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“Thanks to my solid academic training, today I can write hundreds of words on virtually any topic without possessing a shred of information, which is how I got a good job in journalism.”

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Abstract

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by Asier RODRÍGUEZ ESCALANTE

The Thesis Abstract is written here (and usually kept to just this page). The page is kept centered vertically so can expand into the blank space above the title too...

Acknowledgements

The acknowledgments and the people to thank go here, don't forget to include your project advisor...

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List of Abbreviations

DFT	D ensity F unctional T heory
HK	H ohenberg- K ohn
KS	K ohn- S ham
NEGF	N on E quilibrium G reen's F unction

Physical Constants

Speed of Light $c_0 = 2.997\,924\,58 \times 10^8 \text{ m s}^{-1}$ (exact)

List of Symbols

a	distance	m
P	power	W (J s ⁻¹)
ω	angular frequency	rad

For/Dedicated to/To my...

Chapter 1

Theoretical and computational tools

1.1 Density Functional Theory

Density-functional theory (DFT) is an approach to study the electronic structure of many-body problems, which allows the computational treatment large and complex systems. In fact, one of the reasons why DFT has become an essential tool in many areas of physics including condensed-matter theory is the increasing availability and power of computational processing. DFT is mainly based on the fact that any property of a system of many interacting particles can be viewed as a functional of the ground state density [**martin]. The famous paper by Hohenberg and Kohn in 1964 [** in martin] laid the groundwork of modern DFT, while the formulation presented in a 1965 paper by Kohn and Sham [** in martin] has prevailed as one of the most useful approaches up to this day. In the following subsections we will present the basics of this method, and then review a specific implementation, namely SIESTA, which will be used throughout this work.

1.1.1 Basics of DFT

The main problem to be solved is the many-body time-independent Schrödinger's equation, in the spin-unpolarized case:

$$H |\Psi(\{\mathbf{r}\}, \{\mathbf{R}\})\rangle = E |\Psi(\{\mathbf{r}\}, \{\mathbf{R}\})\rangle, \quad (1.1)$$

where $\{\mathbf{r}\}$ and $\{\mathbf{R}\}$ are the electron and ion position vectors, respectively. The most basic Hamiltonian contains a kinetic term plus a potential energy term describing two particle interactions: electron-ion, electron-electron and ion-ion [** martin]:

$$\begin{aligned} H &= T_e + V_{en} + V_{ee} + T_n + V_{nn} \\ &= -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 - \sum_{i,I} \frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \\ &\quad - \sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|}, \end{aligned} \quad (1.2)$$

which after the well-known Born-Oppenheimer approximation [** martin], whereby electrons are adiabatically separated from ions owing to their large mass difference, can be replaced with

$$H \equiv H_e = T_e + V_{en} + V_{ee}, \quad (1.3)$$

so that the corresponding electron eigenfunctions only depend on $\{\mathbf{R}\}$ parametrically. As the name implies, DFT is based upon electron density rather than the explicit wavefunctions, and it does so through two theorems first proved by Hohenberg and Kohn [** martin], which we will now describe. The ground-state wavefunction satisfies¹

$$\mathbf{H} |\Psi_0\rangle = (\mathbf{T}_e + \mathbf{V}_{\text{ext}} + \mathbf{V}_{\text{ee}}) |\Psi_0\rangle = E_0 |\Psi_0\rangle, \quad (1.4)$$

so along with the ground-state energy it is determined by the external potential. Therefore, so is the density, since the wavefunction is a unique functional of this quantity by the relation [** Solyom]

$$n_e(\mathbf{r}) = N_e \int d\mathbf{r}_2 \cdots \int d\mathbf{r}_{N_e} |\Psi(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_{N_e})|^2 \quad (1.5)$$

where N_e is the total number of electrons. The first Hohenberg-Kohn theorem states that this relationship between the external potential and the density is bilateral.

Theorem 1 *The ground-state wavefunction $|\Psi_0\rangle$, and hence the ground-state expectation values of any observable, is a unique functional of the ground-state density $n_e(\mathbf{r})$.*

