Appendix C

Density functional theory

Density Functional Theory (DFT) is used in order to model the atoms of a material. This theory allows to study several properties (electronic, structural, optical,...) of isolated molecules as well as of periodic crystals. A description of DFT is now done, as the ABINIT code is based on this theory. The first four subsections rely on Ref. [46].

C.1 Born-Oppenheimer approximation

The Born-Oppenheimer approximation uncouples the movement of the electrons and the one of the nuclei in a crystal. The approximation is justified by the fact that the mass of a nucleus is by far larger than the mass of an electron. The nuclei can then be considered to be fixed when studying electrons. Under this assumption, the system of N electrons is completely characterised by the wave function

$$\Psi = \Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) \tag{C.1}$$

where $\mathbf{r}_i$ is the position of the electron i. These electrons interact with each other as well as with an external potential $V_{\text{ext}}(\mathbf{r})$ created by the fixed nuclei. The wave function is obtained by solving the Schrödinger equation

$$\hat{H}\Psi = \sum_n \left(-\frac{\nabla_n^2}{2} + V_{\text{ext}}(\mathbf{r}_n) + \sum_{m>n} \frac{1}{|\mathbf{r}_n - \mathbf{r}_m|} \right) \Psi = E\Psi. \tag{C.2}$$

This equation may be written as

$$\left(\hat{T}_e + \sum_n V_{\text{ext}}(\mathbf{r}_n) + \hat{V}_{ee} \right) \Psi = E\Psi \tag{C.3}$$

where $\hat{T}_e = \sum_n -\frac{\nabla_n^2}{2}$ is the kinetic energy of electrons and $\hat{V}_{ee} = \sum_n \sum_{m>n} \frac{1}{|\mathbf{r}_n - \mathbf{r}_m|}$ is the potential describing the interaction between electrons. Many methods have been developed in order to solve this equation (i.e. the Hartree-Fock method [47]). DFT is an alternative method considering the electronic density as the building block allowing to characterize the system.

C.2 Self-consistent field method

Hohenberg and Kohn have shown that the electronic density of the fundamental state of a system of N electrons defined as

$$n(\mathbf{r}) = N \int \Psi^*(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) d\mathbf{r}_1 d\mathbf{r}_2 \ldots \mathbf{r}_N \tag{C.4}$$

determines to a constant the external potential $V_{\text{ext}}(\mathbf{r})$. This potential is then a functional of the electronic density. If the constant is arbitrarily fixed, then the total energy is also a functional of the density :

$$E = \langle \Psi | \hat{H} | \Psi \rangle = E[n] \tag{C.5}$$

because the Hamiltonian is uniquely defined when the external potential is fixed. Starting from the variational principle, the energy is determined by

$$E[n] = \min_n \left\{ F[n] + \int n(\mathbf{r}) V_{\text{ext}}(\mathbf{r}) d\mathbf{r} \right\} \tag{C.6}$$

where $F[n] = \min_{\phi \to n} \left\{ \langle \phi | \hat{T}_e + \hat{V}_{ee} | \phi \rangle \right\}$ is a functional of the density which is not explicitly known. It is necessary to approximate this term in order to obtain a good value of the energy. The kinetic energy of a system of independent electrons with the same density is known :

$$T_0[n] = \min_{\phi \to n} \left\{ \langle \phi | \hat{T}_e | \phi \rangle \right\}. \tag{C.7}$$

Moreover, the Hartree energy associated to this system is

$$E_{\text{H}}[n] = \frac{1}{2} \int \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'. \tag{C.8}$$

These two terms contribute to $F[n]$. The exchange-correlation energy E_{xc} is then simply obtained :

$$E_{\text{xc}}[n] = F[n] - T_0[n] - E_{\text{H}}[n]. \tag{C.9}$$

This exchange-correlation energy is much easier to approximate.

