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Abstract

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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	Density Functional Theory
FFT	Fast Fourier Transform
GGA	Generalized Gradient Approximation
HK	Hohenberg-Kohn
KB	Kleinman-Bylander
KS	Kohn-Sham
LDA	Local Density Approximation
NA	Neutral Atom
NAO	Numerical Atomic Orbital
NEGF	Non Equilibrium Green's Function
PAO	Pseudo Atomic Orbital
PBE	Perdew-Burke-Ernzerhof
PW	Plane Wave
SCF	Self-Consistent Field

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 extract any other property of the material, there is no feasible algorithm to do it in the exact case [** martin].

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

Kohn-Sham equations

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 bmr') 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

SIESTA^[** siesta paper] is an implementation of DFT that solves the Kohn-Sham equations. This code describes the effect of core electrons using soft norm-conserving pseudopotentials, and uses a basis set of numerical atomic orbitals with finite range to represent the electronic structure of valence electrons. All while keeping calculations of order N ($\mathcal{O}(N)$) with respect to system size (number of atoms).

Pseudopotentials

The one particle KS equation presents the numerical difficulty of dealing accurately with both core and valence electrons. Core electrons are those that do not participate in chemical bonding. Core eigenvalues are much lower than valence eigenvalues, and their wavefunctions are highly localized around the nuclei, which make them chemically inert.

Regarding valence electrons, the hermiticity of the Hamiltonian means their wavefunctions are orthogonal to the core wavefunctions. Therefore, the Fourier expansion of their wavefunction has a big contribution of short wavelengths near the nucleus, and in order to get a good approximation a large number of plane waves (or a denser real-space grid) would be needed, which makes calculations more expensive.

In order to overcome this problem, the dynamics of the core electrons is ignored and their effect is replaced by an effective potential. The effect of core electrons on valence wavefunctions can then be eliminated by replacing the oscillating part near the nucleus by a smoother function. This is done by defining an adequate pseudopotential.

Given a reference atomic configuration, Hammann *et al* give a few requirements an adequate pseudopotential must meet^[**Hamann], which ensure the smoothness and transferability of the pseudopotential:

1. All-electron and pseudo-wavefunction valence eigenvalues must be the same.
2. All-electron and pseudo-wavefunctions must be the same beyond a chosen cutoff radius R_c .
3. The logarithmic derivatives of the all-electron and pseudo-wavefunctions must coincide at R_c .
4. The integrals from 0 to R_c of the real and pseudo charge densities must agree for $r > R_c$ for each valence state (norm conservation).

While satisfying these, the user has freedom to specify their desired pseudopotential. In order to generate it, the radial Schrödinger equation for all electrons is solved for the given configuration:

$$\left[-\frac{1}{2} \frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} + V_{\text{eff}}[n_e](r) \right] u_{nl}(r) = \epsilon_{nl} u_{nl}(r), \quad (1.16)$$

where (dropping the KS superscript) $\psi_{nlm}(\mathbf{r}) = \frac{1}{r} u_{nl}(r) Y_{lm}(\theta, \phi)$, and V_{eff} is given by equation 1.15 with $V_{\text{ext}} = -Z/r$. Note that for a single atom V_{eff} only has radial dependence. Next, the pseudo-wavefunctions $u_{nl}^{\text{PS}}(r)$ are created (the part

where $r < R_c$) following the previous specifications, or other similar parametrization schemes like Troullier-Martins [^{**} in telaviv]. Now, one can use equation 1.16, after substituting these pseudo-wavefunctions, in order to solve for V_{eff} , which will now be l -dependent. The unscreened pseudopotential V_l^{PS} is obtained by subtracting the Hartree and exchange-correlation potential (as in equation 1.15) calculated only for the valence electrons with the pseudo-wavefunctions; that is, with the electron density given by

$$n(r) = \sum_l \left| u_{nl}^{\text{PS}}(r) \right|^2. \quad (1.17)$$

The full pseudopotential will be the l -sum of the V_l^{PS} pseudopotentials, which can be further separated into a local (l independent) part that represents the contributions of big l which are similar, and a non-local part which depends strongly on (small) l :

$$\begin{aligned} V^{\text{PS}}(\mathbf{r}) &= \sum_{lm} V_l^{\text{PS}}(\mathbf{r}) |lm\rangle\langle lm| \\ &= V_{\text{local}}(\mathbf{r}) + \sum_{lm} \delta V_l(\mathbf{r}) |lm\rangle\langle lm| \end{aligned} \quad (1.18)$$

In SIESTA, the Kleinman-Bylander form [^{**} in siestapaper] is used which greatly reduces the amount of integrals to be computed. The Hamiltonian used in SIESTA then reads

$$H = T + \sum_l V_l^{\text{local}}(\mathbf{r}) + \sum_l V_l^{\text{KB}} + V_{\text{H}}(\mathbf{r}) + V_{\text{xc}}(\mathbf{r}). \quad (1.19)$$

In this work, we will use GGA-PBE pseudopotentials from ^{***}website.

