

# Key concepts in Density Functional Theory (I)

From the many body problem to the Kohn-Sham scheme

Silvana Botti

European Theoretical Spectroscopy Facility (ETSF)  
CNRS - Laboratoire des Solides Irradiés  
Ecole Polytechnique, Palaiseau - France

Temporary Address:

Centre for Computational Physics  
University of Coimbra - Portugal

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# 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



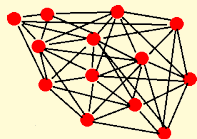
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# The many-body problem

Schrödinger Equation for interacting particles:



$N_e$  electrons

$N_n$  nuclei

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

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

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

# The many-body problem

## Many-particle Hamiltonian in more detail

$$\hat{T}_n = \sum_{I=1}^{N_n} -\frac{\nabla_I^2}{2M_I}, \quad \hat{T}_e = \sum_{i=1}^{N_e} -\frac{\nabla_i^2}{2m},$$

$$\hat{V}_{nn} = \frac{1}{2} \sum_{I,J,I \neq J}^{N_n} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|}, \quad \hat{V}_{ee} = \frac{1}{2} \sum_{i,j,i \neq j}^{N_e} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|},$$

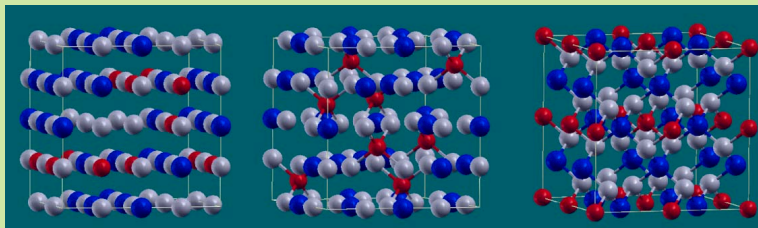
$$\hat{U}_{en} = - \sum_{j,J}^{N_e, N_n} \frac{Z_J}{|\mathbf{R}_J - \mathbf{r}_j|}$$

# Starting approximations

## Born-Oppenheimer separation

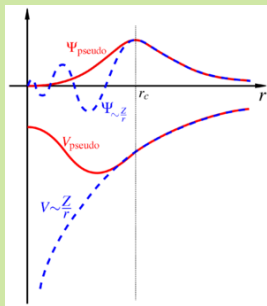
Adiabatic approximation: the nuclei can be frozen in their equilibrium positions.

## 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 logarithmic 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

- 1 **Transferability**: ability to describe the valence electrons in different environments.
- 2 **Efficiency**: softness – few plane waves basis functions.

It is important to find a **compromise**!

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



# The many-body problem

## Many-particle Hamiltonian in more detail

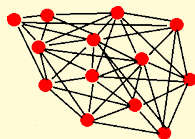
$$\hat{T}_n = \sum_{I=1}^{N_n} -\frac{\nabla_I^2}{2M_I}, \quad \hat{T}_e = \sum_{i=1}^{N_e} -\frac{\nabla_i^2}{2m},$$

$$\text{CONST} \rightarrow \hat{V}_{nn} = \frac{1}{2} \sum_{I,J,I \neq J}^{N_n} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|}, \quad \hat{V}_{ee} = \frac{1}{2} \sum_{i,j,i \neq j}^{N_e} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|},$$

$$\hat{U}_{en} = - \sum_{j,J}^{N_e, N_n} \frac{Z_J}{|\mathbf{R}_J - \mathbf{r}_j|} = \sum_j^{N_e} v_{\text{ext}}(\mathbf{r}_j)$$

# The many-body problem

Schrödinger Equation for  $N_e$  interacting electrons:



$N_e$  electrons

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

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

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

# Why we don't like the electronic wavefunction

## Oxygen atom (8 electrons)

$\Psi(\mathbf{r}_1, \dots, \mathbf{r}_8)$  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
$5 \times 10^9$ bytes per DVD:	$\implies$	$2 \times 10^{14}$ DVDs
10 g per DVD:	$\implies$	$2 \times 10^{15}$ g DVDs
	=	$\times 10^9$ t DVDs

