

Electronic Structure Theory

ab-initio simulations of materials properties

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The many-body problem

The usual approach of quantum mechanics is the solution of the Shroedinger's equation $\hat{H}\Psi = E\Psi$, where:

$$\hat{H} = \underbrace{-\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}}_{\hat{H}_e} - \underbrace{\sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|}}_{\hat{H}_I} - \underbrace{\frac{1}{2} \sum_{i,I} \frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|}}_{\hat{H}_{e-I}}$$

This Hamiltonian cannot be easily diagonalized for systems with more than a few electrons. There are some problems, linked to many-body effects:

- The electron-electron interaction couples electronic variables among them, thus the wavefunction is not separable;
- The electron-phonon interaction couples electronic and phononic variables, introducing another level of correlation;

In order to find the ground-state of the problem we need to use some approximations on \hat{H} : the goal of electronic structure theory is to develop methods which treat electronic correlations with sufficient accuracy.

Ab-initio simulations

We will perform **ab-initio** simulations. That is we will be able to compute the physical properties of a system of interacting atoms and electrons from **first-principles**, i.e. with only the atomic coordinates and chemical nature of atoms. This is very useful when combined with experimental data.



(a)



(b)



(c)

Born-Oppenheimer Approximation

Notice that the kinetic energy of the ions can always be neglected thanks to the **Born-Oppenheimer approximation** (or **adiabatic approximation**): the position of nuclei will then be considered as **parameters**.

The Hamiltonian thus becomes:

$$\hat{H} = \hat{T} + \hat{V}_{\text{ext}} + \hat{V}_{\text{int}} + E_{II}$$

where:

- $\hat{T} = -\frac{1}{2} \sum_i \nabla_i^2$
- $\hat{V}_{\text{ext}} = \sum_{i,I} V_I(|\mathbf{r}_i - \mathbf{R}_I|)$
- $\hat{V}_{\text{int}} = \frac{1}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$

From the electronic wavefunction to the electronic density

Given the operator \hat{H} and by solving the Shroedinger equation we can obtain the eigenvalues and the eigenfunctions of our system.

By the variational principle:

$$\langle \Psi_{\text{tr}} | \hat{H} | \Psi_{\text{tr}} \rangle = E_{\text{tr}} \geq E_0 = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle$$

we can say that the energy is a functional of the wave-function $E[\psi]$ and restate the variational principle as:

$$E_0 = \min_{\Psi \rightarrow N} E[\Psi]$$

Given the number of electrons N , the atomic charge Z_I and the atomic positions \mathbf{R}_I , the problem is fully determined.

A different approach is based on the electronic density, whose properties are:

- It is positive;
- It depends only on the electronic space variables $\mathbf{r} = \{x, y, z\}$;
- It goes to zero as $\mathbf{r} \rightarrow 0$;
- If we integrate it over the whole space, it gives the total number of electrons N ;
- It can be observed by x-ray diffraction experiments;
- It has maxima only at the nuclear positions \mathbf{R} ;
- It has an asymptotic exponential decay for big distances from nuclei;

The electronic density, as the electronic wave-function, has all the ingredients (N , Z_I and \mathbf{R}_I) needed for defining the hamiltonian operator. As we will see in the subsequent sections, we can define the energy as a functional of the density and find the ground-state energy as the minimum of this functional over the physically acceptable electronic densities.

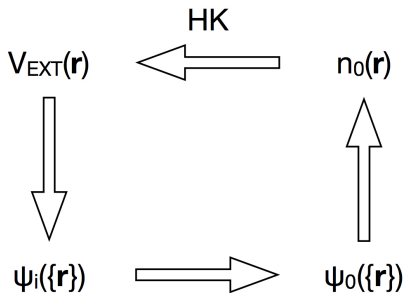
$$E = E[n(\mathbf{r})]$$

$$E_0 = \min_{n \rightarrow \{N, V_{\text{ext}}\}} E[n(\mathbf{r})]$$

Density Functional Theory

The first approach is to formulate DFT as an **exact** theory of many-body systems, which can be applied to any system of interacting particles in an external potential.

DFT is based upon two theorems formulated by Hohenberg and Kohn, which can be summarized in the following sketch:



I Hohenberg-Kohn theorem: the electronic density as central variable

Theorem I For any system of interacting particles in an external potential $V_{EXT}(\mathbf{r})$, the potential $V_{EXT}(\mathbf{r})$ is determined uniquely (except for a constant) by the groundstate particle density $n_0(\mathbf{r})$.

