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Density functional theory

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Institute for Physics, Theoretical Physics
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provided by
Niklas Zwettler, BSc

Supervisor: Ao.Univ.-Prof. Mag. Dr.rer.nat. Ulrich Hohenester

Niklas Zwettler, BSc
Mat-Nr.: 0830682
Ruckerlberggürtel 19
8010 Graz

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Chapter 1

Introduction

Nowadays computers have become an integral part in the world of science, especially when it comes to calculatory problems. For problems which cannot be solved analytically, computers and numerical methods are of crucial importance. The field of computational chemistry deals for instance with the calculatory determination of energies, charge distribution, di- and multipoles as well as spectroscopic quantities of molecules. It's goal is to get insight into molecular processes observed in experiment as well as in order to predict them. The determination of molecular and atomic properties is of similar importance in the fields of molecular physics and solid state physics.

The first steps to deal with the complex and analytically not accessible many-body Schrödinger equation were achieved by Hartree and Fock, who derived a set of self-consistent, wave-function based equations which allowed an iterative calculation of energies and other desired parameters.[1,2] Up to now, the Hartree-Fock method is intensively used in atomic and nuclei physics as well as theoretical chemistry. The method has its flaws, nevertheless, which will be discussed in this thesis. One of the most important ones is the high cost of computation time when large systems are investigated, which arises, among other things, from the dependency of the many-body wave function on $3N$ spatial variables.

An approach to lower computational cost of molecular calculations can therefore be the use of a less complex base variable. The foundation for such an approach has been provided by Hohenberg and Kohn in 1964 when they proofed that the electron density, a variable only depending on 3 spatial variables, in principle contains all information about the ground state properties of a system. This also marked the birth of density functional theory (DFT) to which the main part of this thesis is devoted. In 1998 Kohn got the Nobel prize in chemistry “for his development of the density-functional theory”.[3,4]

In 1965 Kohn and Sham derived a set of self-consistent, iteratively solvable equations which finally allowed to use the up to that point only theoretical concept of Hohenberg and Kohn also in actual computer simulations.[5] And due to the fact that the electron density is a much less complex quantity than the wave function, the computation times of DFT calculations are substantially lower.

At present day, DFT is successfully applied to a broad variety of quantum mechanical problems, such as binding energies of molecules in chemistry or the calculation of band structures of solids in physics.[6] The increasing importance of DFT has been reported by Holthausen and Koch by a comparison of hits for the phrases DFT or density-functional in abstracts from about 100 in 1990 to 2500 in 1999.[7]

This thesis provides an introduction to basic, wave-function based many-body quantum mechanics as well as to the theoretical foundations of DFT up to the point where iteratively accessible, density-based equations for both, time-independent and time-dependent problems are presented.

A major component in DFT is also the choice of the correct approximation for the exchange-correlation functional which arises from the Kohn-Sham approach. A detailed discussion of possible approximation exceeds the coverage of this bachelor thesis, the interested reader is referred to the book of Holthausen and Koch[7] and the articles by Capelle[6] as well as Perdew and Kurth.[8]

Chapter 2

Basic Quantum Mechanics

2.1 Schrödingers groundbreaking equation

Erwin Schrödinger's attempt to describe the so-called 'matter waves' in 1926, where he used de Broglie's relations to describe hypothetical plane waves, led to the most general form of the famous equation named after him, the time-dependent Schrödinger equation[9]

$$i\hbar\frac{\partial}{\partial t}\Psi(\vec{r},t) = \hat{H}\Psi(\vec{r},t). \tag{2.1}$$

It is often impracticable to use a complete relativistic formulation of the formula; therefore Schrödinger himself postulated a non-relativistic approximation which is nowadays often used, especially in quantum chemistry.

Using the Hamiltonian for a single particle

$$\hat{H} = \hat{T} + \hat{V} = -\frac{\hbar^2}{2m}\vec{\nabla}^2 + V(\vec{r},t) \tag{2.2}$$

leads to the (non-relativistic) time-dependent single-particle Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}\Psi(\vec{r},t) = \left[-\frac{\hbar^2}{2m}\vec{\nabla}^2 + V(\vec{r},t)\right]\Psi(\vec{r},t). \tag{2.3}$$

In this thesis, from now on only non-relativistic cases are considered.

For N particles in three dimensions, the Hamiltonian is

$$\hat{H} = \sum_{i=1}^{N}\frac{\hat{p_i}^2}{2m_i} + V(\vec{r}_1,\vec{r}_2,...,\vec{r}_N,t) = -\frac{\hbar^2}{2}\sum_{i=1}^{N}\frac{1}{m_i} + V(\vec{r}_1,\vec{r}_2,...,\vec{r}_N,t). \tag{2.4}$$

The corresponding Schrödinger equation reads

$$i\hbar\frac{\partial}{\partial t}\Psi(\vec{r}_1,\vec{r}_2,...,\vec{r}_N,t)=\left[-\frac{\hbar^2}{2}\sum_{i=1}^{N}\frac{1}{m_i}\nabla_i^2+V(\vec{r}_1,\vec{r}_2,...,\vec{r}_N,t)\right]\Psi(\vec{r}_1,\vec{r}_2,...,\vec{r}_N,t) \quad (2.5)$$

2.2 Time-independent equation

Special cases are the solutions of the time-independent Schrödinger equation, where the Hamiltonian itself has no time-dependency (which implies a time-independent potential $V(\vec{r_1},\vec{r_2},...,\vec{r_N})$, and the solutions therefore describe standing waves which are called stationary states or orbitals). The time-independent Schrödinger equation is not only easier to treat, but the knowledge of its solutions also provides crucial insight to handle the corresponding time-dependent equation.

The time-independent equation is obtained by the approach of separation of variables, i.e. the spatial part of the wave function is separated from the temporal part via[10]

$$\Psi(\vec{r}_1,\vec{r}_2,...,\vec{r}_N,t)=\psi(\vec{r}_1,\vec{r}_2,...,\vec{r}_N)\tau(t)=\psi(\vec{r}_1,\vec{r}_2,...,\vec{r}_N)\cdot e^{-i\omega t}. \quad (2.6)$$

Furthermore, the l.h.s. of the equation reduces to the energy eigenvalue of the Hamiltonian multiplied by the wave function, leading to the general eigenvalue equation

$$E\psi(\vec{r}_1,\vec{r}_2,...,\vec{r}_N)=\hat{H}\psi(\vec{r}_1,\vec{r}_2,...,\vec{r}_N) \quad (2.7)$$

Again, using the many-body Hamiltonian, the Schrödinger equation becomes

$$E\psi(\vec{r}_1,\vec{r}_2,...,\vec{r}_N)=\left[-\frac{\hbar^2}{2}\sum_{i=1}^{N}\frac{1}{m_i}\nabla_i^2+V(\vec{r}_1,\vec{r}_2,...,\vec{r}_N)\right]\psi(\vec{r}_1,\vec{r}_2,...,\vec{r}_N). \quad (2.8)$$

2.3 The wave function

In the last section, the term wave function was repeatedly used. Therefore, and for a better understanding of the following a closer look at the wave function is taken.

The first and most important postulate is that the state of a particle is completely described by its (time-dependent) wave function, i.e. the wave function contains all information about the particle's state.

For the sake of simplicity the discussion is restricted to the time-independent wave function. A question always arising with physical quantities is about possible interpretations as well as observations. The Born probability interpretation of the wave function, which is a major principle of the Copenhagen interpretation of quantum mechanics, provides a physical interpretation for the square of the wave function as a probability density[2,11]

$$|\psi(\vec{r}_1,\vec{r}_2,...,\vec{r}_N)|^2 d\vec{r}_1 d\vec{r}_2 ... d\vec{r}_N. \tag{2.9}$$

Equation (2.9) describes the probability that particles 1,2,...,N are located simultaneously in the corresponding volume element $d\vec{r}_1 d\vec{r}_2 ... d\vec{r}_N$.[7] What happens if the positions of two particles are exchanged, must be considered as well. Following merely logical reasoning, the overall probability density cannot depend on such an exchange, i.e.

$$|\psi(\vec{r}_1,\vec{r}_2,...,\vec{r}_i,\vec{r}_j,...,\vec{r}_N)|^2 = |\psi(\vec{r}_1,\vec{r}_2,...,\vec{r}_j,\vec{r}_i,...,\vec{r}_N)|^2. \tag{2.10}$$

There are only two possibilities for the behavior of the wave function during a particle exchange. The first one is a symmetrical wave function, which does not change due to such an exchange. This corresponds to bosons (particles with integer or zero spin). The other possibility is an anti-symmetrical wave function, where an exchange of two particles causes a sign change, which corresponds to fermions (particles which half-integer spin).[12,13]

