electron density ρ.

Hohenberg-Kohn (HK) theorem – II

The total energy functional has a minimum, the ground state energy E_0, at the ground state density ρ_0.
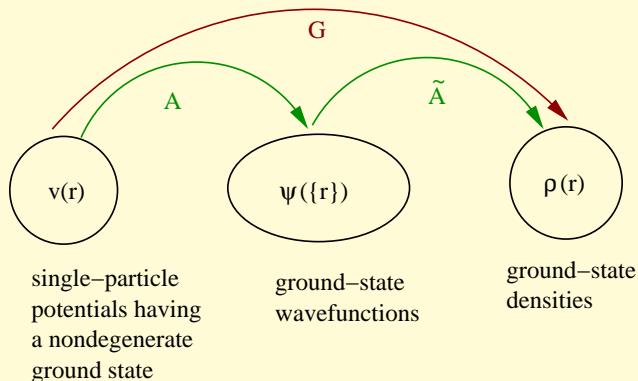
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Density functional theory (DFT)

Restrictions:

- In practice, only ground state properties.
- The original proof is valid for local, spin-independent external potential, non-degenerate ground state.
- There exist extensions to degenerate ground states, spin-dependent, magnetic systems, etc.

Hohenberg-Kohn theorem – I

$G : v(\mathbf{r}) \to \rho(\mathbf{r})$ is obvious.

HK theorem states that G is invertible.

Hohenberg-Kohn theorem – I

Proof:

1. *A* is invertible: the Schrödinger equation can be always solved for the external potential, yielding the potential as a unique function of Ψ.

$$\hat{V} = \sum_i v\left(\mathbf{r}_i\right) = \frac{\left(E - \hat{T} - \hat{V}_{\text{ee}}\right)\Psi}{\Psi} = -\frac{\hat{T}\Psi}{\Psi} - \hat{V}_{\text{ee}} + const.$$

2. $\tilde{A}$ is invertible (proof for non-degenerate ground state):

$$\left(\hat{T} + \hat{W} + \hat{V}\right)\Psi = E\Psi$$

$$\left(\hat{T} + \hat{W} + \hat{V}'\right)\Psi' = E'\Psi'$$

Now what is left to show is that $\Psi \neq \Psi' \Rightarrow \rho \neq \rho'$

Hohenberg-Kohn theorem – I

Applying the variational principle (Rayleigh-Ritz):

$$E = \langle \Psi | \hat{H} | \Psi \rangle < \langle \Psi' | \hat{H} | \Psi' \rangle = E' + \int \mathrm{d}^3 r \, \rho'(\mathbf{r}) \left[v(\mathbf{r}) - v'(\mathbf{r}) \right]$$

$$E' = \langle \Psi' | \hat{H}' | \Psi' \rangle < \langle \Psi | \hat{H}' | \Psi \rangle = E + \int \mathrm{d}^3 r \, \rho(\mathbf{r}) \left[v'(\mathbf{r}) - v(\mathbf{r}) \right]$$

Proof by contradiction:
If $\rho \neq \rho'$ it has to be $E + E' < E + E'$, which is absurd.
Therefore, we deduce that $\Psi \neq \Psi' \Rightarrow \rho \neq \rho'$

Hohenberg-Kohn theorem – I
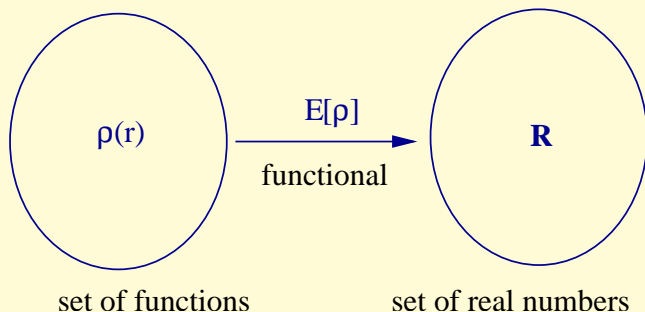
Direct consequence of the 1st HK theorem

The expectation value of any physical observable of a many-electron system is a unique functional of the electron density ρ.

$$\text{Proof:} \quad \rho \xrightarrow{G^{-1}} v\,[\rho] \xrightarrow{\text{solving S.E.}} \Psi_0\,[\rho]$$

Then an observable $\hat{O}\,[\rho] = \langle \Psi_0\,[\rho]\, |\hat{O}|\Psi_0\,[\rho]\rangle$ is a functional of ρ.

