Chapter 12

Density-Functional Theory

Density-Functional Theory (DFT) provides an alternative approach to the "Hartree-Fock plus corrections" paradigm. Unlike Hartree-Fock or more sophisticated methods (Many-Body Perturbation Theory), based on the wave function, it focuses on the charge density as the fundamental quantity. In the last 30 years DFT has become widespread in electronic-structure calculations for materials, especially in the implementation based on plane waves and pseudopotentials.

We will see here in action a basic DFT self-consistent code, using a simple form (Applebaum-Hamann) of atomic pseudopotentials for Si.

12.1 Hohenberg-Kohn theorem

Density-Functional Theory (DFT) is based on the Hohenberg-Kohn theorem (1964). This states that the ground-state charge density, \( \rho(r) \), defined as

\[
\rho(r) = N \int |\Psi(r, r_2, ..., r_N)|^2 d^3r_2 ... d^3r_N
\]

(12.1)

for a system of \( N \) electrons with ground-state many-electron wave-function \( \Psi \), uniquely determines the external (e.g. nuclear) potential \( V \) acting on electrons, and as a consequence the many-body Hamiltonian: \( H = T + V + U \), where \( T \) is the kinetic energy, \( U \) is the electron-electron repulsion.

While it is quite obvious that \( V \) determines \( \rho \), the opposite is much less obvious. The Hohenberg-Kohn theorem demonstrates just this, by showing that no two potentials \( V \) and \( V' \) can have the same \( \rho \) as ground-state charge density (unless they differ by a constant).

A straightforward consequence of the Hohenberg-Kohn theorem is that the energy of the ground state is a functional of the charge density:

\[
E = \langle \Psi | H | \Psi \rangle = \langle \Psi | T + V + U | \Psi \rangle = F[\rho] + \int \rho(r)v(r)d^3r
\]

(12.2)

where \( F[\rho] = \langle \Psi | T + U | \Psi \rangle \) is a universal functional, i.e. independent upon the external potential \( V \), and we have assumed that the potential \( V \) acts locally on the electrons: \( V \equiv \sum_i v(r_i) \).

\footnote{Note that the original DFT applies to \textit{spinless} fermions}
A further consequence is that the energy functional $E[\rho]$ is \textit{minimized} by the ground-state charge density. This suggests a very interesting algorithm to find the ground state: finding a three-dimensional function that minimizes the energy functional is a much easier task than finding the $3N$-dimensional wave function that minimizes the same quantity. Unfortunately it is not easy to minimize an unknown functional, since all we know at this stage is that it exists.\footnote{We actually know a lot more than this about the properties of the exact functional $F[\rho]$, but there is no way to write it down explicitly and in a simple form.}

12.2 Kohn-Sham equations

The transformation of the Hohenberg-Kohn theorem from a curiosity into a useful tool takes place via the Kohn-Sham (KS) approach and via a simple approximation known as Local-Density Approximation, LDA (1965). Since the Hohenberg-Kohn theorem holds irrespective of the electron-electron repulsion $U$, we may introduce an auxiliary system of \textit{non-interacting} electrons having the same density as the true system:

$$\rho(r) = \sum_i |\psi_i(r)|^2,$$

where the $\psi_i$ (\textit{Kohn-Sham orbitals}) are single-electron wavefunctions, to be determined by the condition that $E[\rho]$ is minimized, under orthonormality constraints $\langle \psi_i | \psi_j \rangle = \delta_{ij}$. We still do not know the functional to be minimized, but let us write it as a sum of known terms, large and easy to compute, and the rest:

$$E = T_s[\rho] + E_H[\rho] + \int \rho(r) v(r) d^3r + E_{xc}[\rho],$$

where $T_s$ is the kinetic energy of the non-interacting electrons:

$$T_s = -\frac{\hbar^2}{2m} \sum_i \int \psi_i^*(r) \nabla^2 \psi_i(r) d^3r,$$

(note that in general $T_s \neq \langle \Psi | T | \Psi \rangle$), $E_H$ is the electrostatic (Hartree) energy:

$$E_H[\rho] = \frac{q_e^2}{2} \int \rho(r) \rho(r') \frac{d^3r d^3r'}{|r-r'|},$$

the third term is the interaction energy with the external potential, and all the rest is hidden into the $E_{xc}$ term. The latter is known as \textit{exchange-correlation energy}, for historical reasons coming from Hartree-Fock terminology: in principle, $E_{xc}$ contains \textit{both} the exchange energy of the Hartree-Fock method, \textit{and} the correlation energy that is missing in it.

