Chapter 2

Density-Functional Theory

2.1 The Many-Body Problem

Since the formulation of the Schrödinger equation in the 1920s the ultimate goal of quantum mechanics has been to find at least approximate solutions of this equation for systems containing more then just two mutually interacting particles (like the one-proton and one-electron structure of the hydrogen atom, for which an exact solution can be derived). The result would be a powerful tool to understand and predict material properties without depending on experimental data. The time-independent, non-relativistic Schrödinger equation can be written as

$$H\Psi(\mathbf{x}_i, \mathbf{R}_A) = E\Psi(\mathbf{x}_i, \mathbf{R}_A) \quad . \tag{2.1}$$

The equation describes an eigenvalue problem of the Hamilton operator H with the total energy E of the system as eigenvalue and the many-body wave function $\Psi(\mathbf{x}_i, \mathbf{R}_A)$ as eigenfunction. Any system is then explicitly characterized by the corresponding wave function $\Psi(\mathbf{x}_i, \mathbf{R}_A)$, which depends on the combined spatial and spin coordinates of the electrons $\mathbf{x}_i = (\mathbf{r}_i, \sigma_i)$ and the spatial coordinates of the nuclei $\mathbf{R}_A$ (for an introduction to quantum mechanics see e.g. Refs. [32, 33]). A dependence on the spin coordinates σ_i is necessary, since in contrast to a relativistic treatment, where the electron spin arises naturally, in the non-relativistic approach the electron spin has to be introduced additionally. In atomic units (i.e. $m_\mathrm{e} = \hbar = \mathrm{e} = 1$) the Hamilton operator for a system containing N electrons and M nuclei is given by

$$H = -\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 - \frac{1}{2}\sum_{A=1}^{M}\frac{1}{m_A}\nabla_A^2 - \sum_{i=1}^{N}\sum_{A=1}^{M}\frac{Z_A}{\mathbf{r}_{iA}} + \sum_{i=1}^{N}\sum_{j>i}^{N}\frac{1}{\mathbf{r}_{ij}} + \sum_{A=1}^{M}\sum_{B>A}^{M}\frac{Z_A Z_B}{\mathbf{R}_{AB}} \quad . \tag{2.2}$$

Here, the indices i and j run over the N electrons whereas A and B run over the M nuclei. ∇_i^2 is the Laplacian operator acting on particle i, m_A is the mass of the nucleus A and Z_A its nuclear charge. $\mathbf{r}_{ij}$ is the distance between particles i and j, i.e. $\mathbf{r}_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$, resp. $\mathbf{r}_{iA} = |\mathbf{r}_i - \mathbf{R}_A|$. The Hamilton operator consists of five parts:

the kinetic energy operators T_e and T_n for the electrons and the nuclei, the Coulomb interaction between electrons and nuclei V_en and the repulsive interaction between the electrons V_ee resp. between the nuclei V_nn, so that Eq. (2.2) can be shortly written as

$$H = T_\mathrm{e} + T_\mathrm{n} + V_\mathrm{en} + V_\mathrm{ee} + V_\mathrm{nn} \quad . \tag{2.3}$$

Although the Hamilton operator is known, Eq. (2.1) is far too complex to be solved due to the large number of variables the wave function Ψ depends on. In a system containing N electrons and M nuclei there are $4N + 3M$ degrees of freedom resulting from the $3N$ spatial coordinates, $\{\mathbf{r}_i\}$, and N spin coordinates, $\{\sigma_i\}$, of the electrons and the $3M$ spatial coordinates, $\{\mathbf{R}_A\}$, of the nuclei, respectively. A first step in simplifying Eq. (2.1) is the Born-Oppenheimer approximation [34]. Since the nuclei are much heavier than the electrons (already a factor of $\sim$ 1800 for a proton), it is assumed within the Born-Oppenheimer approximation, that the response of the electrons to an external perturbation is much faster than the response of the nuclei. Thus, the electrons would be able follow any movement of the nuclei quasi instantaneously and might then be considered as basically moving in a constant field generated by the nuclei at fixed positions. The kinetic energy term T_n for the nuclei in Eq. (2.3) is set to zero and the repulsion term for the nuclei V_nn enters the total energy as a constant. With this first approximation the *electronic* Schrödinger equation is given by

