



Center for
Molecular
Modeling



UNIVERSITEIT
GENT



Department of
Materials Science
and Engineering

density-functional theory

molmod.ugent.be

The electronic structure calculations are performed within the DFT framework using the projector augmented wave (PAW) approach for the core-valence interaction and the Perdew-Burke-Ernzerhof (PBE) approximation for the exchange-correlation functional as implemented in the VASP code.³²⁻³⁶ The kinetic energy cutoff is set at 500 eV and special k -point sets of $8 \times 8 \times 8$, $4 \times 4 \times 4$, and $4 \times 4 \times 4$ k -points are used for static self-consistent calculations in the $c111$, $p222$, and the SQS cells, respectively. For the SQS cells a smaller $2 \times 2 \times 2$ k -point set is used during relaxation. To optimize the geometry, a conjugate gradient algorithm is applied. Both ion positions and cell parameters are optimized simultaneously.







$$\begin{aligned}
 \hat{H} = & \sum_A -\frac{\hbar^2 \nabla_{\vec{R}_A}^2}{2M_A} \\
 & + \sum_A -\frac{\hbar^2 \nabla_{\vec{r}_i}^2}{2m_i} \\
 & + \frac{1}{2} \frac{1}{4\pi\epsilon_0} \sum_{A \neq B} \frac{+e^2 Z_A Z_B}{|\vec{R}_A - \vec{R}_B|} \\
 & + \frac{1}{2} \frac{1}{4\pi\epsilon_0} \sum_{i \neq j} \frac{-e^2}{|\vec{r}_i - \vec{r}_j|} \\
 & + \frac{1}{4\pi\epsilon_0} \sum_{i,A} \frac{-e^2 Z_A}{|\vec{r}_i - \vec{R}_A|}
 \end{aligned}$$

HΨ = EΨ

Reminder: a function

$f : \mathbb{R} \mapsto \mathbb{R} : x \mapsto f(x)$

$f_1(x) = 5x + 2$
 $f_2(x) = 3x^2 - 7x + 6$
 $f_3(x) = e^x$

The wave function is a function

$\Psi : ? \mapsto ? : ? \mapsto \Psi(?)$

Exercise:
two spin-less particles

The wave function is a function

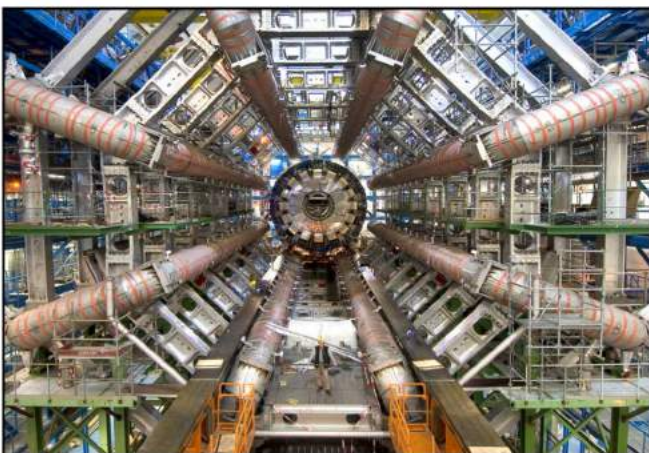
<p>\mathbb{R}^3 A \mathbb{C}^2</p>	<p>\mathbb{R}^6 B \mathbb{C}^2</p>
<p>\mathbb{R}^6 C \mathbb{C}</p>	<p>\mathbb{C}^6 D \mathbb{C}</p>

The wave function is a function

$$\Psi : (\mathbb{R}^3)^N \rightarrow \mathbb{C} : (\dots, \vec{r}_i, \dots) \mapsto \Psi(\dots, \vec{r}_i, \dots)$$

$$N=2 \implies \mathbb{R}^6 \rightarrow \mathbb{C}$$





$\hat{H}\Psi(\vec{r}_1, \dots, \vec{r}_N) = E\Psi(\vec{r}_1, \dots, \vec{r}_N)$
many-body Schrödinger equation

Density
Functional
Theory \downarrow **XC?**

$\hat{H}_{KS}\phi(\vec{r}) = E\phi(\vec{r})$
single-particle Kohn-Sham equations

methods: LAPW, PAW, grids, ...
codes: VASP, QE, WIEN2k, ...