In this text only electrons are from interest, which are fermions. The anti-symmetric fermion wave function leads to the Pauli principle, which states that no two electrons can occupy the same state, whereas state means the orbital and spin parts of the wave function[1] (the term spin coordinates will be discussed later in more detail). The antisymmetry principle can be seen as the quantum-mechanical formalization of Pauli's theoretical ideas in the description of spectra (e.g. alkaline doublets).[14]

Another consequence of the probability interpretation is the normalization of the wave function. If equation (2.9) describes the probability of finding a particle in a volume element, setting the full range of coordinates as volume element must result in a probability of one, i.e. all particles must be found somewhere in space. This corresponds to the normalization condition for the wave function.

$$\int d\vec{r}_1 \int d\vec{r}_2 ... \int d\vec{r}_N |\psi(\vec{r}_1,\vec{r}_2,...,\vec{r}_N)|^2 = 1 \tag{2.11}$$

Equation (2.11) also gives insight on the requirements a wave function must fulfill in order to be physical acceptable. Wave functions must be continuous over the full spatial range and square-integratable.[15]

Another very important property of the wave function is that calculating expectation values of operators with a wave function provides the expectation value of the corresponding observable for that wave function.[6] For an observable $O(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N)$, this can generally be written as

$$O = \langle O \rangle = \int d\vec{r}_1 \int d\vec{r}_2 ... \int d\vec{r}_N \psi^*(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N) \hat{O} \psi(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N). \tag{2.12}$$

2.4 Atoms and molecules

All atomic and molecular systems deal with charged particles. The single electron Schrödinger equation where the electron moves in a Coulomb potential,

$$i\hbar \frac{\partial}{\partial t} \psi(\vec{r}) = \left[-\frac{\hbar^2}{2m} \vec{\nabla}^2 - \frac{e^2}{4\pi\epsilon_0} \cdot \frac{1}{|\vec{r}|} \right] \psi(\vec{r}) \tag{2.13}$$

marks a good starting point.

For the sake of simplicity, the so-called atomic units are introduced at this point for subsequent usage. That means the electron mass m_e, the elementary charge e, the reduced Planck constant (Dirac constant) $\hbar$ as well as the vacuum permittivity factor $4\pi\epsilon_0$ are all set to unity.[16]

The Schrödinger equation for the single electron simplifies to

$$E\psi(\vec{r}) = \left[-\frac{1}{2} \vec{\nabla}^2 - \frac{1}{|\vec{r}|} \right] \psi(\vec{r}). \tag{2.14}$$

This form of the Schrödinger equation is analytically solvable. Although for the description of matter, even atoms, the Schrödinger equation exceeds analytical accessibility soon. Usage of (2.8) allows a construction of a generalized many-body Schrödinger equation for a system composed of N electrons and M nuclei, where external magnetic and electric fields are neglected.

$$E_i \psi_i(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N, \vec{R}_1, \vec{R}_2, ..., \vec{R}_N) = \hat{H} \psi(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N, \vec{R}_1, \vec{R}_2, ..., \vec{R}_N) \tag{2.15}$$

Equation (2.15) doesn't seem overly complicated on the first look, but an examination of the corresponding molecular Hamiltonian

$$\hat{H} = -\frac{1}{2} \sum_{i=1}^{N} \nabla_i^2 - \frac{1}{2} \sum_{k=1}^{M} \nabla_k^2 - \sum_{i=1}^{N} \sum_{k=1}^{M} \frac{Z_k}{r_{ik}} + \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{1}{r_{ij}} + \sum_{k=1}^{M} \sum_{l>k}^{M} \frac{Z_k Z_l}{R_{kl}} \tag{2.16}$$

reveals the real complexity of the equation.

In equation (2.16), M_k represents the nuclear mass in atomic units (i.e. in units of the electron mass), Z_k and Z_l represent the atomic numbers, and $r_{ij} = |\vec{r}_i - \vec{r}_j|$, $r_{ik} = |\vec{r}_i - \vec{R}_k|$ and $R_{kl} = |\vec{R}_k - \vec{R}_l|$ represent the distances between the particles (electron-electron, electron-nucleus and nucleus-nucleus).

A term-by-term interpretation of the right hand side in (2.16) reveals that the first two terms correspond to the kinetic energies of the electrons and nuclei. The latter three terms denote the potential part of the Hamiltonian in terms of electrostatic particle-particle interactions. This is reflected by the corresponding signs, where the negative sign denotes an attractive potential between electrons and nuclei, whereas the positive signs denote repulsive potentials between electrons and electrons as well as the nuclei among themselves.[7]

Taking advantage of the fact, that the mass of a proton is approximately 1800 times larger than the mass of an electron, which is the minimum mass ratio of electron to nucleus (hydrogen atom) and becomes even higher for heavier atoms, another simplification can be introduced. The so called Born-Oppenheimer approximation states that due to the mass difference the nucleus can be, in comparison to the electrons, considered non-moving, i.e. spatially fixed. One can say that the core movement can be neglected on the timescale of electronic transitions which means the core movement has no influence on them.[2,17]

As a consequence, the general Hamiltonian is replaced by the so-called electronic Hamiltonian

$$\hat{H} = -\frac{1}{2}\sum_{i=1}^{N} \nabla_i^2 - \sum_{i=1}^{N}\sum_{k=1}^{M} \frac{Z_k}{r_{ik}} + \sum_{i=1}^{N}\sum_{j>i}^{N} \frac{1}{r_{ij}}, \tag{2.17}$$

or in terms of operators

$$\hat{H}_{el} = \hat{T} + \hat{U} + \hat{V} = \hat{T} + \hat{V}_{tot}. \tag{2.18}$$

Especially for problems of molecular physics and quantum chemistry, the electronic Schrödinger equation is of major interest. But despite all simplifications a simple look at equations (2.15) to (2.18) indicates that there are still a few more crucial points left to deal with until a useful solution can be obtained.

Inspection of equations (2.17) and (2.18) shows that the kinetic energy term $\hat{T}$ doesn't depend on the nuclear coordinates R_{kl}, or in other words, it is only a function of the electron number. Also the electron-electron repulsion $\hat{U}$ is the same for every system with only Coulomb interactions.

Therefore the only part of the electronic Hamiltonian which depends on the atomic respectively molecular system is the external potential $\hat{V}$ caused by the nucleus-electron repulsion.

Subsequently this also means that $\hat{T}$ and $\hat{U}$ only need the electron number N as input and will therefore be denoted as 'universal', whereas $\hat{V}$ is system-dependent. The expectation value of $\hat{V}$ is also often denoted as the external potential V_{ext}, which is consistent as long as there are no external magnetic or electrical fields.[6]

As soon as the external potential is known, the next step is the determination of the wave functions ψ_i which contain all possible information about the system. As simple as that sounds, the exact knowledge of the external potential is not possible for most natural systems, i.e. in similarity to classical mechanics, the largest system which can be solved analytically is a 2-body-system, which corresponds to a hydrogen atom. Using all approximations introduced up to now it is possible to calculate a problem similar to H_2^+, a single ionized hydrogen molecule. To get results for larger systems, further approximations have to be made.

2.5 The Hartree-Fock approach

In order to find a suitable strategy to approximate the analytically not accessible solutions of many-body problems, a very useful tool is variational calculus, similar to the least-action principle of classical mechanics. By the use of variational calculus, the ground state wave function ψ_0, which corresponds to the lowest energy of the system E_0, can be approached. A useful literature source for the principles of variational calculus has been provided by T. Fließbach.[18]

Hence, for now only the electronic Schrödinger equation is of interest, therefore in the following sections we set $\hat{H} \equiv \hat{H}_{el}$, $E \equiv E_{el}$, and so on.