Corollary I Since the hamiltonian is fully determined, the many-body wavefunctions are determined for all states. Therefore all of the properties of the system are completely determined given **only** $n_0(\mathbf{r})$.

HK I theorem: proof

Since all properties are uniquely determined if $n(\mathbf{r})$ is specified, then we can write the total energy functional as:

$$\begin{aligned} E_{HK}[n] &= T[n] + E_{int}[n] + \int d^3r V_{EXT}(\mathbf{r})n(\mathbf{r}) + E_{II} \\ &= F_{HK}[n] + \int d^3r V_{EXT}(\mathbf{r})n(\mathbf{r}) + E_{II} \end{aligned} \quad (1)$$

where $F_{HK}[n]$ includes all internal energies, kinetic and potential, of the interacting electron system and is universal by construction.

II Hohenberg-Kohn theorem: the existence of an energy functional

Theorem II

We can define a universal functional of the energy in terms of the electronic density $E[n]$, valid for any $V_{EXT}(\mathbf{r})$. The exact groundstate of the system is the minimum of this functional and the density which minimizes it is the groundstate electronic density $n_0(\mathbf{r})$.

Corollary II

The functional $E[n]$ alone is sufficient to determine the exact groundstate energy and density.

HK II theorem: proof

Extensions and Problems of HK theorems

HK theorems can be generalized for different type of particles and different situations. Some examples:

- spin-polarized systems;
- $T \neq 0$ systems;
- time-dependent DFT;
- current-dependent DFT;

DFT, as proposed by Hohenberg and Kohn, is an exact theory but it has some limitations:

- Even if this formulation is exact and universal, Hohenberg and Kohn do not provide any guidance for constructing the functionals and no exact functional is known for any system of more than one atom;
- Density functional theory does not provide a way to understand the properties of a material merely by looking at the form of the density;
- The kinetic energy of many interacting electrons cannot be written explicitly in terms of the electron density;

Levy-Lieb Constrained Search

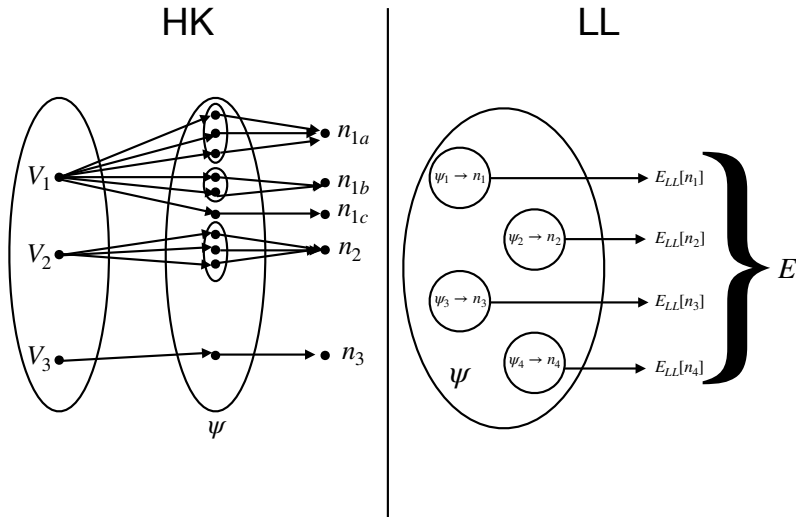
An alternative formulation of DFT was given by M. Levy (1979) and E. Lieb (1983) [M.Levy, Proc.Natl.Acad.Sci.U.S.A. 76, 6062 (1979); E.Lieb, Int. Jour. Quant. Chem. 24, 243-277 (1983)]:

- clear definition of $E[n]$;
- provides a way to determine $E[n]$;
- it is equivalent to the HK formulation;
- applies to degenerate groundstates;

Levy-Lieb Constrained Search: formulation I

Levy-Lieb Constrained Search: formulation II

Hohenberg-Kohn vs Levy-Lieb



Non-Interacting Electrons

KOHN-SHAM ANSATZ: the groundstate density of the original interacting system is equal to that of some chosen non-interacting system.

This leads to independent-(quasi)particle equations for the non interacting system that can be considered soluble (by numerical means) with all difficult many-body terms incorporated into an *exchange-correlation functional of the density*.

By solving the equations one finds the groundstate density and energy of the original interacting system with the accuracy limited only by the approximations in the exchange-correlation functional.