By imposing the condition that the KS orbitals $\psi_i$ minimize the energy, we find the \textit{Kohn-Sham equations} to which KS orbitals obey:

$$\left( -\frac{\hbar^2 \nabla^2}{2m} + V_{KS}(r) \right) \psi_i(r) = \epsilon_i \psi_i(r),$$

$$\left( -\frac{\hbar^2 \nabla^2}{2m} + V_{KS}(r) \right) \psi_i(r) = \epsilon_i \psi_i(r).$$
where the effective, or Kohn-Sham potential, \( V_{KS} = v(r) + V_H(r) + V_{xc}(r) \), is a functional of the charge density:

\[
V_H(r) = q_e^2 \int \frac{\rho(r')}{|r - r'|} d^3r', \quad V_{xc}(r) = \frac{\delta E_{xc}[\rho]}{\delta \rho(r)}.
\] (12.8)

KS equations are reminiscent of Hartree-Fock equations, Eq. (7.13), with the exchange potential replaced by the exchange-correlation potential. Note that the latter is a local potential, while the exchange potential is non-local. The energy can be rewritten using the sum over KS eigenvalues \( \epsilon_i \). It is straightforward to prove that the energy functional can be written as

\[
E = \sum_i \epsilon_i - E_H[\rho] + E_{xc} - \int \rho(r)V_{xc}(r)d^3r.
\] (12.9)

### 12.3 Approximated functionals

Not much progress seems to be done yet: \( E_{xc} \) is still an unknown functional, and so is \( V_{xc} \). There is however a long tradition, pre-dating DFT, of using homogeneous electron gas results to approximate similar functions. The most famous historical method is Slater’s local approximation to the exchange potential:

\[
V_x(r) \simeq -\frac{3q_e^2}{2\pi} (3\pi^2 \rho(r))^{1/3}.
\] (12.10)

Kohn and Sham extend and improve upon such ideas by introducing the local density approximation (LDA): they re-write the the energy functional as

\[
E_{xc} = \int \rho(r)e_{xc}(r)d^3r,
\] (12.11)

using for the exchange-correlation energy density \( e_{xc}(r) \) the result for the homogeneous electron gas of density \( n \), \( e_{xc}(n) \), computed in each point at the local charge density: \( e_{xc}(r) \equiv e_{xc}(\rho(r)) \). The function \( e_{xc}(n) \) can be computed with high accuracy and fitted a some simple analytical form, as e.g. in the following parameterization (Perdew-Zunger) of the Monte-Carlo results by Ceperley and Alder. In Ry atomic units:

\[
e_{xc}(n) = \begin{cases} 
-0.9164 - 0.2846(1+1.0529\sqrt{r_s}+0.3334r_s), & r_s \geq 1 \\
-0.9164 - 0.0960 + 0.0622 \ln r_s - 0.0232 r_s + 0.0040 r_s \ln r_s, & r_s \leq 1.
\end{cases}
\] (12.12)

Here \( r_s = (3/4\pi n)^{1/3} \), a parameter traditionally used in the theory of metals. One recognizes in the first term Hartree-Fock exchange energy, so the remaining terms are refereed to as “correlation”. The exchange-correlation potential can be computed as functional derivative of the energy, Eq. (12.8), that in this case reduces to simple derivation:

\[
V_{xc}(r) = \left( e_{xc}(n) + \rho \frac{de_{xc}(n)}{dn} \right)_{n=\rho(r)}.
\] (12.13)
In spite of its simplicity, and of its derivation from an electron gas model that wouldn’t look suitable to describe real, highly inhomogeneous materials, LDA gives surprising good results for several properties (e.g. bond lengths, crystal structures, vibrational frequencies) of a large class of materials (e.g. sp bonded semiconductors). It also gives (unsurprisingly) bad results for other properties (e.g. band gap) and for other cases (e.g. transition metals). A number of functionals have been proposed with various degrees of sophistication, extending DFT to a much larger class of properties and of materials. The search for better functionals is currently a very active field of research.