Observables in quantum mechanics are calculated as the expectation values of operators.[2,10] The energy as observable corresponds to the Hamilton operator, therefore the energy corresponding to a general Hamiltonian can be calculated as

$$E = \langle \hat{H} \rangle = \int d\vec{r}_1 \int d\vec{r}_2 ... \int d\vec{r}_N \psi^*(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N) \hat{H} \psi(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N) \tag{2.19}$$

The central idea of the Hartree-Fock approach is that the energy obtained by any (normalized) trial wave function, different from the actual ground state wave function, is always an upper bound, i.e. higher than the actual ground state energy. If the trial function happens to be the desired ground state wave function, the energies are equal

$$E_{trial} \geq E_0, \tag{2.20}$$

with

$$E_{trial} = \int d\vec{r}_1 \int d\vec{r}_2 ... \int d\vec{r}_N \psi^*_{trial}(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N) \hat{H} \psi_{trial}(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N) \tag{2.21}$$

and

$$E_0 = \int d\vec{r}_1 \int d\vec{r}_2 ... \int d\vec{r}_N \psi_0^*(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N) \hat{H} \psi_0(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N). \tag{2.22}$$

The expressions above are usually inconvenient to handle. For the sake of a compact notation, in the following the bra-ket notation of Dirac is introduced. For a detailed description of this notation, the reader is referred to the original publication.[19]

In that notation, equations (2.20) to (2.22) are expressed as

$$\langle \psi_{trial} | \hat{H} | \psi_{trial} \rangle = E_{trial} \geq E_0 = \langle \psi_0 | \hat{H} | \psi_0 \rangle \tag{2.23}$$

Proof:[2] The eigenfunctions ψ_i of the Hamiltonian $\hat{H}$(each corresponding to an energy eigenvalue E_i) form a complete basis set, therefore any normalized trial wave function ψ_{trial} can be expressed as linear combination of those eigenfunctions.

$$\psi_{trial} = \sum_i \lambda_i \psi_i \tag{2.24}$$

The assumption is made that the eigenfunctions are orthogonal and normalized. Hence it is requested that the trial wave function is normalized, it follows that

$$\langle \psi_{trial} | \psi_{trial} \rangle = 1 = \langle \sum_i \lambda_i \psi_i | \sum_j \lambda_j \psi_j \rangle = \sum_i \sum_j \lambda_i^* \lambda_j \langle \psi_i | \psi_j \rangle = \sum_j |\lambda_j|^2. \tag{2.25}$$

On the other hand, following (2.23) and (2.25)

$$E_{trial} = \langle \psi_{trial} | \hat{H} | \psi_{trial} \rangle = \langle \sum_i \lambda_i \psi_i | \hat{H} | \sum_j \lambda_j \psi_j \rangle = \sum_j E_j |\lambda_j|^2 \tag{2.26}$$

Together with the fact that the ground state energy E_0 is per definition the lowest possible energy, and therefore has the smallest eigenvalue ($E_0 \leq E_i$), it is found that

$$E_{trial} = \sum_j E_j |\lambda_j|^2 \geq E_0 \sum_j |\lambda_j|^2 \tag{2.27}$$

what resembles equation (2.23). $\square$

The mathematical framework used above, i.e. rules which assign numerical values to functions, so called functionals, is also one of the main concepts in density functional theory. A function gets a numerical input and generates a numerical output whereas a functional gets a function as input and generates a numerical output.[20]

Equations (2.19) to (2.27) also include that a search for the minimal energy value while applied on all allowed (physically possible, cf. chapter 2.3) N-electron wave-functions will always provide the ground-state wave function (or wave functions, in case of a degenerate ground state where more than one wave function provides the minimum energy). Expressed in terms of functional calculus, where $\psi \rightarrow N$ addresses all allowed N-electron wave functions, this means[7]

$$E_0 = \min_{\psi \rightarrow N} E\left[\psi\right] = \min_{\psi \rightarrow N} \langle \psi | \hat{H} | \psi \rangle = \min_{\psi \rightarrow N} \langle \psi | \hat{T} + \hat{V} + \hat{U} | \psi \rangle. \tag{2.28}$$

For N-electron systems this search is, due to the large number of possible wave functions on the one hand and limitations in computational power and time, practically impossible. What is possible is the restriction of the search to a smaller subset of possible wave function, as it is done in the Hartree-Fock approximation.

In the Hartree-Fock approach, the search is restricted to approximations of the N-electron wave function by an antisymmetric (cf. chapter 2.3) product of N (normalized) one-electron wave-functions, the so called spin-orbitals $\chi_i(\vec{x}_i)$.[1] A wave function of this type is called Slater-determinant, and reads[1,7]

$$\psi_0 \approx \phi_{SD} = (N!)^{-\frac{1}{2}} \begin{vmatrix} \chi_1(\vec{x}_1) & \chi_2(\vec{x}_1) & \cdots & \chi_N(\vec{x}_1) \\ \chi_1(\vec{x}_2) & \chi_2(\vec{x}_2) & \cdots & \chi_N(\vec{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(\vec{x}_N) & \chi_2(\vec{x}_N) & \cdots & \chi_N(\vec{x}_N) \end{vmatrix} \tag{2.29}$$

It is important to notice that the spin-orbitals $\chi_i(\vec{x}_i)$ are not only depending on spatial coordinates but also on a spin coordinate which is introduced by a spin function, $\vec{x}_i = \vec{r}_i, s$.

A detailed discussions of the spin orbitals and their (necessary) properties is omitted in this text, a detailed treatise is provided in the books by Szabo[1] and Holthausen.[7] As spin orbitals e.g. hydrogen-type orbitals (for atomic calculations) and linear combinations of them are used.[21]

Returning to the variational principle and equation (2.28), the ground state energy approximated by a single slater determinant becomes

$$E_0 = \min_{\phi_{SD} \rightarrow N} E\left[\phi_{SD}\right] = \min_{\phi_{SD} \rightarrow N} \langle \phi_{SD} | \hat{H} | \phi_{SD} \rangle = \min_{\phi_{SD} \rightarrow N} \langle \phi_{SD} | \hat{T} + \hat{V} + \hat{U} | \phi_{SD} \rangle \tag{2.30}$$

A general expression for the Hartree-Fock Energy is obtained by usage of the Slater determinant as a trial function

$$E_{HF} = \langle \phi_{SD} | \hat{H} | \phi_{SD} \rangle = \langle \phi_{SD} | \hat{T} + \hat{V} + \hat{U} | \phi_{SD} \rangle \tag{2.31}$$

For the sake of brevity, a detailed derivation of the final expression for the Hartree-Fock energy is omitted. It is a straightforward calculation found for example in the Book by Schwabl.[10] The final expression for the Hartree-Fock energy contains three major parts:[7]

$$E_{HF} = \langle \phi_{SD}|\hat{H}|\phi_{SD}\rangle = \sum_{i}^{N}(i|\hat{h}|i) + \frac{1}{2}\sum_{i}^{N}\sum_{j}^{N}[(ii|jj) - (ij|ji)] \tag{2.32}$$

with

$$(i|\hat{h}_i|i) = \int \chi_i^*(\vec{x}_i)\left[-\frac{1}{2}\vec{\nabla}_i^2 - \sum_{k=1}^{M}\frac{Z_k}{r_{ik}}\right]\chi_i(\vec{x}_i)d\vec{x}_i, \tag{2.33}$$

$$(ii|jj) = \int\int |\chi_i(\vec{x}_i)|^2\frac{1}{r_{ij}}|\chi_j(\vec{x}_j)|^2 d\vec{x}_i d\vec{x}_j, \tag{2.34}$$

$$(ii|jj) = \int\int \chi_i(\vec{x}_i)\chi_j^*(\vec{x}_j)\frac{1}{r_{ij}}\chi_j(\vec{x}_j)\chi_i^*(\vec{x}_i)d\vec{x}_i d\vec{x}_j. \tag{2.35}$$

The first term corresponds to the kinetic energy and the nucleus-electron interactions, $\hat{h}$ denoting the single particle contribution of the Hamiltonian, whereas the latter two terms correspond to electron-electron interactions. They are called Coulomb and exchange integral, respectively.[1,7]

Examination of equations (2.32) to (2.35) furthermore reveals, that the Hartree-Fock energy can be expressed as a functional of the spin orbitals $E_{HF} = E[\{\chi_i\}]$. Thus, variation of the spin orbitals leads to the minimum energy.[7]

An important point is that the spin orbitals remain orthonormal during minimization. This restriction is accomplished by the introduction of Lagrangian multipliers λ_i in the resulting equations, which represent the Hartree-Fock equations. For a detailed derivation, the reader is referred to the book by Szabo and Ostlund.[1,7,18]

Finally, one arrives at

$$\hat{f}\chi_i = \lambda_i\chi_i \qquad i = 1, 2, ..., N \tag{2.36}$$

with

$$\hat{f}_i = -\frac{1}{2}\vec{\nabla}_i^2 - \sum_{k=1}^{M}\frac{Z_k}{r_{ik}} + \sum_{i}^{N}[\hat{J}_j(\vec{x}_i) - \hat{K}_j(\vec{x}_i)] = \hat{h}_i + \hat{V}^{HF}(i), \tag{2.37}$$

the Fock operator for the i-th electron. In similarity to(2.32) to (2.35), the first two terms represent the kinetic and potential energy due to nucleus-electron interaction, collected in the core Hamiltonian $\hat{h}_i$, whereas the latter terms are sums over the Coulomb operators $\hat{J}_j$ and the exchange operators $\hat{K}_j$ with the other j electrons, which form the Hartree-Fock potential $\hat{V}^{HF}$.