Thus, $n_e(\mathbf{r})$ univocally determines \mathbf{V}_{ext} , and so we can write the following functional relation

$$E[n_e(\mathbf{r})] = F[n_e(\mathbf{r})] + \int d\mathbf{r} V_{\text{ext}}(\mathbf{r}) n_e(\mathbf{r}), \quad (1.6)$$

where F is the Hohenberg-Kohn functional defined by [** papi]

$$\begin{aligned} F[n_e(\mathbf{r})] &= \langle \Psi_0 | \mathbf{T}_e + \mathbf{V}_{\text{ee}} | \Psi_0 \rangle = T_e[n_e(\mathbf{r})] + E_{\text{ee}}[n_e(\mathbf{r})] \\ &= T_e[n_e(\mathbf{r})] + E_{\text{H}}[n_e(\mathbf{r})] + E_{\text{Q}}[n_e(\mathbf{r})], \end{aligned} \quad (1.7)$$

where we detach from the electron-electron interaction energy the Hartree term, which describes the classical self-interaction of the electron density:

$$E_{\text{H}}[n_e(\mathbf{r})] = \frac{e^2}{2} \int d\mathbf{r} d\mathbf{r}' \frac{n_e(\mathbf{r}) n_e(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \quad (1.8)$$

and express the rest as a non-classical part. Without prior knowledge of the ground-state density, one may find it using the second Hohenberg-Kohn theorem, which is based on the variational principle.

Theorem 2 *The energy as a functional of some trial density takes its minimum at the true ground-state density.*

Thus, the ground-state energy satisfies

$$E_0 = \min E[n_e(\mathbf{r})], \quad \text{with} \quad \int d\mathbf{r} n_e(\mathbf{r}) = N_e. \quad (1.9)$$

However, this minimization cannot be easily carried out in practice, due to the many-body nature of the problem which hinders finding the form of the Hohenberg-Kohn functional. Moreover, even though the density is in principle sufficient to

¹Note that we write \mathbf{V}_{ext} instead of the electron-ion potential for generality, but the former usually includes the latter.

extract any other property of the material, there is no feasible algorithm to do it in the exact case [** martin]. In order to circumvent this problem, Kohn and Sham proposed a way to approximate this functional[** in martin]. The main idea is to replace the interacting system with a non-interacting one, where a functional for the kinetic energy is known, and which contains an effective one-particle potential V_{eff} such that the original density is reproduced. Therefore, the individual particles in this auxiliary problem satisfy

$$\left(-\frac{1}{2} + \nabla^2 + V_{\text{eff}}(\mathbf{r})\right) \psi_i^{\text{KS}} = \epsilon_i \psi_i^{\text{KS}}, \quad (1.10)$$

so that the total auxiliary wavefunction $|\Psi_{\text{KS}}\rangle$ is given by the Slater determinant of these one-particle wavefunctions. The density is then given by

$$n_e(\mathbf{r}) = \sum_{i=1}^{N_e} \left| \psi_i^{\text{KS}}(\mathbf{r}) \right|^2, \quad (1.11)$$

and the kinetic energy functional in this system is now

$$T_{\text{KS}} = \langle \Psi_{\text{KS}} | T | \Psi_{\text{KS}} \rangle = \frac{1}{2} \sum_{i=1}^{N_e} \int d\mathbf{r} \left| \nabla \psi_i^{\text{KS}}(\mathbf{r}) \right|^2. \quad (1.12)$$

This is of course different from the many body kinetic energy, because we have neglected many body effects. Since the density is the same in both problems, these can be taken into account via the so-called exchange-correlation energy, defined as

$$E_{\text{xc}}[n_e] = T_e[n_e] - T_{\text{KS}}[n_e] + E_{\text{Q}}[n_e]. \quad (1.13)$$

Thus, the Hohenberg-Kohn functional reads

$$F[n_e] = T_{\text{KS}}[n_e] + E_{\text{H}}[n_e] + E_{\text{xc}}[n_e], \quad (1.14)$$

so the minimization of the energy functional 1.6 reveals that[**martin]

$$V_{\text{eff}} = V_{\text{ext}}(\mathbf{r}) + e^2 \int d\mathbf{r}' \frac{n_e(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + V_{\text{xc}}[n_e], \quad (1.15)$$

where the middle term is the Hartree potential $V_{\text{H}}[n_e]$. Then, if the exchange-correlation potential were known, the Kohn-Sham equation 1.10 could be solved self-consistently, by using an initial guess of n_e , calculating V_{eff} with it, solving the Kohn-Sham equations to obtain the wavefunctions which define n_e , and so on until convergence is reached.

However, the exact form for E_{xc} is unknown[** martin], so DFT is reduced to finding the useful approximations. The simplest approximation is the local-density approximation (LDA)[**ks in kretz] which assumes E_{xc} only depends on the density locally, that is, the density never simultaneously evaluated at two points (\mathbf{r} and \mathbf{r}') inside the integral. Another widely used approximation is the generalized-gradient approximation (GGA)[**martin], where the gradient is also allowed to appear inside the integral, which introduces some non-locality. Throughout this work we will be using the PBE[** in kretz] flavour of GGA.

1.1.2 SIESTA

summary: In this method the effect of the core electrons is described by soft norm-conserving pseudopotentials and the electronic structure of the valence electrons is expanded in a basis set of numerical atomic orbitals with finite range

Bibliography

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