Quantum Mechanical First Principles Calculations of the Electronic and Magnetic Structure of Fe-bearing Rock-forming Silicates

Danylo Zherebetskyy

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ABSTRACT

The focus of this thesis is the study of the electronic and magnetic structure of three representative members of Fe-bearing rock-forming silicates, viz. orthoferrosilite ($Fe^{2+}{}_2Si_2O_6$), almandine ($Fe^{2+}{}_3Al_2(SiO_4)_3$) and andradite ($Ca_3Fe^{3+}{}_2(SiO_4)_3$). These minerals have attracted significant attention due to their abundance in the Earth's crust and mantle, and because crystallised silicates are main components of cosmic dust which is the most abundant raw material in the Universe. For this purpose quantum mechanical first principles electronic structure calculations are performed by the most efficient DFT method in the local spin-density approximation for calculating spectroscopic data: the spin-polarized self consistent charge Xα method.

The specific feature and strength of these investigations consist in the theoretical characterization of these complex systems based on experimental results. This means that, on one hand, experimental spectroscopic and crystallographic data are being used to judge the reliability of the calculations, whereas, on the other hand, experimental data are interpreted and explained by the theoretical results.

This work comprises seven chapters. After a brief introduction (Chapter 1) Chapter 2 describes the theoretical bases, ideas, approximations and advantages of the SCC- Xα method and basics of the art of cluster construction. Chapter 3 considers physical bases of crystal field theory, absorption, Mössbauer spectroscopy and magnetic interactions, as well as the calculation of spectroscopic data within the frame of the SCC-Xα method. In addition, tetragonally, trigonally and angularly distorted octahedral sites with various degrees of the distortions are calculated and analyzed. The electronic and magnetic structures of orthoferrosilite, almandine and andradite are described in the following chapters. In the case of orthoferrosilite the magnetic interactions between the iron spins within the ribbons and between neighboring ribbons are characterized. Two identical interpenetrating magnetic sublattices of circles of 10 edge-shared dodecahedra are revealed and characterized in almandine. The calculated spin structure explains and solves the controversy in the interpretation of the Mössbauer spectra of almandine below the Néel temperature. For andradite a model of the magnetic structure is proposed based on geometrical considerations and the calculated spin coupling constants for the various interaction pathways. According to this model, the magnetic structure of andradite consists of two frustrated equivalent magnetic sublattices. The spins of the Fe ions within each sublattice are coupled antiferromagnetically. The derived spin pattern explains two sextets in the Mössbauer spectra of andradite below the Néel temperature. Finally, the main results are summarized in Chapter 7.

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Chapter 1

INTRODUCTION

Silicates are the main constituents of the Earth's crust and mantle comprising 95% of the crust and 97% of the mantle, by most estimates, and the most important rock-forming minerals. Correspondingly, about one fourth of the known minerals of the crust are silicates, and the nine most abundant elements in the Earth´s crust, viz. O (61.2 %), Si (20.8 %), Al (6.4 %), Na (2.6 %), Fe (1.9 %), Ca (1.9 %), Mg (1.8 %), K (1.4 %), H (1.0 %), appear as the most major constituting atoms of the various silicate minerals. Moreover, the European Space Agency's Infrared Space Observatory discovered in 1998 that crystallised silicates are main components of dust which is the most abundant raw material in the Universe (planets, comets etc. are all made from reprocessed dust). This finding named "crystalline revolution" that is one of the main results of ESA's infrared space telescope, opens a totally new field astro-mineralogy.

Among the most abundant elements listed above only iron can carry a magnetic moment because of its partly-filled *d* shell, while all the other ions have a closed shell configuration in their common oxidation state. In fact, the reason for the magnetic properties of Fe-bearing silicates is that iron in both of its two common oxidation states occurs in the high-spin state with 5 unpaired 3*d* electrons (Fe^{3+} with spin S=5/2) and 4 unpaired 3*d* electrons (Fe^{2+} with spin S=2), respectively. Since the abundance of any other magnetic ion is more than an order of magnitude smaller than that of iron, e.g. Mn with 0.05 % as the second most abundant open shell ion, the discussion of the magnetic properties of minerals must necessarily focus on iron oxides and iron silicates and a proper understanding of the physics and chemistry of our planet and Universe requires information on their properties.