$$H_\mathrm{e}\Psi_\mathrm{e}(\mathbf{x}_i) = [T_\mathrm{e} + V_\mathrm{en} + V_\mathrm{ee}]\Psi_\mathrm{e}(\mathbf{x}_i) = E_\mathrm{e}\Psi_\mathrm{e}(\mathbf{x}_i) \tag{2.4}$$

with the electronic Hamilton operator H_e, the electronic wave function $\Psi_\mathrm{e}(\mathbf{x}_i, \mathbf{R}_A)$ and the electronic energy $E_\mathrm{e}(\mathbf{R}_A)$. The Born-Oppenheimer potential energy surface can then be obtained by calculating the electronic energy $E_\mathrm{e}(\mathbf{R}_A)$ via Eq. (2.4) and the interaction term between the nuclei V_nn for any given position $\{\mathbf{R}_A\}$ of the nuclei.

Although the Born-Oppenheimer approximation simplifies the original Schrödinger equation considerably, the electronic part in Eq. (2.4) is still only numerically solvable by introducing further approximations. One fundamental approach to solve the electronic Schrödinger equation is the Hartree-Fock approximation [35, 36]. Here the many-body problem is transferred into a single particle problem by approximating the electronic wave function $\Psi_\mathrm{e}(\mathbf{x}_i)$ by a Slater-determinant of single particle wave functions, which ensures the antisymmetry of the wave function. In the Hartree-Fock approach the exchange between electrons as well as the correlated motion of electrons of like spin due to the Pauli principle is taken into account. The correlation resulting from the Coulomb repulsion for all electrons of like and unlike spins is missing. Although Hartree-Fock theory therefore contains a part of the correlation, the so-called Pauli correlation, it is commonly agreed that the term correlation is used for all that is missing in Hartree-Fock. To improve on the original Hartree-Fock approach more involved theories have been developed [32, 33]. Among the most popular are second/fourth order perturbation theory by Møller and Plesset (MP2/MP4) [37], configuration interaction (CI) [32], multiconfiguration self-consistent field (MCSCF) [38] and coupled cluster approaches (CC) [39]. These so-called wave function based methods are mainly used for calculating atoms and molecules (containing up to 50 atoms),

since on the one hand they can be quite accurate, but on the other they also become quite demanding with an increasing number of electrons.

An alternative approach is given by density-functional theory (DFT). In DFT the central quantity is not the wave function $\Psi_\mathrm{e}(\mathbf{x}_i)$, but the electron density $n(\mathbf{r})$. Originating mainly from solid state physics DFT has become more and more popular also in quantum chemistry [40–42].

2.2 The Thomas-Fermi Model

The very first approach to use the electron density $n(\mathbf{r})$ of a system to calculate its total energy was already formulated by Thomas and Fermi in 1927 [43, 44]. The electron density determines the probability of finding any of the N electrons in a volume element $d\mathbf{r}_1$, while the other $N-1$ electrons have arbitrary positions, and is given by

$$n(\mathbf{r}_1) = N \int \cdots \int |\Psi_\mathrm{e}(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N)|^2 d\sigma_1 d\mathbf{x}_2 \ldots d\mathbf{x}_N \quad . \tag{2.5}$$

Compared to the wave function the electron density has the advantage, that it only depends on 3 instead of $3N$ spatial coordinates, but still contains all information needed to determine the Hamiltonian, i.e. the number of electrons N, the positions of the nuclei $\mathbf{R}_A$ and the charge of the nuclei Z_A. N is simply given by the integral over $n(\mathbf{r})$

$$\int n(\mathbf{r}) d\mathbf{r} = N \quad . \tag{2.6}$$

Furthermore $n(\mathbf{r})$ exhibits cusps only at the positions $\mathbf{R}_A$ and the properties of each cusp are clearly related to the nuclear charge Z_A. Taking into account these considerations it seems at least plausible that $n(\mathbf{r})$ is sufficient to determine all properties of a system.