Sun + Earth : 2-body problem.
Analytic solution possible (ellipsoid)

Sun + Earth + Jupiter : 3-body problem.
No analytical solution.

Problem: Earth-Jupiter interaction
(planet-planet interaction)



Density Functional Theory :

Switch off planet-planet interaction

The exact motion of every planet can be reproduced by adding a well-chosen externally applied static gravitational field

A universal generator exists to find this 'magic field' for every problem.



Density Functional Theory :

Replace electrons by non-interacting quasi-electrons

They interact with the nuclei and with an externally applied exchange-correlation field...

...which can be derived from the universal exchange-correlation functional



The electron density is a function
 $\rho : ? \mapsto ? : ? \mapsto \rho(?)$

Exercise:
two spin-less particles

The electron density is a function

<p>A</p> <p>\mathbb{R} \mathbb{R}</p>	<p>B</p> <p>\mathbb{R}^6 \mathbb{R}</p>
<p>C</p> <p>\mathbb{R}^6 \mathbb{C}</p>	<p>D</p> <p>\mathbb{R}^3 \mathbb{R}</p>

$$\hat{\rho}(\vec{r}) = \delta(\vec{r}' - \vec{r})$$

$$\begin{aligned} \rho(\vec{r}) &= \langle \Psi | \hat{\rho}(\vec{r}) | \Psi \rangle \\ &= \int \Psi^*(\vec{r}') \Psi(\vec{r}') \delta(\vec{r}' - \vec{r}) d\vec{r}' \\ &= \Psi^*(\vec{r}) \Psi(\vec{r}) \\ &= |\Psi(\vec{r})|^2 \end{aligned}$$

We know from quantum mechanics that all information about a system is contained in its wave function.

How much information does the density contain ?

- A) Less than the wave function.
- B) As much as the wave function.
- C) More than the wave function.

We know from quantum mechanics that all information about a system is contained in its wave function.

How much information does the density contain ?

- A) Less than the wave function.
- B) As much as the wave function.
- C) More than the wave function.

Exploited in **Density Functional Theory**.
Important corner stone: **1st theorem of Hohenberg and Kohn**.

Note : what is a functional ?

A function maps *numbers* onto (complex) numbers :

$$f : \mathbb{R} \rightarrow \mathbb{R} : x \mapsto f(x) \quad f : \mathbb{C} \rightarrow \mathbb{C} : x \mapsto f(x)$$

A functional maps *functions* onto (complex) numbers :

$$F : \mathcal{F} \rightarrow \mathbb{C} : f \mapsto F[f]$$

Examples :

$$F[f] = \int_{-\infty}^{\infty} f(x)e^{-x^2} dx$$

$$F[f] = f(0)$$

Functional derivative: generalization of derivative for functions.

Example:

$$F_v[\rho] = \int \rho(r)v(r)dr$$

$$\frac{\delta F_v[\rho]}{\delta \rho} = v(r)$$

$$\hat{H} = \sum_A \left[\frac{\hbar^2 \nabla_A^2}{2M_A} + \frac{\hbar^2 \nabla_i^2}{2m_i} \right] + \frac{1}{2} \sum_{A \neq B} \frac{+e^2 Z_A Z_B}{|R_A - R_B|} + \frac{1}{2} \frac{1}{4\pi\epsilon_0} \sum_{i \neq j} \frac{-e^2}{|\vec{r}_i - \vec{r}_j|} + \hat{V}_{\text{ext}}$$

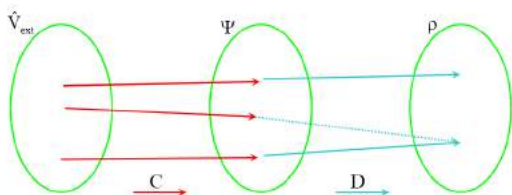
$$\hat{V}_{\text{ext}} = \frac{1}{4\pi\epsilon_0} \sum_{i,A} \frac{-e^2 Z_A}{|\vec{r}_i - \vec{R}_A|}$$