There the major approximation of Hartree-Fock can be seen. The two electron repulsion operator from the original Hamiltonian is exchanged by a one-electron operator $\hat{V}^{HF}$ which describes the repulsion in average.[7]

2.6 Limitations and failings of the Hartree-Fock approach

Atoms as well as molecules can have an even or odd number of electrons. If the number of electrons is even and all of them are located in double occupied spatial orbitals ϕ_i, the compound is in a singlet state. Such systems are called *closed-shell systems*. Compounds with an odd number of electrons as well as compounds with single occupied orbitals, i.e. species with triplet or higher ground state, are called *open-shell systems* respectively. These two types of systems correspond to two different approaches of the Hartree-Fock method. In the *restricted* HF-method (RHF), all electrons are considered to be paired in orbitals whereas in the *unrestricted* HF (UHF)-method this limitation is lifted totally. It is also possible to describe open-shell systems with a RHF approach where only the single occupied orbitals are excluded which is then called a *restricted open-shell* HF (ROHF) which is an approach closer to reality but also more complex and therefore less popular than UHF.[7]

There are also closed-shell systems which require the unrestricted approach in order to get proper results. For instance, the description of the dissociation of H_2 (i.e. the behavior at large internuclear distance), where one electron must be located at one hydrogen atom, can logically not be obtained by the use of a system which places both electrons in the same spatial orbital. Therefore the choice of method is always a very important point in HF calculations.[1]

The size of the investigated system can also be a limiting factor for calculations. Kohn states a number of $M = p^5$ with $3 \leq p \leq 10$ parameters for a result with sufficient accuracy in the investigation of the H_2 system.[4] For a system with $N = 100$ (active) electrons the number of parameters rises to

$$M = p^{3N} = 3^{300} \;\; to \;\; 10^{300} \approx 10^{150} \;\; to \;\; 10^{300}. \tag{2.38}$$

Equation (2.38) states, that the minimization of the energy would have to be performed in a space of at least 10^{150} dimension which exceeds the computational possibilities nowadays by far. HF-methods are therefore restricted to systems with a small number of involved electrons ($N \approx 10$). Referring to the exponential factor in (2.38) this limitation is sometimes called *exponential wall*.[4]

Since a many electron wave function cannot be described entirely by a single Slater determinant, the energy obtained by HF calculations is always larger than the exact ground state energy. The most accurate energy obtainable by HF-methods is called the *Hartree-Fock-limit*.[7]

The difference between E_{HF} and E_{exact} is called *correlation energy* and can be denoted as[22]

$$E_{corr}^{HF} = E_{min} - E_{HF}. \tag{2.39}$$

Despite the fact that E_{corr} is usually small against E_{min}, as in the example of a N_2 molecule where

$$E_{corr}^{HF} = 14.9eV < 0.001 \cdot E_{min}, \tag{2.40}$$

it can have a huge influence.[23]

For instance, the experimental dissociation energy of the N_2 molecule is

$$E_{diss} = 9.9eV < E_{corr} \tag{2.41}$$

which corresponds to a large contribution of the correlation energy to relative energies such as reaction energies which are of particular interest in quantum chemistry.[23]

The main contribution to the correlation energy arises from the mean field approximation used in the HF-method. That means one electron moves in the average field of the other ones, an approach which completely neglects the intrinsic correlation of the electron movements. To get a better understanding what that means, one may picture the repulsion of electrons at small distances which clearly cannot be covered by a mean-field approach like the Hartree-Fock-method.[7]

Chapter 3

Density functional theory

3.1 A new base variable - the electron density

In the section 2.3 about the wave function ψ , a general statement about the calculation of observables has been provided. A quantity calculated in a very similar way is the topic of this section. The electron density (for N electrons) as the basic variable of density functional theory is defined as[3,7]

$$n(\vec{r}) = N \sum_{s_1} \int d\vec{x}_2 ... \int d\vec{x}_N \psi^*(\vec{x}_1, \vec{x}_2, ..., \vec{x}_N) \psi(\vec{x}_1, \vec{x}_2, ..., \vec{x}_N). \tag{3.1}$$

What has to be mentioned is that the notation in (3.1) considers a wave function dependent on spin and spatial coordinates. In detail, the integral in the equation gives the probability that a particular electron with arbitrary spin is found in the volume element $d\vec{r}_1$. Due to the fact that the electrons are indistinguishable, N times the integral gives the probability that any electron is found there. The other electrons represented by the wave function $\psi(\vec{x}_1, \vec{x}_2, ..., \vec{x}_N)$ have arbitrary spin and spatial coordinates.[7]

If additionally the spin coordinates are neglected, the electron density can even be expressed as measurable observable only dependent on spatial coordinates[3,4]

$$n(\vec{r}) = N \int d\vec{r}_2 ... \int d\vec{r}_N \psi^*(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N) \psi(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N), \tag{3.2}$$

which can e.g. be measured by X-ray diffraction.[7]

Before presenting an approach using the electron density as variable, it has to be ensured that it truly contains all necessary informations about the system. In detail that means it has to contain information about the electron number N as well as the external potential characterized by $\hat{V}$.[7]

The total number of electrons can be obtained by integration the electron density over the spatial variables[7]

$$N = \int d\vec{r} n(\vec{r}). \tag{3.3}$$

What is left to proof is that also the external potential is characterized uniquely by the electron density, where uniquely means up to an additive constant.

3.2 The Hohenberg-Kohn theorems

The "basic lemma of Hohenberg-Kohn"[4] states that not only $n(\vec{r})$ is a functional of $v(\vec{r})$ but that also $v(\vec{r})$ is up to a constant determined by $n(\vec{r})$ uniquely.[3,4,7]

Since the original publication of Hohenberg and Kohn[3] deals with an electron gas, the Hamiltonian is resembled by the electronic Hamilton operator introduced in equation (2.17), $\hat{H}_{el} = \hat{T} + \hat{V} + \hat{U}$, with the one difference that the non-universal contribution $\hat{V}$ in this case represents a general external potential (which in case of the electronic Hamilton approximated by Born-Oppenheimer contains a nuclear field contribution).[3,6,7]

Following the original approach of Hohenberg and Kohn, accompanied by their proof via reductio ad absurdum, the discussion in this thesis is restricted to non-degenerate ground states.[3] This restriction nevertheless doesn't affect the presented proof for the second theorem and can be lifted as well for the first theorem.[24,25]

The energy of the system can be denoted as

$$E = \langle\psi|\hat{H}|\psi\rangle = \langle\psi|\hat{T} + \hat{V} + \hat{U}|\psi\rangle = \int v(\vec{r})n(\vec{r})d\vec{r} + \langle\psi|\hat{T} + \hat{U}|\psi\rangle, \tag{3.4}$$

which will be used for the proof of Hohenberg and Kohn's first theorem.

Theorem.[3]The external potential $v(\vec{r})$ is a functional of the electron density $n(\vec{r})$ and, up to an unimportant constant, uniquely determined by it.

Proof.[4,26] It is assumed that there exist two external potentials $v(\vec{r})$ and $v'(\vec{r})$ which differ by more than just a trivial constant. Furthermore, the assumption is made, that both potentials give rise to the same electron density $n(\vec{r})$. Clearly, arising from the nature of $\hat{V}$ in that case there have to be two different Hamiltonians $\hat{H}$ and $\hat{H}'$. Furthermore ψ and ψ' have to be different, since they fulfill different Schrödinger equations. Finally also the energies E and E' associated with the particular wave function differ.

Now the two wave functions ψ and ψ' are used as trial functions assuming the other wave function is the ground state wave function. Then the expressions

$$E_0' = \langle\psi'|\hat{H}'|\psi'\rangle < \langle\psi|\hat{H}'|\psi\rangle = \langle\psi|\hat{H} + \hat{V}' - \hat{V}|\psi\rangle = \langle\psi|\hat{H}|\psi\rangle + \langle\psi|\hat{V}' - \hat{V}|\psi\rangle \tag{3.5}$$

and

$$E_0 = \langle\psi|\hat{H}|\psi\rangle < \langle\psi'|\hat{H}|\psi'\rangle = \langle\psi'|\hat{H}' + \hat{V} - \hat{V}'|\psi'\rangle = \langle\psi'|\hat{H}'|\psi'\rangle + \langle\psi'|\hat{V} - \hat{V}'|\psi'\rangle \tag{3.6}$$

are obtained. By the use of (3.4), this can be rewritten as

$$E`_0 < E_0 + \int \left[v'(\vec{r}) - v(\vec{r})\right] n(\vec{r}) d\vec{r} \tag{3.7}$$

and

$$E_0 < E_0' + \int \left[v(\vec{r}) - v'(\vec{r})\right] n(\vec{r}) d\vec{r} \tag{3.8}$$

By summation of (3.7) and (3.8) the inequality

$$E`_0 + E_0 < E_0 + E_0' \tag{3.9}$$

is obtained, which represents an inconsistency and therefore provides by *reductio ad absurdum* the proof that $v(\vec{r})$ is truly a unique functional of $n(\vec{r})$.□

The first Hohenberg-Kohn theorem can also be written in another form which is sometimes called the "strong form" of the Hohenberg-Kohn theorem.[6] Here $\Delta v(\vec{r})$ and $\Delta n(\vec{r})$ correspond to the change in potential and electron density respectively:

$$\int \Delta v(\vec{r}) \Delta n(\vec{r}) < 0 \tag{3.10}$$

Whereas equation (3.10) can be derived from the original proof[27]it can also be derived perturbatively.