In their model Thomas and Fermi formulated the total energy of a system in terms of its electron density by using the uniform electron gas as a model for the kinetic energy and treating the nuclear-electron attraction and electron-electron repulsion classically

$$E_\mathrm{TF}[n(\mathbf{r})] = \frac{3}{10}(3\pi^2)^{2/3} \int n^{5/3}(\mathbf{r}) d\mathbf{r} - Z \int \frac{n(\mathbf{r})}{\mathbf{r}} d\mathbf{r} + \int \int \frac{n(\mathbf{r}_1) n(\mathbf{r}_2)}{\mathbf{r}_{12}} d\mathbf{r}_1 d\mathbf{r}_2 \quad . \tag{2.7}$$

The actual results obtained by the Thomas-Fermi model for atoms are not very accurate, since there is neither exchange nor correlation included and the Thomas-Fermi kinetic energy functional is only a very coarse approximation to the true kinetic energy. For molecules the description is even worse, since no molecular binding is predicted in the method, which caused the Thomas-Fermi model to be considered as of only little importance for giving quantitative results in atomic, molecular or solid state physics.

Nevertheless Eq. (2.7) is the first example of an expression of the total energy as a functional of the electronic density $n(\mathbf{r})$ without any information about the wave function Ψ. The correct density is then calculated by applying the variational principle to Eq. (2.7) under the constraint of Eq. (2.6). At that time it was just assumed that the variational principle holds for Eq. (2.7). Mathematical this assumption was not proven until almost 40 years later by Hohenberg and Kohn [45].

2.3 The Hohenberg-Kohn Theorems

In 1964 Hohenberg and Kohn formulated two theorems, which formally justified the use of the electron density as basic variable in determining the total energy and which became the foundation of modern density-functional theory [45]. The first theorem states that for a non-degenerate ground state of an electron gas in an external potential V_{ext}, there exists a one-to-one mapping between the external potential V_{ext}, the wave function Ψ_{e} and the electron density $n(\mathbf{r})$. The electron density therefore uniquely defines the external potential (to within a constant). The electronic energy of a system E can then be formulated as a functional of the electron density $n(\mathbf{r})$

$$E[n(\mathbf{r})] = \int n(\mathbf{r}) V_{\text{ext}} d\mathbf{r} + F_{\text{HK}}[n(\mathbf{r})] \quad . \tag{2.8}$$

Here, $F_{\text{HK}}[n(\mathbf{r})]$ is the Hohenberg-Kohn functional, which does not depend on the external potential and is therefore universal. $F_{\text{HK}}[n(\mathbf{r})]$ contains the electron-electron interaction $E_{\text{ee}}[n]$ as well as the kinetic energy of the electrons $T_{\text{e}}[n]$

$$F_{\text{HK}}[n] = T_{\text{e}}[n] + E_{\text{ee}}[n] \quad . \tag{2.9}$$

If one could find an explicit expression for this functional, Eq. (2.8) would provide an exact solution to the Schrödinger equation. Unfortunately an explicit form of the two functionals in Eq. (2.9) is unknown.

The electron-electron interaction can further be divided into the Coulomb repulsion $J[n]$ and a non-classical part $E_{\text{ncl}}[n]$

$$E_{\text{ee}}[n] = \frac{1}{2} \int \int \frac{n(\mathbf{r}_1) n(\mathbf{r}_2)}{\mathbf{r}_{12}} d\mathbf{r}_1 d\mathbf{r}_2 + E_{\text{ncl}}[n] = J[n] + E_{\text{ncl}}[n] \quad . \tag{2.10}$$

The non-classical part $E_{\text{ncl}}[n]$ contains all contributions arising from self-interaction, exchange and Coulomb correlation. Finding good approximations for $T_{\text{e}}[n]$ and $E_{\text{ncl}}[n]$ is still one of the main tasks in density-functional theory.