First theorem of Hohenberg and Kohn

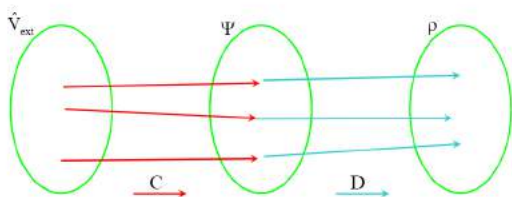
$C: \hat{V}_{\text{ext}} \mapsto \Psi$ surjective by construction
 $D: \Psi \mapsto \rho$ surjective by construction
 Are C and D also injective?

First theorem of Hohenberg and Kohn

$C: \hat{V}_{\text{ext}} \mapsto \Psi$ injective (no surprise)

First theorem of Hohenberg and Kohn

$C: \hat{V}_{\text{ext}} \mapsto \Psi$ injective (no surprise)
 $D: \Psi \mapsto \rho$ injective (very surprising!)
 = first theorem of Hohenberg and Kohn (1964)

First theorem of Hohenberg and Kohn

$C: \hat{V}_{\text{ext}} \mapsto \Psi$ injective (no surprise)
 $D: \Psi \mapsto \rho$ injective (very surprising!)
 = first theorem of Hohenberg and Kohn (1964)

Proof of the first theorem of Hohenberg and Kohn

(for non-degenerate ground states)

To prove: if $\Psi \neq \Psi'$, then $\rho \neq \rho'$ Do this by assuming that $\Psi \neq \Psi'$ and $\rho = \rho'$, which will lead to a contradiction.

Ψ is the ground state of a hamiltonian H , ground state energy is E_{gs}
 Ψ' is the ground state of a hamiltonian H' , ground state energy is E'_{gs}

Same number of electrons (otherwise trivial), hence:
 $H = T + W + V$ and $H' = T + W + V'$ $\rightarrow H = H' - V' + V$

Due to variational principle:

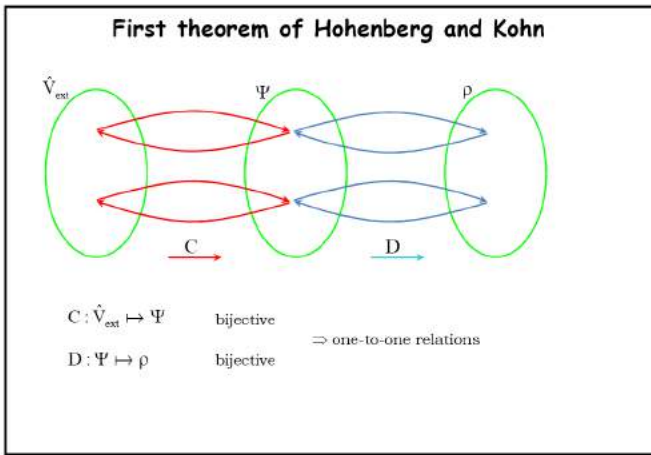
$$E_{\rho'} = \langle \Psi | H | \Psi \rangle = \langle \Psi' | H | \Psi' \rangle = \langle \Psi' | H + V - V' | \Psi' \rangle = E'_{\text{gs}} + \int \rho'(\vec{r}) [v(\vec{r}) - v'(\vec{r})] d\vec{r}$$

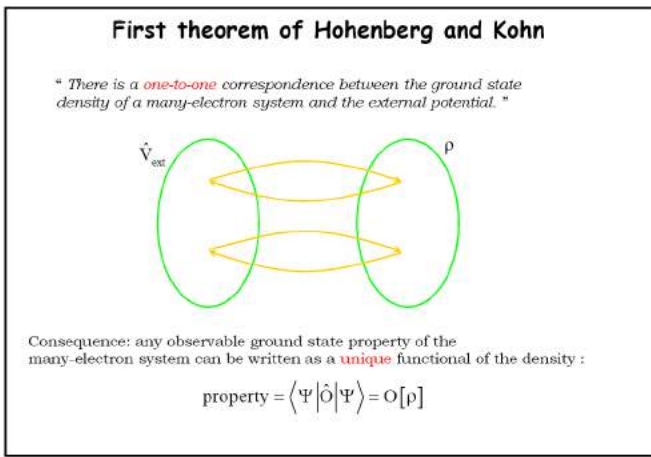
Repeat argument, starting with Ψ' :

$$E'_{\text{gs}} < E_{\rho} + \int \rho(\vec{r}) [v'(\vec{r}) - v(\vec{r})] d\vec{r}$$