The problem is then equivalent to minimizing the functional

$$E[n] = T_0[n] + \int n(\mathbf{r}) V_{\text{ext}}(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \int \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + E_{\text{xc}}[n] \tag{C.10}$$

under the constraint that the number of electrons is fixed :

$$\int n(\mathbf{r}) d\mathbf{r} = N. \tag{C.11}$$

This minimization is equivalent to the resolution of the Kohn-Sham equation

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

where $\phi_n^{\text{KS}}(\mathbf{r})$ is the wave function of an electron, the electronic density is $n(\mathbf{r}) = \sum_{i=1}^{N} |\phi_i^{\text{KS}}(\mathbf{r})|^2$ and $V_{\text{KS}}(\mathbf{r})$ is the Kohn-Sham potential. This potential is defined by

$$V_{\text{KS}}(\mathbf{r}) = V_{\text{ext}}(\mathbf{r}) + V_{\text{H}}(\mathbf{r}) + V_{\text{xc}}(\mathbf{r}) \tag{C.13}$$

where $V_{\text{H}}(\mathbf{r}) = \int \frac{n(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'$ is the Hartree potential and $V_{\text{xc}}(\mathbf{r}) = \frac{\delta E_{\text{xc}}[n]}{\delta n}$ is the exchange-correlation potential. Solving this problem has to be realized self-consistently. Indeed, in order to obtain the Kohn-Sham potential, it is necessary to know the electronic density and thus the wave functions $\phi_i^{\text{KS}}(\mathbf{r})$. But in order to know these wave functions, the Kohn-Sham potential has to be known. Hence, an iteration has to be realized, starting from an initial electronic density and stopping when the convergence of the electronic density and of the total energy is reached. These values are then the exact ones. Fig. C.1 represents the scheme to follow.

A correct approximation of the exchange-correlation energy $E_{\text{xc}}[n]$ still needs to be found. It can be shown that this energy is given by

$$E_{\text{xc}}[n] = \int n(\mathbf{r}) \varepsilon_{\text{xc}}(\mathbf{r}, n) d\mathbf{r} \tag{C.14}$$

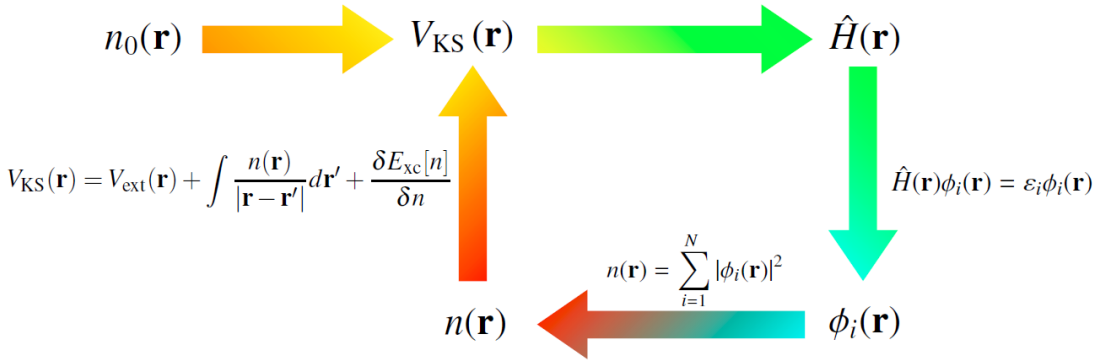

Figure C.1: Self-consistent scheme leading to the knowledge of both the electronic density and the total energy of a system of N electrons in a crystal [46].

where $\varepsilon_{xc}(\mathbf{r}, n)$ is the local exchange-correlation energy per electron. LDA (Local Density Approximation) consists in saying that this local energy depends only on the local electronic density and is equal to the one of a homogeneous electron gas of same density (jellium model) :

$$\varepsilon_{xc}^{LDA}(\mathbf{r}, n) = \varepsilon_{xc}^{hom}[n(\mathbf{r})]. \tag{C.15}$$

The exchange part of $\varepsilon_{xc}^{hom}(n(\mathbf{r}))$ can be analytically determined, and its correlation part may be numerically computed.