12.4 Structure of a DFT code

The basic algorithm for the solution of the DFT problem, as implemented in code \texttt{ah.f90}, consists in a self-consistent loop in which, at iteration \( n \):

1. the KS potential \( V_{KS}^{(n)} \) is computed from \( \rho^{(n)} \).
2. KS equations are solved, yielding KS orbitals \( \psi_i^{(n)} \);
3. the output charge density \( \rho_{\text{out}}^{(n)} \) is calculated by summing the square of all occupied KS orbitals: \( \rho_{\text{out}}^{(n)} = \sum_i |\psi_i^{(n)}|^2 \);
4. the new charge density \( \rho^{(n+1)} \) is computed from a linear combination of previous input \( \rho^{(n)} \) and output \( \rho_{\text{out}}^{(n)} \) charge densities.

The loop is started with some suitable initial choice of the charge density, is iterated until self-consistency is achieved, i.e. \( \rho_{\text{out}}^{(n)} = \rho^{(n)} \) according to some pre-defined criterion (see Ch.\ref{ch-selfconsistency} for an introduction to self-consistency). At the end of the loop, the DFT energy can be computed, using either Eq.\((12.4)\) or Eq.\((12.9)\). The total energy will be given by the sum of the DFT energy and of the nuclear repulsion energy.

Let us focus on a periodic system with a plane-wave basis set. We consider a simple but nontrivial case: Si crystal using Appelbaum-Hamann (Phys. Rev. \textbf{B} \textit{8}, 1777 (1973)) pseudopotentials. We use the definitions of lattice, reciprocal lattice, Bloch vector, plane-wave basis set as in code \texttt{cohenbergstresser}, introduced in Ch.\ref{ch-reverse} as well as conventional (LAPACK) diagonalization and the “simple mixing” algorithm of Sec.\ref{sec-simple-mixing}:

\[
\rho^{(n+1)} = \beta \rho_{\text{out}}^{(n)} + (1 - \beta) \rho^{(n)}, \quad 0 < \beta \leq 1. \tag{12.14}
\]

for achieving self-consistency.\footnote{But not the only one: it is also possible to directly minimize the energy functional \url{http://www.fisica.uniud.it/%7Egiannozz/Corsi/MQ/Software/F90/ah.f90}}

New algorithms in code \texttt{ah.f90} deal with the calculation of

1. matrix elements of the pseudopotential;\footnote{Serious codes use iterative diagonalization, similar to the Lanczos method of Ch.\ref{ch-lanczos} and more sophisticated algorithms for self-consistency.}
2. charge density from KS orbitals;
3. self-consistent potential from the charge density.

In the following we examine in some detail these cases.

### 12.4.1 Matrix elements of the potential

In order to compute matrix elements of the Hamiltonian, we need the pseudopotential form factors, Eq. (10.16). This is done in function \texttt{form\_factor}. The Appelbaum-Hamann pseudopotential for Si is given as the sum of two terms, one long-ranged, one short-ranged. The former is the electrostatic potential $v_{lr}$ generated by a charge density distribution $\rho$: 

$$v_{lr}(r) = -q_e^2 \int \frac{\rho_{at}(r')}{|r - r'|} d^3 r', \quad \rho_{at}(r) = 4 \left(\frac{\alpha}{\pi}\right)^{3/2} e^{-\alpha r^2}. \quad (12.15)$$

Note that both $\rho_{at}$ and $v_{lr}$ are spherically symmetric, and so are their Fourier transforms. You may want to verify that $\rho_{at}$ integrates to four. Appelbaum-Hamann pseudopotentials describe in fact a Si$^{4+}$ (pseudo-)ion, interacting with four valence electrons of Si.

The short-ranged potential has the form

$$v_{sr}(r) = e^{-\alpha r^2} (v_1 + v_2 r^2). \quad (12.16)$$

$\alpha, v_1, v_2$ are adjustable parameters provided in the paper. The form factor of the electrostatic term:

$$\tilde{v}_{lr}(G) = -\frac{4\pi q_e^2}{\Omega} \int \rho_{at}(r') e^{-iG \cdot r} d^3 r \quad (12.17)$$

can be computed by rearranging the integral:

$$\tilde{v}_{lr}(G) = -\frac{4\pi q_e^2}{\Omega} \int \left(\frac{1}{|r - r'|} e^{-iG \cdot (r - r')} d^3 r' \right) \rho_{at}(r') e^{-iG \cdot r'} d^3 r'. \quad (12.18)$$

The integral between brackets can be brought by a change of variable to the following known result:

$$\int \frac{1}{r} e^{-i\mathbf{q} \cdot \mathbf{r}} d^3 r = \frac{4\pi}{q_e^2}. \quad (12.19)$$