The importance of this proof lies in the fact, that it not only implies the first Hohenberg Kohn theorem (if $\Delta v(\vec{r}) \neq 0$ clearly also $\Delta n(\vec{r})$ must not vanish) but also provides an assertion about the signs of $\Delta v(\vec{r})$ and $\Delta n(\vec{r})$, i.e. a (mostly) positive potential $\Delta v(\vec{r})$ requires a (mostly) negative electron density $\Delta n(\vec{r})$ to ensure the negativity of the integral in (3.10).[6]

From the first Hohenberg Kohn theorem it is obvious that also the ground state wave function is a unique functional of the ground state electron density

$$\psi_0(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N) = \psi\left[n_0(\vec{r})\right]. \tag{3.11}$$

Furthermore, recalling (2.12), the ground state expectation value of any observable is a functional of $n_0(\vec{r})$ too, i.e.

$$O_0 = O\left[n_0(\vec{r})\right] = \langle\psi\left[n_0(\vec{r})\right]|\hat{O}|\psi\left[n_0(\vec{r})\right]\rangle. \tag{3.12}$$

Among these observables is the ground state energy, the expectation value of the Hamiltonian, which is of great importance. Recalling equation (3.4), the ground state energy corresponding to an potential $v(\vec{r})$ can be denoted as

$$E_{v,0} = E_v\left[n_0(\vec{r})\right] = \langle\psi\left[n_0(\vec{r})\right]|\hat{H}\psi\left[n_0(\vec{r})\right]\rangle = \int v(\vec{r})n_0(\vec{r})d\vec{r} + \langle\psi\left[n_0(\vec{r})\right]|\hat{T}+\hat{U}|\psi\left[n_0(\vec{r})\right]\rangle. \tag{3.13}$$

To obtain a more convenient handling of equation 3.13, the Hohenberg-Kohn functional $F_{HK}\left[n(\vec{r})\right]$ and subsequently, the energy functional $E_v\left[n(\vec{r})\right]$ are defined:[3]

$$F_{HK}\left[n(\vec{r})\right] \equiv \langle\psi\left[n_0(\vec{r})\right]|\hat{T}+\hat{U}|\psi\left[n_0(\vec{r})\right]\rangle \tag{3.14}$$

$$E_v\left[n(\vec{r})\right] \equiv \int v(\vec{r})n_0(\vec{r})d\vec{r} + F_{HK}\left[n(\vec{r})\right] \tag{3.15}$$

In similarity to the terminology introduced in the section about the Hartree-Fock method, the Hohenberg-Kohn functional represents the system-independent or universal part. Equation (3.13) furthermore leads to another crucial finding of the original paper by Hohenberg and Kohn, which is often addressed as the second theorem of Hohenberg and Kohn.[3]

Theorem II.[3,28] The ground state energy can be derived from the electron density by the use of variational calculus. The electron density, which provides a minimum of the ground state energy, is therefore the exact ground state density.

Originally this second theorem has been proved by variation calculus,[3] the proof provided subsequently is a different one, namely the so called *constrained-search* approach, introduced by Levy and Lieb[29,30] and subsequently thoroughly examined in the books by Parr, Yang as well as Kryachko and Ludena.[31,32]

Since the wave function is a unique functional of the electron density, every trial wave function ψ' corresponds to a trial density $n'(\vec{r})$ following equation (3.2). According to the Rayleigh-Ritz principle, the ground state energy is obtained as

$$E_{v,0} = \min_{\psi'}\langle\psi'|\hat{H}|\psi'\rangle. \tag{3.16}$$

Proof.[4] In principle, the minimization can be carried out in two steps. In the first step, a trial electron density $n'(\vec{r})$ is fixed. The class of trial functions corresponding to that electron density is then denoted by $\psi_{n'}^{\prime\alpha}$. Then, the constrained energy minimum is defined as

$$E_v\left[n'(\vec{r})\right] \equiv \min_{\alpha}\langle\psi_{n'}^{\prime\alpha}|\hat{H}|\psi_{n'}^{\prime\alpha}\rangle = \int v(\vec{r})n'(\vec{r})d\vec{r} + F\left[n'(\vec{r})\right]. \tag{3.17}$$

In that notation, $F\left[n'(\vec{r})\right]$ is the universal functional

$$F\left[n'(\vec{r})\right] \equiv \min_{\alpha} \langle \psi'^{\alpha}_{n'} | \hat{T} + \hat{U} | \psi'^{\alpha}_{n'} \rangle \tag{3.18}$$

which is clearly related to the Hohenberg-Kohn functional in (3.13). What is important to notice at this point is that the universal functional $F\left[n'(\vec{r})\right]$ requires no explicit knowledge of $v(\vec{r})$.

In the second step, equation (3.17) is minimized over all trial densities $n'(\vec{r})$:

$$E_{v,0} = \min_{n'(\vec{r})} E_v\left[n'(\vec{r})\right] = \min_{n'(\vec{r})} \{ \int v(\vec{r}) n'(\vec{r}) d\vec{r} + F\left[n'(\vec{r})\right] \} \tag{3.19}$$

Now, for a non-degenerate ground state, the energy in (3.19) is attained, if $n'(\vec{r})$ is the actual ground state density. □

Furthermore, the constrained search approach finally lifts the restriction to non-degenerate ground states. If a ground state density corresponding to a number of wave functions is selected, only one of the wave functions connected with the energy of the degenerate ground state is found.[7]

Recapitulating, it has been shown that density functional theory provides a clear and mathematical exact framework for the use of the electron density as base variable. Nevertheless, nothing of what has been derived is of practical use. Or in other words, the Hohenberg-Kohn theorems, as important as they are, do not provide any help for the calculation of molecular properties and also don't provide any information about approximations for functionals like $F\left[n(\vec{r})\right]$. In the direct comparison to the variational approach of the Hartree-Fock method, the variational principle introduced in the second theorem of Hohenberg and Kohn is even more tricky. Whereas in wave-function based approaches like Hartree-Fock or configuration interaction[1] (CI) the obtained energy value provides information about the quality of the trial wave function (the lower E, the better the wave function), this is not the case in the variational principle based on the electron density. More than that, it can even happen that some functionals provide energies lower than the actual ground state energy in particular calculations.[7]

Also important to mention is that there are certain functions $n(r)$ which would fulfill the requirements[4] and be therefore possible ground state densities, but do not correspond to a potential $v(\vec{r})$. Therefore another requirement on the electron density is its v-representability, i.e. it must correspond to some potential.[4]

3.3 The Kohn-Sham equations

The framework by Hohenberg and Kohn is exact, yet not very useful in actual calculations. The only possibility would be the direct use of the second Hohenberg-Kohn theorem for energy minimization, a way that is possible in general but has proven itself to be impractical. The most desirable way in which quantities can be calculated for problems without an exact analytical solution is one that allows iterations.[6]

An early example of an iterative approach are the self-consistent single particle Hartree-equations.[4,33] Of course, the Hartree-equations are clearly wave-function based and not directly related to the work of Hohnberg and Kohn, yet they have been proven very useful. Hartree's approximation assumes that every electron moves in an effective single-particle potential of the form

$$v_H(\vec{r}) = -\frac{Z}{|\vec{r}|} + \int \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}'. \tag{3.20}$$

The first term is an attractive Coulomb potential of a nucleus with atomic number Z, whereas the integral term corresponds to the potential caused by the mean electron density distribution $n(\vec{r})$.

The mean density can be denoted in terms of the single particle wave functions

$$n(\vec{r}) = \sum_{j=1}^{M} |\phi_j(\vec{r})|^2. \tag{3.21}$$

It is important to mention that the sum in (3.21) runs over the M lowest eigenvalues in accordance to the Pauli principle.

Since the electron-electron interactions are taken into account in the potential term, the N-electron and therefore (neglecting the spin coordinates) 3N-dimensional Schrödinger equation can be approximately replaced by N 3-dimensional single particle equations for electrons moving in an effective potential defined in (3.20):

$$\left[-\frac{1}{2}\vec{\nabla}^2 + v_H(\vec{r})\right] \phi_j(\vec{r}) = \epsilon_j \phi_j(\vec{r}) \qquad j = 1, ..., N \tag{3.22}$$

To solve these self consistent Hartree-equations iteratively an electron density $n(\vec{r})$ and subsequently a potential $v_H(\vec{r})$ are defined, which is then used to solve (3.22) for the chosen wave function. Via comparison of the l.h.s. and the r.h.s. in equation (3.21) one then can determine the deviation of the square-sum of the calculated wave functions from the initially used density. This procedure is repeated with adapted densities in every step until the difference between the l.h.s. and r.h.s. deceeds a certain threshold.