GGA (Generalized Gradient Approximation) is still a local approximation, but it also takes into account the gradient of the density :

$$\varepsilon_{xc}^{GGA}(\mathbf{r}, n) = \varepsilon_{xc}[n(\mathbf{r}), \nabla n(\mathbf{r})]. \tag{C.16}$$

If the obtained total energy and electronic density are exact, the wave functions and eigen energies from Kohn-Sham equation correspond to a fictive group of free electrons. LDA and GGA generally lead to good results. However, when it comes to the computation of a band gap, both techniques give wrong values even if the shape of the band structures is usually qualitatively good. Other formalisms have been developed in order to be able to compute a better value for the band gap of a material (GW,...).

C.3 Pseudopotentials

Schrödinger equation (C.3) can be greatly simplified if electrons are divided in two categories : core electrons and valence ones. Indeed, core electrons are strongly bonded and do not play an important role in interatomic bonds, so that many properties of materials depend only on valence electrons. The electronic density is

$$n(\mathbf{r}) = \sum_{i \in \text{core}}^{N_{\text{core}}} \phi_i^*(\mathbf{r})\phi_i(\mathbf{r}) + \sum_{i \in \text{val}}^{N_{\text{val}}} \phi_i^*(\mathbf{r})\phi_i(\mathbf{r}). \tag{C.17}$$

The frozen core approximation consists in considering that the behavior of core electrons do not change when the atom is isolated or in a random medium :

$$\phi_{i \in \text{core}}(\mathbf{r}) = \phi_{i \in \text{core}}^{\text{atome}}(\mathbf{r}). \tag{C.18}$$

This approximation leads to results which are not exact anymore. Depending on the desired precision, it will be necessary to consider more or less valence electrons.

A pseudopotential is an approximation of the potential that valence electrons undergo. Many pseudopotentials exist, depending on the atom, the number of considered valence electrons, considered interactions (spin-orbit coupling,...), imposed conditions (norm-conserving,...), studied properties,...

C.4 Plane wave basis set

It is useful to describe the way ABINIT treats wave functions. In periodic systems, Bloch theorem gives

$$\phi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r}) \tag{C.19}$$

with $u_{n\mathbf{k}}(\mathbf{r}+\mathbf{R}) = u_{n\mathbf{k}}(\mathbf{r})$ and where $\phi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{R}}\phi_{n\mathbf{k}}(\mathbf{r})$. $\mathbf{R}$ is a vector describing the periodicity of the crystal. $u_{n\mathbf{k}}(\mathbf{r})$ then has the same periodicity. The reciprocal space, characterized by $\mathbf{G}$ vectors, is defined by

$$e^{i\mathbf{G}\cdot\mathbf{R}} = 1. \tag{C.20}$$

The periodic part of wave functions can be written as

$$u_{n\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} \sum_{\mathbf{G}} u_{n\mathbf{k}}(\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{r}} \tag{C.21}$$

where Ω is the volume of the primitive cell and $u_{n\mathbf{k}}(\mathbf{G})$ are the coefficients of this Fourier series. These coefficients decrease exponentially with the kinetic energy $\frac{(\mathbf{k}+\mathbf{G})^2}{2}$. The selection of the plane waves used in the sum (C.21) depends on a maximal kinetic energy called the cut-off energy. This cut-off energy is represented by `ecut` in ABINIT.

C.5 Projector-augmented wave method

The projector-augmented wave (PAW) method is an alternative to the use of a plane-wave basis set and pseudopotentials. The description of this method is mainly based on Refs. [48, 49].