The second theorem of Hohenberg and Kohn proofs that the variational principle holds for the minimization of the energy with respect to the electron density, i.e. for any arbitrary, well behaved electron density $n(\mathbf{r})$

$$n(\mathbf{r}) \geq 0 \quad \text{and} \quad \int n(\mathbf{r}) d\mathbf{r} = N \tag{2.11}$$

the lowest energy E_0 is only given as a functional of the true ground state density $n_0(\mathbf{r})$

$$E_0 = E[n_0(\mathbf{r})] \leq E[n(\mathbf{r})] \quad . \tag{2.12}$$

As mentioned above an exact form of the Hohenberg-Kohn functional $F_{\mathrm{HK}}[n]$ is not known. Concerning the variational principle this means that the ground state energy obtained with an approximate functional $F_{\mathrm{HK}}[n]$ does not necessarily have to be an upper bound for the energy of the true system ground state. The variational principle can then only give the ground state energy of the system specified by the approximate functional. The minimization of the energy is performed under the constraint of a constant number of electrons N (cf. Eq. (2.11)), which results in the Euler-Lagrange equation

$$\mu = \frac{\delta E[n(\mathbf{r})]}{\delta n(\mathbf{r})} = V_{\mathrm{ext}}(\mathbf{r}) + \frac{\delta F_{\mathrm{HK}}[n(\mathbf{r})]}{\delta n(\mathbf{r})} \tag{2.13}$$

Here, the Lagrange multiplier μ corresponds to the chemical potential of the electrons.

2.4 The Kohn-Sham Equations

In 1965, about a year after the Hohenberg-Kohn theorems were published, Kohn and Sham proposed a way to approximate the universal functional $F_{\mathrm{HK}}[n]$ [46]. The basic concept of their approach is to separate the kinetic energy functional T_{e} into the kinetic energy of a non-interacting reference system T_{s} and an unknown part T_{c}, which contains the corrections due to the interaction between the electrons in the real system. For a non-interacting system of electrons the kinetic energy can be computed exactly using one-particle wave functions φ,

$$T_{\mathrm{s}} = \sum_{i=1}^{N} \langle \varphi_i | -\frac{1}{2}\nabla^2 | \varphi_i \rangle \quad . \tag{2.14}$$

The Hohenberg-Kohn functional can then be expressed as

$$F_{\mathrm{HK}}[n] = T_{\mathrm{s}}[n] + J[n] + E_{\mathrm{xc}}[n] \tag{2.15}$$

with the exchange-correlation energy E_{xc} defined as

$$E_{\mathrm{xc}}[n] \equiv T_{\mathrm{e}}[n] - T_{\mathrm{s}}[n] + E_{\mathrm{ee}}[n] - J[n] \quad . \tag{2.16}$$

The exchange-correlation energy contains the difference in the kinetic energy between the real, interacting system and the non-interacting system as well as the non-classical part of the electron-electron repulsion, E_{ncl}. Following this approach the many-body problem is again mapped onto an effective single particle problem and all unknown

terms are merged into the exchange-correlation part. The one-particle wave functions can now be determined by effective one-particle equations under the constraint to reproduce the density of the real, interacting system. This yields the so-called Kohn-Sham (KS) equations

$$[-\frac{1}{2}\nabla^2 + V_{\text{eff}}(\mathbf{r})]\varphi_i = \epsilon_i \varphi_i \quad , \tag{2.17}$$

with the effective potential $V_{\text{eff}}(\mathbf{r})$ containing the external potential $V_{\text{ext}}(\mathbf{r})$, the classical Coulomb potential and the exchange-correlation potential $V_{\text{xc}}(\mathbf{r})$

$$V_{\text{eff}}(\mathbf{r}) = V_{\text{ext}}(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + V_{\text{xc}}(\mathbf{r}) \quad . \tag{2.18}$$

The density of the real system $n(\mathbf{r})$ can be expressed in terms of the Kohn-Sham orbitals φ_i

$$n(\mathbf{r}) = \sum_i^N |\varphi_i(\mathbf{r})|^2 \quad , \tag{2.19}$$

and the exchange-correlation potential is given by the derivative of the exchange-correlation energy in Eq. (2.16) with respect to the density

$$V_{\text{xc}}(\mathbf{r}) = \frac{\delta E_{\text{xc}}[n(\mathbf{r})]}{\delta n(\mathbf{r})} \quad . \tag{2.20}$$