Since the framework of Hohenberg and Kohn is formally exact, an extraction of the Hartree equations from their variational principle for the energy should provide even improvements and, more than that, an alternative and finally practically useful formulation of the second theorem.[4]

Therefore, Kohn and Sham investigated the density functional theory applied to a system of N non-interacting electrons in an external potential, similar to Hartree's approach.

Recalling (3.17) and (3.18), the expression for the energy of such a system is of the form

$$E_{v(\vec{r})}\left[n'(\vec{r})\right] \equiv \int v(\vec{r})n'(\vec{r})d\vec{r} + T_S\left[n'(\vec{r})\right] \geq E \tag{3.23}$$

where $n'(\vec{r})$ is a v-representable density for non-interacting electrons and $T_S\left[n'(\vec{r})\right]$ the kinetic energy of the ground state of those non-interacting electrons.[4]

Setup of the Euler-Lagrange equation[18] for the non-interacting case (3.23) with the density defined in (3.21) as argument provides[4]

$$\delta E_v\left[n'(\vec{r})\right] \equiv \int \delta n'(\vec{r})\left[v(\vec{r}) + \frac{\delta}{\delta n'(\vec{r})}T_S\left[n'(\vec{r})\right]|_{n'(\vec{r})=n(\vec{r})} - \epsilon\right]d\vec{r} = 0 \tag{3.24}$$

with $n'(\vec{r})$, the exact ground state density for the potential $v(\vec{r})$, and the Lagrangian multiplier ϵ to ensure particle density conservation.

Via equations (3.20) to (3.22), where the approximated Hartree-potential is replaced by a simple external potential, it is possible to calculate the ground state energy and particle density of the non-interacting single particles. For a system of non-interacting electrons, the total ground state energy and particle density can therefore simply be denoted as the sums

$$E = \sum_{j=1}^{N}\epsilon_j \tag{3.25}$$

and

$$n(\vec{r}) = \sum_{j=1}^{N}|\phi_j(\vec{r})|^2. \tag{3.26}$$

In addition, Kohn and Sham used the universal functional in equations (3.17) to (3.19) as an alternative formulation, namely[4,5]

$$F\left[n'(\vec{r})\right] \equiv T_S\left[n'(\vec{r})\right] + \frac{1}{2}\int\frac{\left[n'(\vec{r})\right]\left[n'(\vec{r'})\right]}{|\vec{r}-\vec{r'}|}d\vec{r}d\vec{r'} + E_{xc}\left[n'(\vec{r})\right]. \tag{3.27}$$

In (3.27) $T_S\left[n'(\vec{r})\right]$ is the kinetic energy functional of non-interacting electrons (which is not even for the same density $n(\vec{r})$ the true kinetic energy of the interacting system[7]) and the second term is the so-called Hartree term which describes the electrostatic self-repulsion of the electron density.[8] The last term is called *exchange-correlation* term. It is implicitly defined by (3.27) and can in practice only be approximated. The quality of the approximation for $E_{xc}\left[n'(\vec{r})\right]$ is therefore one of the key issues in DFT.[4]

Construction of the Euler-Lagrange equations for the interacting case in equation (3.27) provides[4]

$$\delta E_v\left[n'(\vec{r})\right] \equiv \int \delta n'(\vec{r}) \left[v_{eff}(\vec{r}) + \frac{\delta}{\delta n'(\vec{r})} T_S\left[n'(\vec{r})\right]|_{n'(\vec{r})=n(\vec{r})} - \epsilon\right] d\vec{r} = 0 \tag{3.28}$$

with

$$v_{eff}(\vec{r}) \equiv v(\vec{r}) + \int \frac{[n(\vec{r}')]}{|\vec{r}-\vec{r}'|} d\vec{r}' + v_{xc}(\vec{r}) \tag{3.29}$$

and the functional derivative

$$v_{xc}(\vec{r}) \equiv \frac{\delta}{\delta n'(\vec{r})} E_{xc}\left[n'(\vec{r})\right]|_{n'(\vec{r})=n(\vec{r})} \tag{3.30}$$

whereas the Euler-Lagrange equation resembles (3.24) up to the potential term.

Because of that, the minimizing density can be calculated in a way similar to the Hartree-approach described in equations (3.20) to (3.22). The corresponding equations are the single-particle Schrödinger equations

$$\left[-\frac{1}{2}\vec{\nabla}^2 + v_{eff}(\vec{r})\right]\phi_j(\vec{r}) = \epsilon_j \phi_j(\vec{r}) \qquad j = 1, ..., N \tag{3.31}$$

as well as the defining equation for the particle density

$$n(\vec{r}) = \sum_{j=1}^{M} |\phi_j(\vec{r})|^2, \tag{3.32}$$

which form together with the effective potential $v_{eff}(\vec{r})$ in (3.29) the self-consistent Kohn-Sham equations.[4,5]

The accurate ground state energy, as one of the most important quantities, can be expressed as[4]

$$E = \sum_j \epsilon_j + E_{xc}\left[n(\vec{r})\right] - \int v_{xc}(\vec{r}) n(\vec{r}) dv - \frac{1}{2}\int \frac{[n(\vec{r})]\,[n(\vec{r}')]}{|\vec{r}-\vec{r}'|} d\vec{r} d\vec{r}'. \tag{3.33}$$

Equation (3.33) can be seen as an generalization of the energy expression obtained with the Hartree-approach (note that the neglect of $E_{xc}\left[n(\vec{r})\right]$ and$v_{xc}\left[n(\vec{r})\right]$ leads back to equation (3.25)).[4]

Similar to the Hohenberg-Kohn theorems, also equations (3.31) to (3.33) are formally exact, which means, if the exact $E_{xc}\left[n(\vec{r})\right]$ and $v_{xc}\left[n(\vec{r})\right]$ would be used, one would obtain the exact solution.

3.4 Problems and limitations of DFT

In summary, both the Hohenberg-Kohn formulation as well as the approach by Kohn-Sham are formally exact and therefore allow in principle an exact solution provided that the functional $E_{xc}\left[n(\vec{r})\right]$ is exactly known.

In practice this is never the case, which reveals the crucial point in (ground state) density functional theory. Every calculatory approach in DFT stands and falls with the quality of the approximation for the unknown functionals $F\left[n(\vec{r})\right]$ and $E_{xc}\left[n(\vec{r})\right]$.[4,7] As stated in the introduction, possible approximations of the functional $E_{xc}\left[n(\vec{r})\right]$ are not discussed in this thesis but can be found in several literature sources.[1,6,7,8]

There are also a few other points which have to be taken into consideration. In section 3.1 about the electron density, the term v-representability has been introduced, accompanied by the fact that there do exist particle densities which do not correspond to a potential $v(\vec{r})$[7,4]

The same question can also be asked for an antisymmetric N-body wave function $\psi(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N)$. How can it be assured that a given density $n(\vec{r})$ corresponds to such a wave function? Both of these questions are very important, because an energy calculated from a "physically impossible density" would provide a useless solution.[6,7]

Nevertheless, the problem of N-representability has been solved and it has been proofed that every nonnegative function can be written in the form (3.1) by the use of some anti-symmetric wave function $\psi(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N)$[34,35] The v-representability problem on the other hand lacks of a solution. But instead of a solution, it is referred to the proof which has been presented for the second HK-theorem (Levy and Lieb) and the subsequent statement that a knowledge of $v(\vec{r})$ and therefore v-representability of the density is not a necessity.[29,30]

Another problem arises as soon as information about excited states is required. Recalling that the minimum of the functional $E_v\left[n'(\vec{r})\right]$ in (3.17) corresponds to the ground state energy, it could be assumed that the other extrema of the functional correspond to excited state densities as well, even if the variational principle is in general only valid for the ground state. This is in fact the case, but on the other hand not every excited state density corresponds to an extremum of the functional .[6,36]

Therefore, to obtain trustful information about the excited states of a system, other methods have to be found. A variety of different methods have been investigated,[37,38,39,40] one of the most prominent among them is the so called time-dependent DFT,[7,6,41] to which the final part of this thesis is assigned.

3.5 Time dependent DFT

In general, time-dependent DFT is an alternative yet exact formulation of time-dependent quantum mechanics.[42] The density functional theory discussed up to now solely dealed with equivalence to time-independent wave functions $\psi(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N)$ which fulfill time-independent Schrödinger equations of a form presented in section 2.2.