Whereas the magnetic properties of most iron oxide minerals, some of them known since ancient times, have extensively been investigated and are thus rather well known, the magnetic behaviour of iron bearing silicates is far less well understood. The obvious reason is the complexity of their structure so that

(i) the interpretation of the experimental results is more difficult and

(ii) reliable theoretical calculations can hardly be found.

Moreover, none of the most abundant rock forming iron silicates is magnetically ordered at ambient temperature, but almost all of them exhibit complex low-temperature magnetic structure, usually characterized by antiferromagnetic ordering with Néel temperatures T_N in the range between 1 and 100 K.

Nevertheless, the occurrence of magnetic ordering at low temperatures can still have a significant influence on the thermodynamic properties at elevated temperatures since crystal-field effects and magnetic ordering can contribute up to 10% and more to the specific heat, and thus to the enthalpy and entropy at room temperature. In general, the Mg- and Al-silicates show considerably different physico-chemical properties in comparison with the isotypic Fe-silicates, e.g. enstatite, $Mg_2Si_2O_6$, vs. ferrosilite, $Fe^{2+}{}_2Si_2O_6$, pyrope, $Mg_3Al_2(SiO_4)_3$, vs. almandine, $Fe^{2+}{}_3Al_2(SiO_4)_3$, and grossular, $Ca_3Al_2(SiO_4)_3$, vs. andradite, $Ca_3Fe^{3+}{}_2(SiO_4)_3$. Thus, the presence of magnetic ions in a solid solution may change its macroscopic properties in a fundamental manner. Additionally, magnetic ions provide a sensitive probe of the local chemical environment, and chemical disorder may induce spin glass behaviour.

The basic aim of the present study is to understand the origin and the details of the low-temperature magnetic structure of representative iron-bearing silicates as an important class of rock-forming minerals. Since a qualitatively correct model of the electronic structure is the necessary basis for understanding the magnetic properties, this aim is expected to be achieved by systematic theoretical investigations of the electronic structure from which spin density distributions, magnetic moments, and the parent magnetic interaction constants can be derived. These results are utilized to trace back the reasons for the different strengths of the magnetic interactions, as expected, e.g., in the different ordering temperatures T_N, to the electronic and geometrical structure. The specific feature and strength of these investigations consist in the theoretical characterization of these complex systems based on experimental results. This means that, on one hand, experimental spectroscopic and crystallographic data are being used to judge the reliability of the calculations, whereas, on the other hand, experimental data are interpreted and explained by the theoretical results. For, in many cases different physical effects contribute to a certain observable and the influence and significance of the various contributions can usually not be estimated from experiments alone, while calculations may help to settle this type of questions.

The innovative aspects of these investigations consist in quantum mechanical first principles calculations, i.e. without using empirically derived parameters. To the best of our knowledge calculations on this level of sophistication have not yet been applied for the determination of magnetic interaction constants in Fe-bearing silicates. The theoretical derivation of quantitatively correct values for the Heisenberg coupling constants for systems of such a complexity as provided by the iron-silicates is certainly the most important and challenging step towards describing and explaining the magnetic properties not just of the Fe-bearing silicates but also of other similarly complex systems. Consequently, investigating and understanding the magnetic properties and magnetic structures of iron silicates is of basic importance and will substantially contribute to the understanding of these phenomena as well as to the thermodynamic properties of Fe-bearing rock-forming silicates.

In summary, Fe-bearing silicates exhibit a variety of interesting magnetic properties reflecting peculiarities of the silicate structure. Very often minor changes of the crystal structures and chemical compositions have a great influence on the magnetic properties such as magnetic ordering temperatures, sizes of the local magnetic fields, magnetic coupling, etc. However, the complete relations between crystal structures and magnetic properties of the various Fe-bearing silicates are not yet understood.