Reminder: what is a functional?

set of functions   set of real numbers

$v_{\mathbf{r}}\left[\rho\right] = v\left[\rho\right](\mathbf{r})$ is a functional that depends parametrically on $\mathbf{r}$

$\Psi_{\mathbf{r}_1 \ldots \mathbf{r}_N}\left[\rho\right] = \Psi\left[\rho\right](\mathbf{r}_1 \ldots \mathbf{r}_N)$ is a functional that depends parametrically on $\mathbf{r}_1 \ldots \mathbf{r}_N$

Hohenberg-Kohn (HK) theorem – II

2nd HK theorem: Variational principle

The total energy functional has a minimum, the ground state energy E_0, at the ground state density ρ_0.

$$\langle \Psi_0 | \hat{H} | \Psi_0 \rangle = \min \{ E_{\mathrm{HK}} [\rho] \} = E_0 [\rho_0]$$

Euler-Lagrange equation:

$$\frac{\delta}{\delta \rho(\mathbf{r})} \left[E_{\mathrm{HK}} [\rho] - \mu \left(\int \mathrm{d}^3 r \, \rho(\mathbf{r}) - N \right) \right] = 0$$

It yields the exact ground-state energy E_0 and density $\rho_0(\mathbf{r})$.

Hohenberg-Kohn (HK) theorem – II

Formal construction of $E_{\mathrm{HK}}[\rho]$:

- For an arbitrary ground state density it is always true $\rho(\mathbf{r}) \xrightarrow{\tilde{A}^{-1}} \Psi[\rho]$
  $\Rightarrow$ we can define the functional of the density:

$$E_{\mathrm{HK}}[\rho] = \langle \Psi[\rho] | \hat{T} + \hat{U} + \hat{V} | \Psi[\rho] \rangle$$

- $E_{\mathrm{HK}}[\rho] > E_0$ for $\rho \neq \rho_0$
  $E_{\mathrm{HK}}[\rho] = E_0$ for $\rho = \rho_0$
- $E_{\mathrm{KS}}[\rho] = F_{\mathrm{HK}}[\rho] + \int \mathrm{d}^3 r\, v(\mathbf{r}) \rho(\mathbf{r})$
  $F_{\mathrm{HK}}[\rho]$ is universal, as it does not depend on the external potential.

Hohenberg-Kohn (HK) theorem – II

In principle: the Euler-Lagrange equation allows to calculate $\rho_0(\mathbf{r})$ without introducing a Schrödinger equation.

The universal functional

$$E_{\mathrm{KS}}[\rho] = F_{\mathrm{HK}}[\rho] + \int \mathrm{d}^3 r\, v(\mathbf{r})\rho(\mathbf{r})$$

$$F_{\mathrm{HK}}[\rho] = \langle \Psi | \hat{T} + \hat{U} | \Psi \rangle$$

The HK theorem proofs the existence of the universal functional $F_{\mathrm{HK}}[\rho]$ but it does not say how to determine it.

In practice: $F_{\mathrm{HK}}[\rho]$ needs to be approximated and approximations of $T[\rho]$ lead to large errors in the total energy.
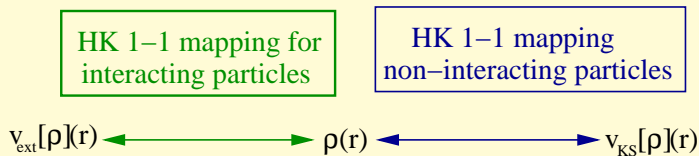
Outline

Reformulation: Kohn-Sham scheme

HK 1−1 mapping for interacting particles

HK 1−1 mapping non−interacting particles

$$v_{ext}[\rho](r) \longleftrightarrow \rho(r) \longleftrightarrow v_{KS}[\rho](r)$$

Essence of the mapping

The density of a system of interacting particles can be calculated exactly as the density of an auxiliary system of non-interacting particles

$\implies$ Reformulation in terms of single-particle orbitals!