Writing the energy functional

Consider a system of N_e electrons obeying the hamiltonian:

$$\hat{H} = -\frac{1}{2} \sum_i^{N_e} \nabla_i^2 - \sum_i^{N_e} \sum_I^{N_I} \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} + \frac{1}{2} \sum_{i \neq j}^{N_e} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \quad (2)$$

The **density** is defined as:

$$n(\mathbf{r}) = \langle \psi | \sum_i^{N_e} \delta(\mathbf{r} - \mathbf{r}_i) | \psi \rangle = N \int d^3 r_2 \cdots d^3 r_N |\psi(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N)|^2 \quad (3)$$

The **joint density** is defined as:

$$n(\mathbf{r}, \mathbf{r}') = \langle \psi | \sum_{i \neq j}^{N_e} \delta(\mathbf{r} - \mathbf{r}_i) \delta(\mathbf{r}' - \mathbf{r}_j) | \psi \rangle = N(N-1) \int d^3 r_3 \cdots d^3 r_N |\psi(\mathbf{r}, \mathbf{r}', \mathbf{r}_3, \dots, \mathbf{r}_N)|^2 \quad (4)$$

The joint density and the density are connected by the relation:

$$n(\mathbf{r}, \mathbf{r}') = n(\mathbf{r})n(\mathbf{r}') + \underbrace{\Delta n(\mathbf{r}, \mathbf{r}')}_{\text{it is } 0 \text{ for independent electrons}} \quad (5)$$

Writing the energy functional

First of all let's consider the *electron-ion* interaction. We can write it as a functional of the density:

$$E_{e-i}[n] = \langle \psi | - \sum_i^{N_e} \sum_I^{N_I} \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} | \psi \rangle = \int n(\mathbf{r}) V_{e-i}(\mathbf{r}) d^3r \quad (6)$$

In general, we can put together electron-ion interaction and any other interaction with an external field, thus defining an *external* potential $V_{\text{ext}}(\mathbf{r})$. The energy functional will therefore become:

$$E_{\text{ext}}[n] = \int n(\mathbf{r}) V_{\text{ext}}(\mathbf{r}) d^3r \quad (7)$$

Writing the energy functional

For what concerns the electron-electron interaction, we can write the energy functional as:

$$\begin{aligned}
 E_{e-e}[n] &= \frac{1}{2} \int d^3r d^3r' \frac{n(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} = \\
 &= \frac{1}{2} \int d^3r d^3r' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \frac{1}{2} \int d^3r d^3r' \frac{\Delta n(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} = \\
 &= E_{\text{Hartree}}[n] + E_{\text{ncI}}[n]
 \end{aligned} \tag{8}$$

The electron-electron interaction is the term which makes the many-body problem so hard to solve. We have split it into two terms, one regarding the classical coulomb interaction of the density with itself and the non-classical part.

Writing the energy functional

As we have said before, we cannot directly write the kinetic energy functional due to the presence of the laplacian operator. Here's where Kohn-Sham assumption comes in help: instead of the full many-particle system we consider an auxiliary system of single-particle orbitals that have the same groundstate density as the real system.

Therefore we can write:

$$T[n] = -\frac{1}{2} \sum_i^{N_e} \int d^3r |\nabla \psi_i(\mathbf{r})|^2 + \Delta T[n] \quad (9)$$

Notice that the kinetic energy of this fictitious system cannot be the same of the original one, therefore in order to impose this equality we add a corrective term $\Delta T[n]$.

The Kohn-Sham functional is therefore:

$$E_{KS}[n] = T_{KS}[n] + \int n(\mathbf{r}) V_{\text{ext}}(\mathbf{r}) d^3r + E_{\text{Hartree}}[n] + E_{II} + E_{XC}[n] \quad (10)$$

and the exchange-correlation functional can be viewed as:

$$E_{XC}[n] = \{\langle \hat{T} \rangle - T_{KS}[n]\} + \{\langle \hat{V}_{int} \rangle - E_{\text{Hartree}}[n]\} \quad (11)$$

so that:

- $E_{XC}[n]$ is a functional of the density;
- $E_{XC}[n]$ corresponds to the difference between the interacting and non-interacting system;

Kohn-Sham variational equations

We would like to obtain an effective one-particle hamiltonian of the form:

$$\hat{H}_{eff} = -\frac{\hbar^2}{2m_e} \nabla^2 + \hat{V}_{eff} \quad (12)$$

If we now apply Hohenberg-Kohn second theorem, i.e. we find the minimum of the energy functional in terms of the electron density, subject to the fact that $\langle \psi_i | \psi_j \rangle = \delta_{i,j}$:

$$\frac{\delta E_{KS}[n(\mathbf{r})]}{\delta n(\mathbf{r}')} = 0 \Rightarrow (\hat{H}_{KS} - \epsilon_i) \psi_i(\mathbf{r}) = 0 \quad (13)$$

We obtain the Kohn-Sham Schrödinger-like equations.