The selection of suitable Fe-silicates for investigating magnetic ordering is dictated by several boundary conditions that must be fulfilled for successfully carrying out of this work, namely:

- Spectroscopic data, e.g. from Mössbauer, and/or optical spectroscopy, and/or magnetic susceptibility should be available for the selected systems in order to have an independent measure for judging the reliability of the calculations.
- The systems should be representative and relevant from the mineralogical and geochemical point of view. In this respect pyroxenes and garnets belong to the most important Fe-bearing rock-forming silicates

Based on these considerations, the orthopyroxene solid solution series, as well as end-member garnets almandine and andradite have been selected. The quantum mechanical first principles electronic structure calculations are performed by the most efficient DFT method in the local spin-density approximation for calculating spectroscopic data: the spin-polarized self consistent charge Xα method.

In the first part of this thesis, the theoretical bases, ideas, approximations and advantages of the SCC- Xα method and basics of the art of cluster construction are described (Chapter 2) and, furthermore, we considered the physical bases of absorption and Mössbauer spectroscopy, crystal field theory, evaluation of the main spectroscopic values within the frames of the SCC- Xα method and magnetic interaction between atoms (Chapter 3). In addition, the splitting patterns of the 3*d* orbitals of the Fe^{2+} ion in tetragonally, trigonally and angularly distorted octahedral site for variable degrees of the distortions are calculated and analyzed. It is shown, that the point charge model for description of the crystal-field splitting is inappropriate and the model based on the overlap integrals is very appropriate for the description of the crystal-field splitting.

In the second part of this work (Chapter 4-6) the electronic and magnetic structures of orthoferrosilite $Fe^{2+}{}_2Si_2O_6$, almandine $Fe^{2+}{}_3Al_2(SiO_4)_3$ and andradite $Ca_3Fe^{3+}{}_2(SiO_4)_3$ are investigated and characterized by electronic structure calculations in the local spin density approximation.

Chapter 2

THEORETICAL BASES

2.1 Born-Oppenheimer Approximation

The quantum mechanical description of an electronic system requires the solution of the (time-independent) Schrödinger equation (SE). Neglecting magnetic interactions and relativistic effects, the full *nonrelativistic Hamiltonian* for a molecule, cluster or solid comprises contributions from all the nuclei and the electrons of the system:

$$\hat{H} = \hat{T}_N + \hat{T}_e + \hat{U}_{Ne} + \hat{U}_{ee} + \hat{U}_{NN}, \qquad (2.1)$$

where $\hat{T}_N$ and $\hat{T}_e$ are the operators of the kinetic energy of the nuclei and electrons, respectively, $\hat{U}_{Ne}$ is the operator of the attractive electrostatic interaction between electrons and nuclei, $\hat{U}_{ee}$ and $\hat{U}_{NN}$ are the operators of the electrostatic electron-electron and nuclear-nuclear repulsion, respectively. For a system of N nuclei and K electrons, this Hamiltonian explicitly can be written as:

$$\hat{H} = -\frac{\hbar^2}{2M_I}\sum_{I=1}^{N}\nabla_I^2 - \frac{\hbar^2}{2m_e}\sum_{i=1}^{K}\nabla_i^2 - \sum_{I=1}^{N}\sum_{i=1}^{K}\frac{Z_I e^2}{|\vec{R_I}-\vec{r_i}|} +$$

$$+\sum_{i=1}^{K}\sum_{j<i}^{K}\frac{e^2}{|\vec{r_i}-\vec{r_j}|} + \sum_{I=1}^{N}\sum_{J<I}^{N}\frac{Z_I Z_J e^2}{|\vec{R_I}-\vec{R_J}|}, \qquad (2.2)$$

where M_I is the mass of I^{th} nucleus and m_e is the electron mass, e is the elementary charge, $\vec{r_i}$ is the position of the i^{th} electron, $\vec{R_I}$ and Z_I are the position and the atomic number of the I^{th} nucleus, respectively. In equations (2.1-2.2), relativistic effects, such as spin-orbit or spin-spin coupling are neglected.