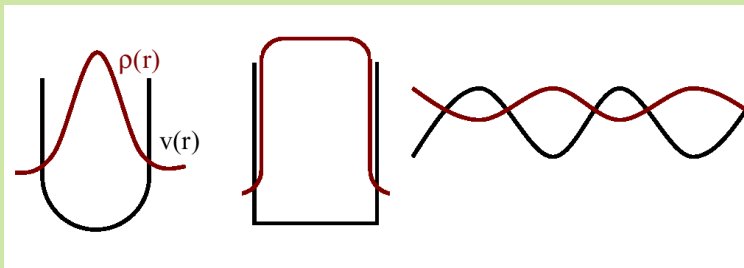
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# Ground state densities vs potentials

Are the ground state densities  $\rho(\mathbf{r})$  coming from different external potentials  $v(\mathbf{r})$  always different?



# Density functional theory (DFT): the essence

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

- (i) every observable quantity of a quantum system can be calculated from the **density** of the system alone.
- (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).

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# Density functional theory (DFT)

## Hohenberg-Kohn (HK) theorem – I

The ground state expectation value of any physical observable of a many-electron system is a unique functional of the electron density  $\rho$ .

## Hohenberg-Kohn (HK) theorem – II

The total energy functional has a minimum, the ground state energy  $E_0$ , in correspondence to the ground state density  $\rho_0$ .



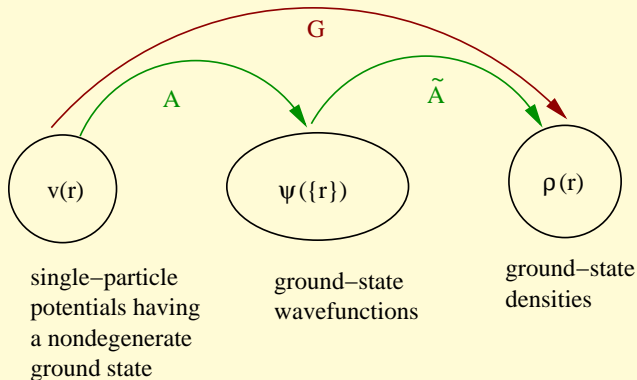
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# Density functional theory (DFT)

## Restrictions:

- 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



$G : v(\mathbf{r}) \rightarrow \rho(\mathbf{r})$  is invertible

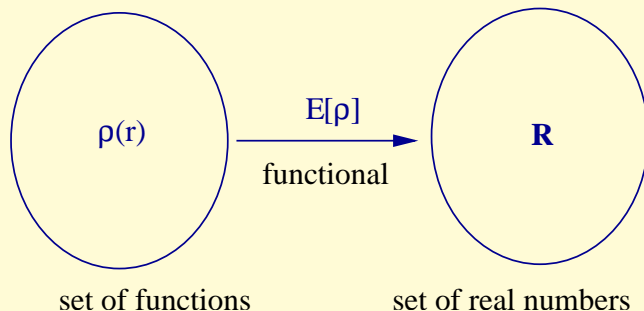
# Hohenberg-Kohn theorem – I

The ground state expectation value of any physical observable of a many-electron system is a unique functional of the electron density  $\rho$ .

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

$$\hat{O}[\rho] = \langle \Psi_0[\rho] | \hat{O} | \Psi_0[\rho] \rangle$$

# What is a functional?



## Generalization:

$v_{\mathbf{r}} = v[\rho](\mathbf{r})$  is a functional depending parametrically on  $\rho$

$\Psi_{\mathbf{r}_1 \dots \mathbf{r}_N} = \Psi[\rho](\mathbf{r}_1 \dots \mathbf{r}_N)$  is a functional depending parametrically on  $\rho$

# Hohenberg-Kohn (HK) theorem – II

How to calculate the ground state density  $\rho_0$  of a given system without recourse to the Schrödinger equation?

## Variational principle

The total energy functional has a minimum, the ground state energy  $E_0$ , in correspondence to the ground state density  $\rho_0$ .