Finally:

$$\tilde{v}_{lr}(G) = -4\pi q_e^2 \tilde{\rho}_{at}(G), \quad \tilde{\rho}_{at}(G) = \frac{1}{\Omega} \int \rho_{at}(r) e^{-iG \cdot r} d^3 r. \quad (12.20)$$

The equation on the left has a general validity: it is the solution of the Poisson equation in Fourier space and is used also to compute the Hartree potential from the charge. The Fourier transform of a Gaussian is known (see Eq. (9.16)). One finally finds

$$\tilde{v}_{lr}(G) = -4\pi q_e^2 e^{-G^2/4\alpha} \frac{1}{G^2}, \quad (12.21)$$
and for the short-range term:

$$v_{sr}(G) = q^2 e^\left(\frac{\pi}{\alpha}\right)^{3/2} \left( v_1 + v_2 \left( \frac{3}{2} - \frac{G^2}{4\alpha} \right) \right) e^{-G^2/4\alpha}. \quad (12.22)$$

The careful reader will notice that the $G = 0$ term diverges as $-4q^2_e/G^2$. This is due to the presence of the long-range Coulomb term. The divergence, however, cancels out, at least in neutral systems, with the divergence of opposite sign coming from the Hartree potential of electrons. The $G = 0$ term can be evaluated in practice by taking the $G \to 0$ limit and throwing away the divergent term $-4\pi q^2_e/G^2$.

### 12.4.2 FFT and FFT grids

The three-dimension generalization of the Discrete Fourier-Transform algorithm introduced in Sec. 9.1.5 is needed. We define a real-space grid of points $r_{jmn}$, spanning the unit cell, as

$$r_{jmn} = \frac{j}{n_1} a_1 + \frac{m}{n_2} a_2 + \frac{n}{n_3} a_3, \quad (12.23)$$

where the integer indices $j, m, n$ run from 0 to $n_1 - 1, n_2 - 1, n_3 - 1$, respectively; and a corresponding reciprocal-space grid of vectors $G_{hkl}$, as

$$G_{hkl} = \frac{h}{n_1} b_1 + \frac{k}{n_2} b_2 + \frac{l}{n_3} b_3, \quad (12.24)$$

where the integer indices $h, k, l$ run from 0 to $n_1 - 1, n_2 - 1, n_3 - 1$ and are known as Miller’s indices. These are stored into array $\text{mill}$, while array $\text{indg}$ returns the index of the $G$ vector as a function of Miller indices. The factors $n_1, n_2, n_3$ are chosen big enough to include all Fourier components (see next section). These grids are referred to as “FFT grids”.

It can be easily verified that the discretized version of the three-dimensional Fourier Transform:

$$\tilde{F}(G) = \frac{1}{\Omega} \int F(r) e^{-i G \cdot r} d^3 r, \quad (12.25)$$

where $\Omega$ is the volume of the unit cell, can be written as follows:

$$\tilde{F}_{hkl} = \frac{1}{n_1 n_2 n_3} \sum_{j=0}^{n_1-1} e^{-2\pi i h j/n_1} \sum_{m=0}^{n_2-1} e^{-2\pi i k m/n_2} \sum_{n=0}^{n_3-1} e^{-2\pi i l n/n_3} F_{jmn}. \quad (12.26)$$

while the corresponding inverse transform:

$$F(r) = \sum_G \tilde{F}(G) e^{i G \cdot r} \quad (12.27)$$

(valid for periodic functions) can be written as

$$F_{jmn} = \sum_{h=0}^{n_1-1} e^{2\pi i h j/n_1} \sum_{k=0}^{n_2-1} e^{2\pi i k m/n_2} \sum_{l=0}^{n_3-1} e^{2\pi i l n/n_3} \tilde{F}_{hkl}. \quad (12.28)$$

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6 Handle with care! there are many subtleties about divergent terms in periodic system, but they are beyond the scope of these lecture notes.
Routine `invfft` implements Eq. (12.28), while routine `fwfft` implements Eq. (12.26) without the factor $1/n_1n_2n_3$. Note that, as in Sec. 9.1.3, both the real- and the reciprocal-space grids are periodic, so $\mathbf{G}$–vectors with negative indices $hkl$ appear “at the other end of the box”. Also note that the “inverse” transform is exactly so: if you apply a FT to a function and then the inverse FT, or vice versa, you get exactly the starting function.