The vast majority of electronic structure calculations on molecules, clusters and solids is based on the experience that the motions of the nuclei and electrons are, in general, only weakly coupled due to the large difference in the masses of the electrons and protons (nuclei)

$$\frac{m_{el}}{M_{prot}} = \frac{1}{1836.15} \Rightarrow \frac{m_{el}}{M_{nuc}} \approx 2\cdot 10^{-4} \dots 10^{-6}. \qquad (2.3)$$

In addition, since the absolute values of the electric charge of the electron and the proton are identical, attractive and repulsive electrostatic interactions between the particles are of the same order of magnitude. Due to this difference in masses the electronic and nuclear motions take place on different time scales, i.e.:

1) the electrons move much faster, and adjust to each change of nuclear positions almost instantaneously;

2) with respect to the motion of the electrons, the ions can be assumed as frozen.

The formal separation of electronic and nuclear motion is known as *the Born-Oppenheimer approximation*, adiabatic or clamped-nuclei approximation (Born and Oppenheimer 1927). In this approximation the total wavefunction is written as the product of a nuclear and an electronic part

$$\Psi(\vec{R},\vec{r}) = \psi_{nuc}(\vec{R})\psi_{el}(\vec{r}), \qquad (2.4)$$

where $\vec{R}$ are all nuclear coordinates and $\vec{r}$ are the coordinates of all electrons. Substituting this wavefunction into the Hamiltonian (2.1) yields two separate SE, viz.:

$$\left(\hat{T}_e + \hat{U}_{ee} + \hat{U}_{Ne}\right)\psi_{el} = E_{el} \cdot \psi_{el} \qquad (2.5)$$

which refers to the electronic system, where the energy E_{el} and wavefunction ψ_{el} depend parametrically on the nuclear positions $\vec{R}$, and

$$\left(\hat{T}_N + \hat{U}_{NN} + E_{el}\right)\psi_{nuc} = E \cdot \psi_{nuc} \qquad (2.6)$$

describing the nuclear motions.

The corresponding electronic Hamiltonian in the Born-Oppenheimer (BO) approximation is

$$\hat{H}_{el} = -\frac{\hbar^2}{2m_e}\sum_{i=1}^{K}\nabla_i^2 - \sum_{I=1}^{N}\sum_{i=1}^{K}\frac{Z_I e^2}{|\vec{R_I}-\vec{r_i}|} + \sum_{i=1}^{K}\sum_{j<i}^{K}\frac{e^2}{|\vec{r_i}-\vec{r_j}|}\,. \qquad (2.7)$$

Solving SE (2.5) for the electronic wavefunction gives the eigenvalue $E_{el}(\vec{R})$ of the electronic Hamiltonian (2.7). One must remember during the treatment of the electronic SE that the nuclei move relatively slowly and each new relative positions of the nuclei $\vec{R}$ provide a new solution to the SE. Accordingly, the total energy of the system E_T is the sum of electronic energy E_{el} and the nuclear repulsion term U_{NN}:

$$E_T(\vec{R}) = U_{NN} + E_{el}(\vec{R})\ . \qquad (2.8)$$

In this picture the electrons move in the field of the fixed nuclei (2.5) while the nuclei move on a potential energy surface (2.8), where the electronic energy compensates the nuclear-nuclear repulsion. Consequently, there is no stable nuclear system without electrons. Furthermore, solution of the SE (2.6) for the nuclear wave function leads to energy levels for molecular vibrations and rotations.

The BO approximation is the first step towards simplifying the solution of the SE. However, the approximation contradicts with respect to the nuclei one of the fundamental principles of quantum mechanics, namely the Heisenberg uncertainty principle. Since the uncertainty principle does not allow simultaneously certain impulse and certain position any particle, it is wrong to say that the nuclei are frozen having certain coordinates. Therefore, the Born-Oppenheimer approximation cannot be realized within the frames of QM. The conceptual basis of the BO approximation consists in the classical description of the nuclear motion. Correspondingly, the nuclear positions $\overrightarrow{R_I}$ are treated as parameters and not as dynamical variables. Consequently, the conceptual basis of molecular and solid state physics (structure, bond, potential curve, electronic state, molecular vibration, etc.) is not defined within the frame of a purely quantum mechanical description. Therefore, the two fundamental concepts of any theory of condensed matter, viz. structure and dynamics, are not defined within the frames of a purely quantum mechanical description (Grodzicki 2007).