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

The solution of the Euler-Lagrange equation:

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

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



# Hohenberg-Kohn (HK) theorem – II

## The unknown universal functional

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

The HK theorem shows the **existence** of the universal functional **without determining** it:

$$F_{\text{HK}}[\rho] = \langle \Psi_0 | \hat{T} + \hat{U} | \Psi_0 \rangle$$

In practice:

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



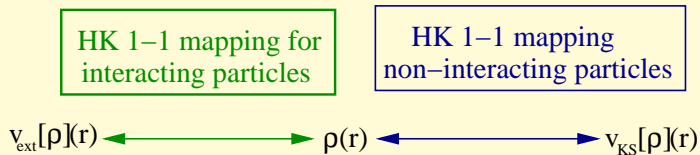


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# Reformulation: Kohn-Sham scheme



## Essence

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

⇒ Reformulation in terms of **single-particle orbitals**!



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

# From the Hohenberg-Kohn variational principle

For a non-interacting system:

$$E_{\text{KS}}[\rho] = \langle \Psi[\rho] | \hat{T} + \hat{V}_{\text{KS}} | \Psi[\rho] \rangle = T_s[\rho] + \int d^3r \rho(\mathbf{r}) v_{\text{KS}}(\mathbf{r})$$

Euler-Lagrange equation for the non-interacting system

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

$$\frac{\delta}{\delta \rho(\mathbf{r})} T_s[\rho] + v_{\text{KS}}(\mathbf{r}) = \mu$$

# Using a one-particle Schrödinger equation

## Kohn-Sham equations

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

$$\rho(\mathbf{r}) = \sum_{i, \text{ lowest } \varepsilon_i} |\phi_i(\mathbf{r})|^2$$

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

What about  $v_{\text{KS}}$  for the non-interacting electron system?

- Uniqueness follows from **HK 1-1 mapping**
- Existence follows from **V-representability** theorem

Proof:  $v_{\text{KS}}(\mathbf{r}) = v_{\text{KS}}[\rho_0](\mathbf{r})$



# Problem of V-representability

By construction, the HK mapping is well-defined for all  $\rho(\mathbf{r})$  that are ground-state densities of some potential (so called V-representable functions  $\rho(\mathbf{r})$  )

## 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) ensemble-V-representable.



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

# Problem of V-representability

## Answer: V-representability theorem

In other words:

For any given  $\rho(\mathbf{r})$  normalizable, positive, compatible with Pauli principle there exists a potential,  $v[\rho](\mathbf{r})$ , yielding  $\rho(\mathbf{r})$  as interacting ground-state density, and there exists another potential,  $v_s[\rho](\mathbf{r})$ , yielding  $\rho(\mathbf{r})$  as non-interacting ground-state density.

In the worst case, the potential has degenerate ground states such that the given  $\rho(\mathbf{r})$  is representable as a linear combination of the degenerate ground-state densities (ensemble-V-representable).



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

# Reformulation: Kohn-Sham scheme

## Kohn-Sham one-particle equations

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

$$\rho(\mathbf{r}) = \sum_i |\phi_i(\mathbf{r})|^2$$

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

which is the form of  $v_{\text{KS}}$  for the non-interacting electrons?

Hartree potential

$$v_{\text{KS}}(\mathbf{r}) = v(\mathbf{r}) + v_{\text{H}}(\mathbf{r}) + v_{\text{xc}}(\mathbf{r})$$

unknown exchange-correlation (xc) potential



# Kohn-Sham scheme: Hartree and xc potentials

## Hartree potential

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

$v_{\text{H}}$  describes classic electrostatic interaction

## Exchange-correlation (xc) potential

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

$v_{\text{xc}}$  encompasses many-body effects



# Approximations for the xc potential

- LDA:

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

- LSDA:

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

- GGA:

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

- meta-GGA:

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

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



# Approximations for the xc potential

- **LDA:**

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

- **LSDA:**

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

- **GGA:**

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

- **meta-GGA:**

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

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



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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  $\rho$ .
- The total energy functional  $E_{\text{HK}}[\rho]$  has a minimum, the ground state energy  $E_0$ , in correspondence to the ground state density  $\rho_0$ .
- The **universal functional**  $F_{\text{HK}}[\rho]$  is hard to approximate
- The Kohn-Sham scheme allows a reformulation in terms of **one-particle orbitals**.



# Suggestion of essential bibliography

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