But there are a lot of problems which require the consideration of time-dependency. Such problems would be, for example, photoabsorption spectra, scattering processes, interaction of matter with laser fields and various more.[41,42]

The starting point is the time-dependent Schrödinger equation[41,42] already introduced in 2.1 which is, due to its importance for the following considerations, repeated briefly at this point.

$$i\hbar\frac{\partial}{\partial t}\Psi(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N, t) = \hat{H}(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N, t)\Psi(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N, t) \tag{3.34}$$

with a time-dependent Hamilton operator similar to the electronic Hamiltonian introduced in section 2.4

$$\hat{H}(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N, t) = \hat{T}(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N) + \hat{V}(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N, t) + \hat{W}(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N). \tag{3.35}$$

It contains of the operators

$$\hat{T}(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N) = -\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2, \tag{3.36}$$

$$\hat{W}(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N) = \frac{1}{2}\sum_{i=1}^{N}\sum_{i>j}^{N}\frac{1}{|\vec{r}_i - \vec{r}_j|}, \tag{3.37}$$

$$\hat{V}(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N, t) = \sum_{i=1}^{N} v_{ext}(\vec{r}_i, t) = \sum_{i=1}^{N}\sum_{k=1}^{M}\frac{Z_k}{|\vec{r}_i - \vec{R}_k(t)|}, \tag{3.38}$$

and the initial condition reads

$$\Psi(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N, t = t_0) = \Psi_0. \tag{3.39}$$

The next section will deal with the major distribution in this field, the paper of Erich Runge and E.K.U. Gross from 1984, who provided a comparable theorem for time-dependent systems as Hohenberg and Kohn did it for time-independent systems.[3] This theorem is nowadays known as the "Runge-Gross-theorem"[41,42]

Since the Rayleigh-Ritz minimum principle doesn't exist in time-dependent systems, and an appropriate action integral provides only a stationary point at the solution of a Schrödinger equation similar to (3.34), another approach has to be found.

Runge and Gross achieved that by showing the invertibility of the map $G : v(\vec{r},t) \rightarrow n(\vec{r},t)$ up to a merely time dependent constant.

Theorem.[41]The map $G : v(\vec{r},t) \rightarrow n(\vec{r},t)$ is obtained for a single particle potential $v(\vec{r},t)$ which is Taylor-expandable at $t = t_0$, by solving the time-dependent Schrödinger equation with a fixed initial state $\Psi(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N, t = t_0) = \Psi_0$ and subsequent calculation of the corresponding densities $n(\vec{r},t)$. It is invertible up to a merely time-dependent function $c(t)$ in the potential.

Proof.[41]It is assumed, that the two potentials $v(\vec{r},t)$ and $v'(\vec{r},t)$ differ by more than a merely time-dependent function, i.e. $v(\vec{r},t) - v'(\vec{r},t) \neq c(t)$. These potentials can of course, still be identical at $t = t_0$. Furthermore due to the prerequisite of the theorem that the two potentials have to be Taylor-expandable at $t = t_0$, there must exist a minimal and non-negative integer k fulfilling

$$\frac{\partial^k}{\partial t^k} \left[v(\vec{r},t) - v'(\vec{r},t)) \right] |_{t=t_0} \neq const. \tag{3.40}$$

Now it has to be proven that the corresponding densities $n(\vec{r},t)$ and $n'(\vec{r},t)$ are in fact different, if equation (3.40) holds for a $k \geq 0$.

The first step of the proof shows that the corresponding current densities $j(\vec{r},t)$ and $j'(\vec{r},t)$ are, in fact, different. The identicallity of the current and particle densities is ensured by the evolution from a fixed initial state Ψ_0.

The time-dependency of the current density can be expressed by the equation of motion

$$\begin{aligned} & i\frac{\partial}{\partial t}\langle \Psi(\{\vec{r}_i\},t)|\hat{O}(\{\vec{r}_i\},t)|\Psi(\{\vec{r}_i\},t)\rangle = \\ & = \langle \Psi(\{\vec{r}_i\},t)|i\frac{\partial}{\partial t}\hat{O}(\{\vec{r}_i\},t) + \left[\hat{O}(\{\vec{r}_i\},t), \hat{H}(\{\vec{r}_i\},t)\right] |\Psi(\{\vec{r}_i\},t)\rangle. \end{aligned} \tag{3.41}$$

Usage of

$$j(\vec{r},t) = \langle \Psi(\{\vec{r}_i\},t)|\hat{\vec{j}}(\vec{r})(\{\vec{r}_i\},t)|\Psi(\{\vec{r}_i\},t)\rangle \tag{3.42}$$

where

$$\hat{\vec{j}}(\vec{r}) = \frac{1}{2i}\sum_{s=1}^{N}\left[\hat{\psi}_s^*(\vec{r})\vec{\nabla}\hat{\psi}_s(\vec{r}) - (\vec{\nabla}\hat{\psi}_s^*(\vec{r}))\hat{\psi}_s(\vec{r})\right] \tag{3.43}$$

leads to

$$i\frac{\partial\vec{j}(\vec{r},t)}{\partial t} = \langle \Psi(\{\vec{r}_i\},t)|\left[\hat{\vec{j}}(\vec{r}),\hat{H}(\{\vec{r}_i\},t)\right]|\Psi(\{\vec{r}_i\},t)\rangle. \tag{3.44}$$

Due to the fixed initial state Ψ_0 from which $\Psi(\{\vec{r}_i\},t)$ and $\Psi'(\{\vec{r}_i\},t)$ evolve, equation (3.44) subsequently leads to

$$\begin{aligned} i\frac{\partial\vec{j}(\vec{r},t)}{\partial t}\left[\vec{j}(\vec{r},t)-\vec{j}'(\vec{r},t))\right]|_{t=t_0} = \langle\Psi_0|\left[\hat{\vec{j}}(\vec{r}),\hat{H}(\{\vec{r}_i\},t_0)-,\hat{H}'(\{\vec{r}_i\},t_0)\right]|\Psi_0\rangle = \\ = i\,n(\vec{r},t_0)\vec{\nabla}\left[v(\vec{r},t_0)-v'(\vec{r},t_0)\right]. \end{aligned} \tag{3.45}$$

If now $v(\vec{r},t)$ and $v'(\vec{r},t)$ differ at $t=t_0$, which is equivalent to equation (3.40) holding for k=0, the r.h.s. does not vanish and the current densities $j(\vec{r},t)$ and $j'(\vec{r},t)$ differ at every time infinitesimally later than t_0. If equation (3.40) holds for a minimum integer $k>0$, equation (3.41) must be applied k times. The prerequisite, that the $k-$th derivatives of the potentials with respect to the spatial coordinates, is assumed to be fulfilled within this proof.[41]

All that can, after some rearrangements and algebra, be expressed mathematically as

$$\left(i\frac{\partial}{\partial t}\right)^{k+1}\left[\vec{j}(\vec{r},t)-\vec{j}'(\vec{r},t))\right]|_{t=t_0} = i\,n(\vec{r},t_0)\vec{\nabla}\left[\left(i\frac{\partial}{\partial t}\right)^{k}\left[v(\vec{r},t)-v'(\vec{r},t))\right]|_{t=t_0}\right]\neq 0 \tag{3.46}$$

what completes the proof for the current densities.

The discussion for the corresponding particle densities starts at the continuity equation

$$\frac{\partial}{\partial t}\left[n(\vec{r},t)-n'(\vec{r},t))\right] = -div\ \left[\vec{j}(\vec{r},t)-\vec{j}'(\vec{r},t))\right]. \tag{3.47}$$

By the use of the result in (3.46) and the $(k+1)$-th derivative of the continuity equation above, the expression

$$\left(\frac{\partial}{\partial t}\right)^{k+2}\left[n(\vec{r},t)-n'(\vec{r},t))\right]|_{t=t_0} = -div\ n(\vec{r},t)\cdot\vec{\nabla}\left[\left(\frac{\partial}{\partial t}\right)^{k}\left[v(\vec{r},t)-v'(\vec{r},t))\right]|_{t=t_0}\right] \tag{3.48}$$

is obtained.

The last remaining step is now to proof that the r.h.s. of equation (3.48) doesn't vanish as long as equation (3.40) holds.