Why is FFT important? because it allows to quickly jump between real to reciprocal space, performing the required operations in the space where it is more convenient. Such “dual-space” technique is fundamental in modern DFT codes based on plane waves to achieve high performances in terms of speed.

### 12.4.3 Computing the charge density

The calculation of the charge density requires a sum (actually, an integral) over an infinitely dense set of Bloch vectors (or ”k-points”) covering the entire Brillouin Zone. This apparently hopeless task can in fact be accomplished by approximating the integral with a discrete sum over a finite grid of Bloch vectors. For insulators and semiconductors, quite accurate results can be obtained with relatively coarse grids of points. This method is often referred to as ”special points technique”. In our sample code, we use a really ”special” k-point:

$$\mathbf{k}_0 = \frac{2\pi}{a_0} (0.6223, 0.2953, 0)$$

(12.29)

fully exploiting the fcc lattice symmetry, also known as mean-value point\(^7\). The calculation of the charge density reduces to

$$\rho(\mathbf{r}) = \sum_{\nu=1}^{4} |\psi_{\mathbf{k}_0,\nu}(\mathbf{r})|^2.$$  

(12.30)

In spite of its simplicity, this approximation is remarkably good. Since the expensive part of the calculation is typically the diagonalization of the KS Hamiltonian, that must be done for each k-point, this choice reduces the computational burden to the strict minimum.

The actual calculation of the charge density is performed in real space using FFT’s (see subroutine `sum_charge`), but it is instructive to look at how the same calculation would appear if performed in reciprocal space. With straightforward algebra:

$$\rho(\mathbf{G}) = \sum_{\nu, \mathbf{G}'} \psi_{\mathbf{k}_0,\nu}(\mathbf{G} - \mathbf{G}') \psi_{\mathbf{k}_0,\nu}(\mathbf{G}').$$

(12.31)

As a consequence is that the largest $\mathbf{G}$-vector appearing in $\rho(\mathbf{G})$ has modulus twice as large as the largest $\mathbf{G}$-vector appearing in $\psi(\mathbf{G})$. This gives a prescription to choose the $n_1, n_2, n_3$ factors defining the FFT grid: they must be large enough to accommodate $\mathbf{G}$-vectors up to a maximum cutoff $E_\rho = 4E_{cut}$, where $E_{cut}$ is the cutoff for the plane waves basis set, Eq. (10.7). This choice guarantees that no Fourier components are “lost” when computing the charge density.

\(^7\)A. Baldereschi, Phys. Rev. B \textbf{7}, 5212 (1973)
12.4.4 Computing the potential

The self-consistent potential appearing in the Kohn-Sham equations, Eq. (12.8), consists of two terms, the Hartree and the exchange-correlation term. Pseudopotentials are built to work in conjunction with a specific kind of exchange-correlation functional. Appelbaum-Hamann pseudopotentials work together with "Slater exchange", Eq. (12.10), the simplest and less accurate functional.

The self-consistent potential is computed in subroutine \texttt{v.of.rho}.

**Calculation of XC potential**  The exchange-correlation potential (exchange only in our case) can be conveniently and directly computed on the real-space grid. In the following few lines, \texttt{rho} is the charge density, \texttt{vr} the potential \( V_{xc}(r) \):

```fortran
do n3=1,nr3
  do n2=1,nr2
    do n1=1,nr1
      vr(n1,n2,n3) = -e2*(3.0_dp*rho(n1,n2,n3)/pi)**(1.0_dp/3.0_dp)
    end do
  end do
end do
```

Since we need \( V(G) \) to fill the Hamiltonian matrix, we Fourier-transform the potential, storing it in vector \texttt{vg}.

**Hartree potential**  The Hartree potential can be conveniently computed in reciprocal space. Straightforward algebra shows that \( V_H(G) \) can be written as

\[
V_H(G) = 4\pi q_e \frac{\rho(G)}{G^2}.
\]  

This is nothing but the solution of the Poisson equation in Fourier space. The diverging \( G = 0 \) term is compensated (in neutral systems) by the same term coming from pseudopotentials. The lines

```fortran
do ng =1, ngm
  if ( g2(ng) > eps ) vg(ng) = vg(ng) + fpi*e2*rhog(ng)/g2(ng)
end do
```

add, for \( G \neq 0 \), to \texttt{vg} the Hartree potential directly computed from \texttt{rhog} (charge in reciprocal space) and \texttt{g2}, square modulus of \( G \).