Kohn-Sham variational equations: derivation I

Kohn-Sham variational equations: derivation II

Kohn-Sham variational equations: derivation III

Kohn-Sham variational equations

The Kohn-Sham equations can be summarized as follows:

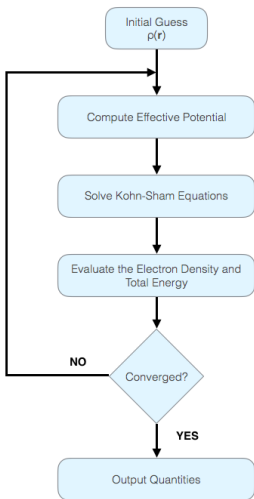
$$\hat{H}_{KS}^{\sigma} \psi_i^{\sigma}(\mathbf{r}) = \left[-\frac{\hbar^2}{2m_e} \nabla_i^2 + \hat{V}_{KS}^{\sigma}(\mathbf{r}) \right] \psi_i^{\sigma}(\mathbf{r}) = \epsilon_i^{\sigma} \psi_i^{\sigma}(\mathbf{r})$$

$$\hat{V}_{KS}^{\sigma}(\mathbf{r}) = \hat{V}_{\text{ext}}(\mathbf{r}) + \hat{V}_{\text{Hartree}}(\mathbf{r}) + \hat{V}_{XC}^{\sigma}(\mathbf{r})$$

$$n(\mathbf{r}) = \sum_{\sigma} \sum_{i=1}^{N_e} |\psi_i^{\sigma}(\mathbf{r})|^2$$

- We have independent particle equations that have to be solved in a self-consistent way with the resulting density;
- These equations are independent of any approximation to the functional $E_{XC}[n]$, therefore it would lead to the exact groundstate density and energy for the interacting system if the exact $E_{XC}[n]$ were known;

Solving Kohn-Sham equations



- Kohn-Sham equations are a set of Schrödinger-like independent-particle equations that have to be solved in a self-consistent way;
- We iteratively change V_{eff} and n in order to approach a self consistent solution;
- Except at the exact solution, the input and output potentials and densities do not agree. We need some criterion to stop the cycle;

Ingredients for a DFT Computation

In order to solve the Kohn-Sham variational equations, we need three ingredients:

- A suitable approximation to the Exchange-Correlation potential;
- A suitable basis for the expansion of the electronic wavefunction;
- A way to treat the external potential, that is the interaction of electrons with atomic nuclei;

These ingredients are to be approximated according to the system under study, the level of accuracy desired and the computational effort.

The Total Energy Functional

For an independent particle system, the total energy can be simply written as the sum of the single-particle eigenvalues. However, in the case of the Kohn-Sham problem it is not simply that. Indeed:

$$E_{KS}[V^{\sigma,in}] = \left[\sum_{i,\sigma} \epsilon_i^{\sigma} \right]_{V^{\sigma,in}} - \sum_{\sigma} \int d\mathbf{r} V_{KS}^{\sigma,in}(\mathbf{r}) n^{\text{out}}(\mathbf{r}) \quad (14)$$

where:

- in \rightarrow input of the KS equations;
- out \rightarrow output of the KS equations;

The Total Energy Functional: derivation I

The Total Energy Functional: derivation II

Meaning of Kohn-Sham Eigenvalues

KS eigenvalues have no physical meaning in absolute value. The only exception is the highest eigenvalue in a finite system, which is minus the ionization energy.

Within KS formalism, eigenvalues have a well definite mathematical meaning (Slater-Janak theorem):

$$\epsilon_i = \frac{dE_{total}}{dn_i} = \int \frac{dE_{total}}{dn(\mathbf{r})} \frac{dn(\mathbf{r})}{dn_i} d\mathbf{r}$$

$\frac{dE_{total}}{dn(\mathbf{r})}$ contains the derivative of the exchange-correlation energy, which is discontinuous and give problems to the self-interaction correction. This leads to problems in the band-gap computation for example.

The band-gap problem I

The band-gap problem II

The band-gap problem III