Add, assuming that $\rho = \rho'$ $\rightarrow E_{\text{gs}} + E'_{\text{gs}} < E_{\text{gs}} + E'_{\text{gs}}$ \rightarrow contradiction

P. Hohenberg and W. Kohn, Phys. Rev. 136B (1964) 864

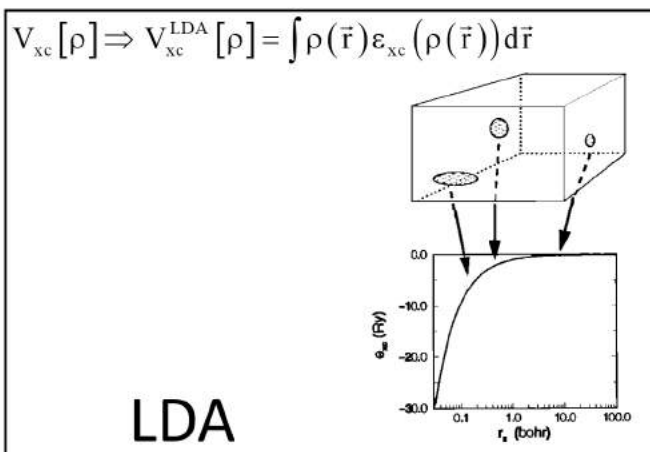






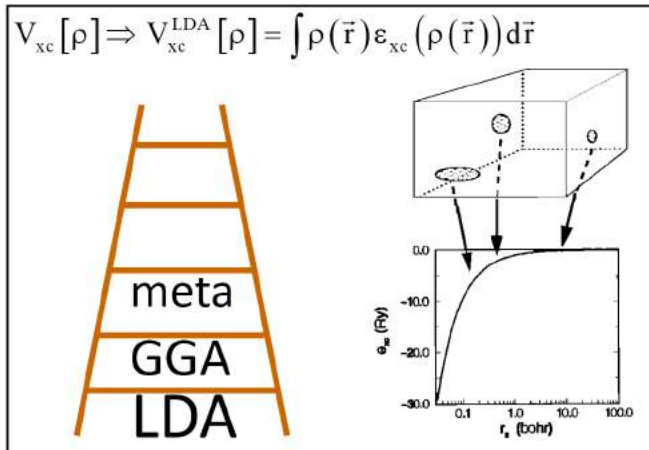






where the electronic density $n(\mathbf{r})$ is relatively slowly varying, so that our approximation (2.3) for ϵ_{xc} is expected to be satisfactory as discussed in case (a) above. (3) The “surface” of atoms and the overlap regions in molecules. Here our approximation (2.3) has no validity and therefore we expect this region to be the main source of error. **We do not expect an accurate description of chemical binding.** In large atoms, of course, this “surface” region becomes of less importance. (The surface is more satisfactorily handled in the nonlocal method described under *B* below.)

For metals, alloys, and small-gap insulators we have,











The electronic structure calculations are performed within the DFT framework using the projector augmented wave (PAW) approach for the core-valence interaction and the Perdew-Burke-Ernzerhof (PBE) approximation for the exchange-correlation functional as implemented in the VASP code.³²⁻³⁶ The kinetic energy cutoff is set at 500 eV and special k -point sets of $8 \times 8 \times 8$, $4 \times 4 \times 4$, and $4 \times 4 \times 4$ k -points are used for static self-consistent calculations in the $c111$, $p222$, and the SQS cells, respectively. For the SQS cells a smaller $2 \times 2 \times 2$ k -point set is used during relaxation. To optimize the geometry, a conjugate gradient algorithm is applied. Both ion positions and cell parameters are optimized simultaneously.