📄 W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

Back to the Hohenberg-Kohn variational principle

For a non-interacting system:

$$E_{\mathrm{KS}}\left[\rho\right] = \langle \Psi[\rho] | \hat{T}_{\mathrm{s}} + \hat{V}_{\mathrm{KS}} | \Psi[\rho] \rangle = T_{\mathrm{s}}[\rho] + \int \mathrm{d}^3 r \, \rho(\mathbf{r}) v_{\mathrm{KS}}(\mathbf{r})$$

Euler-Lagrange equation for the non-interacting system

$$\frac{\delta}{\delta \rho(\mathbf{r})} \left[E_{\mathrm{KS}}\left[\rho\right] - \mu \left(\int \mathrm{d}^3 r \, \rho(\mathbf{r}) - N \right) \right] = 0$$

$$\frac{\delta T_{\mathrm{s}}\left[\rho\right]}{\delta \rho(\mathbf{r})} + v_{\mathrm{KS}}(\mathbf{r}) = \mu$$

Using a one-particle Schrödinger equation

Kohn-Sham equations

$$\left[-\frac{\nabla^2}{2} + v_{\mathrm{KS}}\left(\mathbf{r}\right)\right]\phi_i\left(\mathbf{r}\right) = \varepsilon_i\phi_i\left(\mathbf{r}\right)$$

$$\rho_0\left(\mathbf{r}\right) = \sum_{i,\ \mathrm{lowest}\ \varepsilon_i}\left|\phi_i\left(\mathbf{r}\right)\right|^2$$

$\varepsilon_i =$ KS eigenvalues, $\phi_i(\mathbf{r}) =$ KS single-particle orbitals

Can we always build v_{KS} for the non-interacting electron system?

- Uniqueness of v_{KS} follows from HK 1-1 mapping.
- Existence of v_{KS} is guaranteed by V-representability theorem.

Problem of V-representability

Definition

$\rho(\mathbf{r})$ is V-representable if it is the ground-state density of some potential V.

Question

Are all reasonable functions $\rho(\mathbf{r})$ V-representable?

Answer: V-representability theorem

On a lattice (finite or infinite) any normalizable positive function $\rho(\mathbf{r})$, that is compatible with the Pauli principle, is both interacting and non-interacting V-representable. For degenerate ground states such a $\rho(\mathbf{r})$ is ensemble V-representable, i.e. representable as a linear combination of the degenerate ground-states densities.

📄   Chayes, Chayes, Ruskai, J Stat. Phys. 38, 497 (1985).

Reformulation: Kohn-Sham scheme

Kohn-Sham one-particle equations

$$\left[-\frac{\nabla^2}{2} + v_{\mathrm{KS}}\left(\mathbf{r}\right) \right] \phi_i\left(\mathbf{r}\right) = \varepsilon_i \phi_i\left(\mathbf{r}\right)$$

to solve self-consistenlty with $\rho_0\left(\mathbf{r}\right) = \sum_i \left|\phi_i\left(\mathbf{r}\right)\right|^2$

$\varepsilon_i =$ KS eigenvalues, $\phi_i(\mathbf{r}) =$ KS single-particle orbitals

Which is the form of v_{KS} for the non-interacting electrons?

Hartree potential

$$v_{\mathrm{KS}}\left(\mathbf{r}\right) = v\left(\mathbf{r}\right) + v_{\mathrm{H}}\left(\mathbf{r}\right) + v_{\mathrm{xc}}\left(\mathbf{r}\right)$$

unknown exchange-correlation (xc) potential

Kohn-Sham scheme: Hartree and xc potentials

Hartree potential

$$v_{\mathrm{H}}\left[\rho\right](\mathbf{r}) = \int \mathrm{d}^3 r' \, \frac{\rho\left(\mathbf{r'}\right)}{\left|\mathbf{r} - \mathbf{r'}\right|}$$

v_{H} describes classic electrostatic interaction

Exchange-correlation (xc) potential

$$v_{\mathrm{xc}}\left[\rho\right](\mathbf{r}) = \frac{\delta\, E_{\mathrm{xc}}\left[\rho\right]}{\delta\,\rho\left(\mathbf{r}\right)}$$

v_{xc} encompasses many-body effects

Kohn-Sham scheme: xc potential

Proof:

- We define

$$E_{\mathrm{xc}}\left[\rho\right] = F_{\mathrm{HK}}\left[\rho\right] - E_{\mathrm{H}}\left[\rho\right] - T_{\mathrm{s}}\left[\rho\right]$$

- We use the variational principle (and $\frac{\delta E_{\mathrm{H}}[\rho]}{\delta \rho(\mathbf{r})} = v_{\mathrm{H}}\left(\mathbf{r}\right)$)

$$\frac{\delta F_{\mathrm{HK}}\left[\rho\right]}{\delta \rho(\mathbf{r})} + v(\mathbf{r}) = \mu \Rightarrow \frac{\delta F_{\mathrm{HK}}\left[\rho\right]}{\delta \rho(\mathbf{r})} = -v(\mathbf{r}) + \mu$$

$$\frac{\delta T_{\mathrm{s}}\left[\rho\right]}{\delta \rho(\mathbf{r})} + v_{\mathrm{KS}}(\mathbf{r}) = \mu \Rightarrow \frac{\delta T_{\mathrm{s}}\left[\rho\right]}{\delta \rho(\mathbf{r})} = -v_{\mathrm{KS}}(\mathbf{r}) + \mu$$

- To obtain $v_{\mathrm{KS}}\left(\mathbf{r}\right) = v\left(\mathbf{r}\right) + v_{\mathrm{H}}\left(\mathbf{r}\right) + v_{\mathrm{xc}}\left(\mathbf{r}\right)$, $\frac{\delta E_{\mathrm{xc}}[\rho]}{\delta \rho(\mathbf{r})} = v_{\mathrm{xc}}\left(\mathbf{r}\right)$

Approximations for the xc potential

- **LDA**:

$$E_{xc}^{LDA}[\rho] = \int d^3r\, \rho(\mathbf{r})\, \epsilon_{xc}^{HEG}(\rho(\mathbf{r}))$$

- LSDA:

$$E_{xc}^{LSDA}[\rho_\uparrow, \rho_\downarrow] = \int d^3r\, \rho(\mathbf{r})\, \epsilon_{xc}^{HEG}(\rho_\uparrow, \rho_\downarrow)$$

- GGA:

$$E_{xc}^{GGA}[\rho_\uparrow, \rho_\downarrow] = \int d^3r\, \rho(\mathbf{r})\, \epsilon_{xc}^{GGA}(\rho_\uparrow, \rho_\downarrow, \nabla\rho_\uparrow, \nabla\rho_\downarrow)$$

- meta-GGA:

$$E_{xc}^{MGGA}[\rho_\uparrow, \rho_\downarrow] = \int d^3r\, \rho(\mathbf{r})\, \epsilon_{xc}^{MGGA}(\rho_\uparrow, \rho_\downarrow, \nabla\rho_\uparrow, \nabla\rho_\downarrow, \nabla^2\rho_\uparrow, \nabla^2\rho_\downarrow, \tau_\uparrow, \tau_\downarrow)$$

- EXX, SIC-LDA, hybrid Hartree-Fock/DFT functionals, . . .

Approximations for the xc potential

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- EXX, SIC-LDA, hybrid Hartree-Fock/DFT functionals, . . .

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Summary

- The electron density is the key-variable to study ground-state properties of an interacting electron system.
- The ground state expectation value of any physical observable of a many-electron system is a unique functional of the electron density ρ.
- The total energy functional $E_{HK}[\rho]$ has a minimum, the ground state energy E_0, in correspondence to the ground state density ρ_0.
- The universal functional $F_{HK}[\rho]$ is hard to approximate.
- The Kohn-Sham scheme allows a reformulation in terms of one-particle orbitals.

Suggestion of essential bibliography

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