Appendix A

Density Functional Theory

This section was inspired by [45].
The ABINIT program allows to solve the Kohn-Sham equations. These equations come from the density functional theory (DFT), a quantum calculation method allowing the study of the electronic structure of materials in an exact way.

Traditional methods in electronic structure theories, in particular Hartree-Fock theory, are based on a multielectronic wavefunction. The objective of the DFT is to replace this complex wavefunction by the electronic density as the important quantity for calculation. When the multielectronic wavefunction depends of 3N variables (where N is the total number of particles of the system), the electronic density only depends of 3 variables. It's then a much simpler quantity to process, mathematically and conceptually.

The DFT idea is to reformulate the quantum n-body problem in a 1-body problem with electronic density as parameter.

The fundamental equation to solve in order to describe the electronic structure of a system with many nuclei and electrons is the Schrödinger equation. This equation can be simplified thanks to the Born-Oppenheimer approximation which consists in taking the nucleus position as fixed; the kinetic energy can be neglected and the interaction term between ions considered as a constant.

This approximation is justified by the ratio between the masses of particles constituting the nucleus (the protons and neutrons) and the mass of the electron. The equation can then be written :

$$\hat{H}\psi = \sum_n \left(-\frac{\nabla_n^2}{2} + V_{ext}(\mathbf{r_n}) + \sum_{m>n} \frac{1}{|\mathbf{r_n} - \mathbf{r_m}|} \right) \psi = E\psi \tag{A.1}$$

The first term corresponds to the kinetic energy of electrons, the second to the external potential created by the ions and the third to the interaction between electrons.

Hohenberg and Kohn demonstrated that the electronic density of the first state, defined by

$$n(r) = N_e \int [\psi(r, r_2, ..., r_{N_e})]^* \psi(r, r_2, ..., r_{N_e}) dr_2 ... dr_{N_E} \tag{A.2}$$

determines in a unique way the potential $V_{ext}(r)$ modulo a global constant.

This constant can be fixed by setting the potential to zero when distance tends to infinity. From this comes that the total electronic energy is also a density functional :

$$E = \langle \psi | \hat{H} | \psi \rangle = E(n) \tag{A.3}$$

Thanks to the variational principle of quantum mechanics, it is possible to show that it results in minimizing

$$E = \min_n \left\{ F[n] + \int n(\mathbf{r}) V_{ext}(\mathbf{r}) d\mathbf{r} \right\} \tag{A.4}$$

with $F[n]$ a functional of the density not known explicitly and defined as

$$F[n] = \min_{\phi \to n} \left\{ \left\langle \phi | \hat{T}_e + \hat{V}_{ee} | \phi \right\rangle \right\} \tag{A.5}$$

Kohn and Sham tried to establish a connection with a system of non-interacting electrons of same electronic density :

$$T_0[n] = \min_{\phi \to n} \left\{ \left\langle \phi | \hat{T}_e | \phi \right\rangle \right\} \tag{A.6}$$

For such a system, the kinetic energy is a known functional of the density. Moreover, the functional for the associated Hartree energy is also known:

$$E_H[n] = \frac{1}{2} \int \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \tag{A.7}$$

When removing these 2 terms from $F[n]$, stays only a much smaller part of the total energy called exchange-correlation energy functional.

$$E_{xc}[n] = F[n] - T_0[n] - E_H[n] \tag{A.8}$$

This term contains a exchange part, a correlation part and the difference of kinetic energy between interacting and non-interacting electron systems.

It is much simpler to find a good approximation for this exchange-correlation term than for the $F[n]$ functional (see below).

The problem consists now in minimizing the functional

$$E[n] = T_0[n] + \int n(\mathbf{r}) V_{ext}(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \int \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + E_{xc}[n] \tag{A.9}$$

under the constraints of a fixed number of electrons :

$$\int n(\mathbf{r}) d\mathbf{r} = N_e \tag{A.10}$$

By introducing the Lagrange multipliers, one obtains an equation strictly equivalent to the one of a non-interacting electron system with the same electronic density in a potential called the Kohn-Sham potential :

$$V_{KS}(\mathbf{r}) = V_{ext}(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc}(\mathbf{r}) \tag{A.11}$$

It is then also exactly as solving the Schrödinger equation for one electron in a self-consistent way :

$$\left[-\frac{1}{2} \nabla^2 + V_{KS}(\mathbf{r}) \right] \phi_n^{KS}(\mathbf{r}) = \varepsilon_n^{KS} \phi_n^{KS}(\mathbf{r}) \tag{A.12}$$

with the electronic density :

$$n(\mathbf{r}) = \sum_{i=1}^{N} |\phi_i^{KS}(\mathbf{r})|^2 \tag{A.13}$$

When self-consistency is achieved, the electronic density and then the total energy are exact (assuming the exchange-correlation potential is exact). However, the Kohn-Sham wavefunctions and eigenenergies correspond to a fictive set of independent electrons, not to exact physical quantities.

It still remains to choose an approximation for the exchange-correlation potential. Several approximations exist but the 2 widely used are : *Local density approximation* or LDA and the *Generalized gradient approximation* or GGA. In this work it's the LDA that is chosen for reasons explained below.

The LDA is based on the uniform electrons gas model and is the simplest approach to approximate the exchange-correlation term. It is described as :

$$E_{xc}[n] = \int n(\boldsymbol{r})\varepsilon_{xc}[n]dr \tag{A.14}$$

where $\varepsilon_{xc}[n]$ is the exchange-correlation energy of one particle in an homogeneous electron gas.

The function $\varepsilon_{xc}[n]$ can be decomposed in an exchange part $\varepsilon_x[n]$ and a correlation part $\varepsilon_c[n]$.

$$\varepsilon_{xc}[n] = \varepsilon_x[n] + \varepsilon_c[n] \tag{A.15}$$

The exchange contribution can be calculated analytically :

$$\varepsilon_x[n(r)] = -\frac{3}{4\pi}(3\pi^2 n(r))^{1/3} \tag{A.16}$$

The correlation contribution is obtained from precise numerical simulation (Quantum Monte Carlo).

In order to lower the number of plane waves needed to solve the equations, another approximation is used : *The frozen core approximation* consisting in considering that core electrons do not change with the environment in which the atom is placed, they are "frozen". This allows to calculate wave function only for valence electrons. This approximation takes place in the construction of pseudo-potentials for atoms.