The PAW method has been developed because of the fact that for elements with strongly localized orbitals like first-row, $3d$ and rare-earth elements, the number of plane waves in the basis set needs to be quite large because the pseudopotentials are quite hard. The strategy of the PAW method is to divide the wave function into parts : one inside a sphere around each atom and a second one outside this sphere, in the so called bonding region.

Only the basic formalism of this method is introduced here. The details can be found in the references cited here above.

C.5.1 Formalism

The all-electron wave function can be decomposed in one-electron wave functions :

$$|\Psi\rangle = \sum_i |\phi_i\rangle\, c_i \qquad \text{within } \Omega_R \tag{C.22}$$

where the index i corresponds to the atomic site $\mathbf{R}$, the angular momentum quantum numbers (l, m) and an additional index n to label the different functions ϕ at the same atomic site and with the same angular momentum. Ω_R is the augmentation region around the atom, approximately corresponding to the core region. The PAW method introduces a new wave function $\left|\tilde{\Psi}\right\rangle$ called the pseudo wave function. All quantities related to the pseudo representation will be noted with a tilde. The transformation between the all-electron and the pseudo wave functions is supposed to be linear and should be different only inside the augmentation region. The same kind of decomposition can be done for the pseudo wave function :

$$\left|\tilde{\Psi}\right\rangle = \sum_i \left|\tilde{\phi}_i\right\rangle c_i \qquad \text{within } \Omega_R \tag{C.23}$$

with the same coefficients c_i. Finally, the projector functions $\langle\tilde{p}_i|$ are defined by the conditions

$$c_i = \left\langle \tilde{p}_i \middle| \tilde{\Psi} \right\rangle \tag{C.24}$$

$$\left\langle \tilde{p}_i \middle| \tilde{\phi}_j \right\rangle = \delta_{ij}. \tag{C.25}$$

With these definitions, the all-electron wave function can be derived from the pseudo wave function with a linear transformation :

$$|\Psi\rangle = \left|\tilde{\Psi}\right\rangle + \sum_i \left(|\phi_i\rangle - \left|\tilde{\phi}_i\right\rangle\right) \left\langle \tilde{p}_i \middle| \tilde{\Psi} \right\rangle. \tag{C.26}$$

In this expression, the all-electron partial waves ϕ_i can be obtained for a reference atom solving the Schrödinger equation and the pseudo partial waves $\tilde{\phi}_i$ are equal to the ϕ_i outside a core radius r_c. The PAW method use the pseudo partial waves to compute the density. These functions are easier to manipulate numerically. The charge density is given by

$$n(\mathbf{r}) = \tilde{n}(\mathbf{r}) + n^1(\mathbf{r}) - \tilde{n}^1(\mathbf{r}) \tag{C.27}$$

where

$$\tilde{n}(\mathbf{r}) = \sum_n f_n \left\langle \tilde{\Psi}_n \middle| \mathbf{r} \right\rangle \left\langle \mathbf{r} \middle| \tilde{\Psi}_n \right\rangle, \tag{C.28}$$

$$n^1(\mathbf{r}) = \sum_{n,(i,j)} f_n \left\langle \tilde{\Psi}_n \middle| \tilde{p}_i \right\rangle \langle \phi_i | \mathbf{r} \rangle \langle \mathbf{r} | \phi_j \rangle \left\langle \tilde{p}_j \middle| \tilde{\Psi}_n \right\rangle, \tag{C.29}$$

and

$$\tilde{n}^1(\mathbf{r}) = \sum_{n,(i,j)} f_n \left\langle \tilde{\Psi}_n \middle| \tilde{p}_i \right\rangle \left\langle \tilde{\phi}_i \middle| \mathbf{r} \right\rangle \left\langle \mathbf{r} \middle| \tilde{\phi}_j \right\rangle \left\langle \tilde{p}_j \middle| \tilde{\Psi}_n \right\rangle. \tag{C.30}$$

Here, f_n is the occupation of the state. The same kind of decomposition can be realized for the energy. The details of this decomposition are given in Refs. [49].