It is assumed, that $div\left[n(\vec{r},t_0)\vec{\nabla}u(\vec{r})\right] = 0$ with $u(\vec{r}) \neq const$, subsequently

$$0 = \int d\vec{r}u(\vec{r})div\left[n(\vec{r},t_0)\vec{\nabla}u(\vec{r})\right] = -\int d\vec{r}n(\vec{r},t_0)\left[\vec{\nabla}u(\vec{r})\right]^2 + \frac{1}{2}\oint n(\vec{r},t_0)\left[\vec{\nabla}u^2(\vec{r})\right]\cdot d\vec{s} \tag{3.49}$$

If the initial density $n(\vec{r},t_0)$ falls off rapidly enough, the surface integral in (3.49) vanishes and it can be concluded that $n(\vec{r},t_0)\left[\vec{\nabla}u(\vec{r})\right]^2 \equiv 0$. This is in contradiction to $u(\vec{r}) \neq const$, neglecting the theoretical possibility that $u(\vec{r}) = const$ in exactly the spatial subregions in which $n(\vec{r},t_0)$ vanishes (if such exist). It proofs by *reductio ad absurdum* that the r.h.s. in (3.48) cannot vanish and $n(\vec{r},t)$ and $n'(\vec{r},t)$ differ infinitesimally later than t_0. □

With that proof at their hands, Runge and Gross also derived a set of, in principle exact, equations similar to the Kohn-Sham equations for ground state DFT.[41]

Theorem II.[41] "The exact time-dependent density of the system can be computed from

$$n(\vec{r},t) = \sum_{j=1}^{M}|\phi_j(\vec{r},t)|^2 \tag{3.50}$$

where the single-particle orbitals fulfill

$$\left[i\frac{\partial}{\partial t} + \frac{1}{2}\vec{\nabla}^2\right]\phi_j(\vec{r},t) = v_{eff}(\vec{r},t;n(\vec{r},t))\phi_j(\vec{r},t) \qquad j = 1,...,N \tag{3.51}$$

with the effective single particle potential

$$v_{eff}(\vec{r},t;n(\vec{r},t)) \equiv v(\vec{r},t) + \int d\vec{r}'\ n(\vec{r}',t)w(\vec{r},\vec{r}') + \frac{\delta A_{xc}}{\delta n(\vec{r},t)} \tag{3.52}$$

."

Proof.[41] Analogous to the stationary case, the *exchange-correlation* part of the action is denoted as

$$\begin{aligned} A_{xc}\left[n(\vec{r},t)\right] = &\int dt\langle\Psi\left[n(\vec{r})\right](t)|\hat{W}|\Psi\left[n(\vec{r})\right](t)\rangle \\ &-\frac{1}{2}\iiint n(\vec{r},t)w(\vec{r},\vec{r}')n(\vec{r}',t) + S_0\left[n(\vec{r},t)\right] - S_W\left[n(\vec{r},t)\right] \end{aligned} \tag{3.53}$$

with the density functional

$$S[n(\vec{r},t)] = \int dt\langle\Psi\left[n(\vec{r})\right](t)|i\frac{\partial}{\partial t}\hat{T}|\Psi\left[n(\vec{r})\right](t)\rangle. \tag{3.54}$$

The stationary action principle is then

$$\frac{\delta A}{\delta n(\vec{r},t)} = 0 = \frac{\delta S_0}{\delta n(\vec{r},t)} - \left[v(\vec{r},t) + \int d\vec{r}'\; n(\vec{r}',t) w(\vec{r},\vec{r}') + \frac{\delta A_{xc}}{\delta n(\vec{r},t)} \right] \tag{3.55}$$

what resembles exactly the Euler equation for a system of non-interacting particles in the effective potential $v_{eff}(\vec{r},t;n(\vec{r},t))$. $\square$

Bibliography

[1] A. Szabo and N.S. Ostlund. *Modern Quantum Chemistry.* McGraw-Hill, 1989.

[2] D.J. Griffiths. *Introduction to Quantum Mechanics.* Pearson, 2005.

[3] P. Hohenberg and W. Kohn. Inhomogeneous electron gas. *Physical Review*, 136:B864–B871, 1964.

[4] W. Kohn. Nobel lecture: Electronic structure of matter - wave functions and density functionals. *Reviews of Modern Physics*, 71:1253–1266, 1999.

[5] W. Kohn and L.J. Sham. Self-consistent equations include exchange and correlation effects. *Physical Review*, 140:A1133–A1138, 1965.

[6] K. Capelle. A bird's-eye view of density-functional theory. *arXiv:cond-mat*, 0211443v5, 2006.

[7] W. Koch and M.C. Holthausen. *A Chemists's Guide to Density Functional Theory.* Wiley-VCH, 2001.

[8] J.P. Perdew and S. Kurth. Density functionals for non-relativistic coulomb systems in the new century. *Lecture Notes in Physics*, 620:1–55, 2003.

[9] E. Schrödinger. An undulatory theory of the mechanics of atoms and molecules. *Physical Review*, 28:1049–1070, 1926.

[10] F. Schwabl. *Quantenmechanik: Eine Einführung (German).* Springer, 2007.

[11] M. Born. On the quantum mechanics of collision processes (german). *Zeitschrift fuer Physik*, 37:863–867, 1926.

[12] W. Pauli. The connection between spin and statistics. *Phys. Rev.*, 58:716–722, 1940.

[13] A. Jabs. Connecting spin and statistics in quantum mechanics. *Found. Phys.*, 40:776–792, 2010.

[14] W. Pauli. On the connexion between the completion of electron groups in an atom with the complex structure of spectra. *Zeitschrift fï¿$\frac{1}{2}$r Physik*, 31:765pp, 1925.

[15] N. Zettili. *Quantum Mechanics: Concepts and Applications.* Wiley-VCH, 2009.

[16] D.A. McQuarrie and J.D. Simon. *Physical Chemistry: A Molecular Approach.* University Sciency Books, 1997.

[17] M. Born and R. Oppenheimer. On the quantum theory of molecules (german). *Annalen der Physik*, 389:457–484, 1927.

[18] T. Fließbach. *Mechanik: Lehrbuch zur Theoretischen Physik I (German).* Spektrum, 2009.

[19] P.A.M. Dirac. A new notation for quantum mechanics. *Mathematical Proceedings of the Cambridge Philosophical Society*, 35:416–418, 1939.

[20] C.B. Lang and N. Pucker. *Mathemathische Methoden in der Physik (German).* Spektrum, 2005.

[21] E. Pavarini, E. Koch, and U. Schollwoeck. *Emergent Phenomena in Correlated Matter.* Forschungszentrum Jï¿$\frac{1}{2}$lich, 2013.

[22] P.O. Löwdin. Scaling problem, virial theorem and connected relations in quantum mechanics. *Journal of Molecular Spectroscopy*, 3:46–66, 1959.

[23] M. Odelius and I. Josefsson. Quantum chemistry - lecture notes, 2009.

[24] A. Berger. *Current-Density Functional in Extended Systems.* PhD thesis, Rijksuniversiteit Groningen, 2006.

[25] W. Kohn. *Proceedings of the International School of Physics "Enrico Fermi"*, LXXXIX:4pp, 1985.

[26] J.C. Cuevas. Introduction to density functional theory (talk notes).

[27] O.V. Gritsenko and E.J. Baerends. The spin-unrestricted molecular kohn-sham solution and the analogue of koopmans's theorem for open-shell molecules. *J. Chem. Phys.*, 120:8364–8372, 2004.

[28] P.P. Rushton. *Towards a Non-Local Density Functional Description of Exchange and Correlation.* PhD thesis, University of Durham, 2002.

[29] M. Levy. Universal variational functionals of electron densities, first order density matrices, and natural spin orbitals and solution of the v-representability problem. *Proc. Natl. Acad. Sci. USA*, 76:6062pp, 1979.

[30] E. Lieb. Density functionals for coulomb systems. *Int. J. Quant. Chem.*, 24:243–277, 1983.

[31] Yang W. Parr, R.G. *Density-Functional Theory of Atoms and Molecules.* Oxford University Press, 1989.

[32] E.V. Kryachko, E.S. Ludena. *Energy Density Functional Theory of Many- Electron Systems.* Kluwer Academic Press, 1990.

[33] D.R. Hartree. The wave mechanics of an atom with a non-coulomb central field. part i. theory and methods. *Mathematical Proceedings of the Cambridge Philosophical Society*, 24:89–110, 1928.

[34] T.L. Gilbert. Hohenberg-kohn theorem for nonlocal external potentials. *Phys. Rev. B.*, 12:2111pp, 1975.

[35] J.E. Harriman. Orthonormal orbitals for the representation of an arbitrary density. *Phys. Rev. A*, 24:680–682, 1981.

[36] J.P. Perdew and M. Levy. Extrema of the density functional for the energy: Excited states from the ground-state theory. *Phys. Rev. B*, 31:6264–6272, 1985.

[37] A. Nagy and I. Andrejkovics. Excitation energies in density functional theory: comparison of several methods for the h2o, n2, co and c2h4 molecules. *Chem. Phys. Lett.*, 296:489pp, 1998.

[38] M. Levy and A. Nagy. Variational density-functional theory for an individual excited state. *Phys. Rev. Lett.*, 83:4361pp, 1999.

[39] K. Capelle. Variational calculation of many-body wave functions and energies from density functional theory. *J. Chem. Phys.*, 119:1285pp, 2003.

[40] R. van Leeuwen, C.O. Almbladh, and U. von Barth. Variational total energies from phi- and psi-derivable theories. *Phys. Rev. Lett.*, 82:3863pp, 1999.

[41] E. Runge and E.K.U. Gross. Density-functional theory for time-dependent systems. *Physical Review Letters*, 52:997–1000, 1984.

[42] M.A. Marques and E.K.U. Gross. Time-dependent density functional theory. *Lecture Notes in Physics*, 620:144–151, 2003.