Basis sets

In order to solve the Kohn-Sham differential equations numerically, these are turned into finite matrix equations by the use of basis sets. One can expand the KS wavefunction in terms of the wavefunctions in the basis set:

$$\psi_i(\mathbf{r}) \simeq \sum_{\mu} \phi_{\mu}(\mathbf{r}) c_{\mu,i}, \quad (1.20)$$

where now we wish to obtain the $c_{\mu,i}$ coefficients. Strict equality is achieved when the basis set is complete, which requires an infinite number of wavefunctions, so the goal is to span as much as possible of the whole Hilbert space with a finite basis set. Using this, the KS equation $H\psi_i = \epsilon_i\psi_i$ becomes

$$\sum_{\mu} H_{\nu\mu} c_{\mu,i} = \epsilon_i \sum_{\mu} S_{\nu\mu} c_{\mu,i}, \quad (1.21)$$

where

$$\begin{aligned} H_{\nu\mu} &\equiv \int d\mathbf{r} \phi_{\nu}^*(\mathbf{r}) H \phi_{\mu}(\mathbf{r}), \\ S_{\nu\mu} &\equiv \int d\mathbf{r} \phi_{\nu}^*(\mathbf{r}) \phi_{\mu}(\mathbf{r}) \end{aligned} \quad (1.22)$$

are the Hamiltonian and overlap matrices. Since the basis set is usually non-orthogonal ($S_{\mu\nu} \neq \delta_{\mu\nu}$), equation 1.21 defines a generalized eigenvalue problem to be solved numerically.

The most popular basis sets are either based on plane waves (for example, in Quantum Espresso^[**]) or atomic-like orbitals, as is done in SIESTA. These are defined by a radial function times a spherical harmonic, and are usually (but not necessarily) centered around the nuclei ^[** siesta paper]:

$$\phi_{Ilmn}(\mathbf{r}) = \phi_{Il n}(r_I) Y_{lm}(\hat{\mathbf{r}}_I), \quad (1.23)$$

where $\mathbf{r}_I = \mathbf{r} - \mathbf{R}_I$ and n labels different wavefunctions with the same angular dependence. Particularly in SIESTA, the radial function has finite support, so it is zero above a certain cutoff radius. This ensures the sparsity of the Hamiltonian and overlap matrices, and allows $\mathcal{O}(N)$ calculations. Then, $\phi_{Il n}(r_I)$ is defined numerically for discrete radial distances. A disadvantage of NAOs when compared to PWs is the lack of systematic convergence, which is done through the choice of basis sets.

Some of the most common basis sets are inherited from quantum chemistry. The minimal (or single- ζ) basis uses atomic orbitals of at least partly occupied states, that is, actual numerical solutions of the single-particle KS for a free (pseudo-)atom. On top of this, a hard confining potential is added, which defines a cutoff radius for the basis wavefunctions. This potential bumps the orbital up in energy, and this energy shift which is related to the cutoff radius can be specified by the user.

In order to add some radial flexibility, multiple- ζ basis sets are used, which have several wavefunctions with different radial part for each spherical harmonic. These radial functions are usually generated using the ‘split-valence’ method ^[** siestapaper 35]. Further, to give some angular flexibility (to account for bond formation, for instance), higher angular momentum shells are used, which are obtained by a perturbative polarization of the an l orbital with an electric field, so that the form of the $l + 1$ is obtained ^[** siestapaper]. In this work, we will mostly use the double- ζ polarized (DZP) basis.

Integrals

The Hamiltonian 1.19 can be rewritten in a more useful way, by noticing that the local potential plus the effect of valence electrons calculated for the free pseudo-atom goes asymptotically to zero, since the atom becomes neutral, and strictly to zero when the basis functions are zero beyond the cutoff radius ^[** siesta paper]. For each atom, we can write the density as $\rho_I = \rho_I^{\text{atom}} + \delta\rho$, where ρ_I^{atom} is the density of the aforementioned valence electrons. The Hartree potential is linear in the density, so summing the contributions from all atoms we can write it similarly as $V_H = V_H^{\text{atom}} + \delta V_H$, we can define

$$V_I^{\text{NA}} = V_I^{\text{local}} + V_I^{\text{atom}}, \quad \text{with} \quad \sum_I V_I^{\text{atom}} = V_H, \quad (1.24)$$

whose terms will exactly cancel beyond the cutoff radius. 1.19 can then be rewritten as

$$H = T + \sum_I V_I^{\text{KB}} + V_I^{\text{NA}}(\mathbf{r}) + \delta V_H(\mathbf{r}) + V_{\text{xc}}(\mathbf{r}). \quad (1.25)$$

The matrix elements of the first two terms of this equation, as well as the overlap integrals, can be calculated using so-called two-centered integrals. Owing to the cutoff radius of the basis functions, there is a maximum distance $R_{\text{max}} = r_1^c + r_2^c$ up to which the matrix elements are nonzero. Taking advantage of this, SIESTA

calculates these integrals in reciprocal space using a special FFT[** siestapaper] and then tabulates and stores the values in a radial grid, so that later an interpolation can be made from that table.

The last three potential terms of equation 1.25 depend on the position, so their matrix elements are calculated on a real-space grid whose fineness is controlled by an energy cutoff, corresponding to the maximum kinetic energy of the planewaves that can be represented in the grid without aliasing [** siestapaper]. The density matrix *****doit***** is essential to calculate $\delta V_H(\mathbf{r})$ and $V_{xc}(\mathbf{r})$.

Self-consistent field cycle

SCF, mixing (pulay)

Forces and relaxation

Forces and relaxation

1.2 The SISL package

Chapter 2

Study of nanoporous graphene

2.1 Plain NPG

2.2 Double-pore NPG

2.3 Functionalized nanoporous graphene