Since the effective potential V_{eff} already depends on the density itself (cf. Eq. (2.18)) the Kohn-Sham equations have to be solved self-consistently. Once a self-consistent density is calculated, the functional in Eq. (2.15) can be evaluated and thus also the electronic energy of the system (Eq. (2.8)). Within the Kohn-Sham formalism the kinetic energy of the non-interacting system is only described indirectly using N one-particle wave functions, but still exact. Solely the exchange-correlation functional $E_{\text{xc}}[n]$ remains unknown. Finding good approximations for $E_{\text{xc}}[n]$ is still one of the greatest challenges is modern DFT. Some of the basic ideas of constructing exchange-correlation functional are outlined in the next Section.

2.5 Exchange-Correlation Functionals

The local-density approximation (LDA) is the simplest, but also most widely used approximation for the exchange-correlation functional. The LDA is based on the homogeneous electron gas, which describes a system of electrons in an infinite region of space with a uniform positive background charge to preserve overall charge neutrality. For any inhomogeneous system it is then assumed that the exchange-correlation energy

can be obtained by approximating the density of the inhomogeneous system locally by the density of the homogeneous electron gas

$$E_{\mathrm{xc}}^{\mathrm{LDA}}[n] = \int n(\mathbf{r})\epsilon_{\mathrm{xc}}(n(\mathbf{r}))d\mathbf{r} \quad , \tag{2.21}$$

with $\epsilon_{\mathrm{xc}}(n(\mathbf{r}))$ being the exchange-correlation energy per particle of the homogeneous electron gas. $\epsilon_{\mathrm{xc}}(n(\mathbf{r}))$ can be written as the sum of exchange and correlation contributions

$$\epsilon_{\mathrm{xc}}(n(\mathbf{r})) = \epsilon_{\mathrm{x}}(n(\mathbf{r})) + \epsilon_{\mathrm{c}}(n(\mathbf{r})) \quad , \tag{2.22}$$

where the exchange part $\epsilon_{\mathrm{x}}(n(\mathbf{r}))$ can be expressed explicitly

$$\epsilon_{\mathrm{x}}(n(\mathbf{r})) = -\frac{3}{4}\sqrt[3]{\frac{3\,n(\mathbf{r})}{\pi}} \quad . \tag{2.23}$$

For the correlation part $\epsilon_{\mathrm{c}}(n(\mathbf{r}))$ there is no such explicit expression, but there are highly accurate quantum Monte Carlo calculations for the homogeneous electron gas [47], which can then be parameterized to be used in DFT [48, 49]. Although the LDA appears to be a crude approximation for any realistic system, it has been widely used (especially in solid state physics) and often gives astonishingly good results. Results obtained within the LDA usually become worse with increasing inhomogeneity of the described system, which is particularly the case for atoms or molecules. Typically, in the LDA binding energies are overestimated and therefore bond lengths underestimated. Nevertheless the LDA forms the base of practically all currently used exchange-correlation functionals.

One of the first extensions to the LDA is the generalized gradient approximation (GGA), where in addition to the density itself, information about the gradient of the density are considered

$$E_{\mathrm{xc}}^{\mathrm{GGA}}[n] = \int n(\mathbf{r})\epsilon_{\mathrm{xc}}(n(\mathbf{r}), \nabla n(\mathbf{r}))d\mathbf{r} \quad . \tag{2.24}$$

Again the functional is usually divided into an exchange $E_{\mathrm{x}}^{\mathrm{GGA}}$ and a correlation part $E_{\mathrm{c}}^{\mathrm{GGA}}$, which are expanded separately. In the development of new functionals some known behavior of the exact, but unknown functional is usually considered as well as empirical parameters. For the description of transition metals, which is the main focus of this work, the many different GGAs provide in most cases better results than the LDA, especially with respect to binding energies.

In this work the functional developed by Perdew, Burke and Ernzerhof (PBE) [50] is used. Since the error introduced by an approximate exchange-correlation functional can not be quantified, some of the calculations in this work have also been repeated using the LDA and the GGA-RPBE [51] functionals. Comparing the different results obtained by using different exchange-correlation functionals is then used to provide a first estimate of the uncertainty arising from the approximate E_{xc}.