2.2 Density Functional Theory

Density functional theory (DFT) is one of the most popular and successful quantum mechanical approaches to simulations of matter. In recent years, it has widely been applied for simulation studies in order to understand the behavior and properties of molecules and solids. The development of the DFT leads to important breakthroughs in chemical calculations and is a very significant contribution to the science of many-particle quantum systems, including problems of electronic structure of molecules and of condensed matter. For the pioneering contributions in developing methods that can be used for theoretical studies of the properties of molecules and the chemical processes in which they are involved, Walter Kohn who played the leading role in the development of the DFT was awarded, jointly with John Pople, the Nobel Prize in chemistry in 1998 (Kohn 1995, 1999).

The knowledge of the energies and wavefunctions of electrons in a system under study enables the calculation of optical, magnetic, thermal properties of the system, and therefore understanding the behaviour of atoms, molecules and solids. However, the wavefunction is a very complicated quantity for an *N*-electron system that depends on 3*N* spatial and *N* spin variables. This huge number of variables makes Hartree-Fock computations very difficult or impossible at all. Within conventional quantum-chemical approaches (HF and beyond), it was common wisdom that the exact description of the electronic structure requires both the *single-particle density* $\rho(\vec{r})$ and the *two-particle density* $\pi(\vec{x}_1, \vec{x}_2)$:

$$\rho(\vec{r}) = N \int \dots \int |\Psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N)|^2 ds_1 d\vec{x}_2 \dots d\vec{x}_N, \qquad (2.9)$$

$$\pi(\vec{x}_1, \vec{x}_2) = N(N-1) \int \dots \int |\Psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N)|^2 d\vec{x}_3 \dots d\vec{x}_N. \qquad (2.10)$$

In equation (2.9), $\vec{x}_i = (\vec{r_i}, s_i)$ and $\rho(\vec{r})$ is the probability to find any of *N* electrons within the volume $d\vec{r}_1$ (at position $\vec{r}_1$) with arbitrary spin while the other electrons of the system have arbitrary positions. In turn, the two-particle density $\pi(\vec{x}_1, \vec{x}_2)$ defines the probability to find two electrons with spins s_1 and s_2 within two volume elements $d\vec{r}_1$ and $d\vec{r}_2$ (at positions $\vec{r}_1$ and $\vec{r}_2$), respectively.

The probability density $\rho(\vec{r})$ is strictly the electron number density and not electron density, which is defined as $-e\rho(\vec{r})$. However, numerous authors speak about probability density and electron density as if it were the same thing. Such sloppy usage is stipulated by the fact that probability density is related to a random variable and the authors want to indicate that the electrons are the particles under consideration. It is clear that the integral of the probability density is the total number of electrons

$$\int \rho(\vec{r})d\vec{r}_1 = N. \tag{2.11}$$

An important property of the probability density is the observability, i.e. it can be measured experimentally by X-ray diffraction.

In turn, the pair density $\pi(\vec{x}_1, \vec{x}_2)$ contains important information about electron correlation. The integral of the pair density is the total number of non-distinct electron pairs

$$\int \pi(\vec{x}_1, \vec{x}_2)d\vec{x}_1 d\vec{x}_2 = N(N-1). \tag{2.12}$$

Since electrons are indistinguishable particles, the pair density may be written as

$$\pi(\vec{x}_1, \vec{x}_2) = \frac{N-1}{N}\rho(\vec{x}_1)\rho(\vec{x}_2)(1 - g(\vec{x}_1, \vec{x}_2)), \tag{2.13}$$

where $g(\vec{x}_1, \vec{x}_2)$ is the pair-correlation function.

With regard to this background it was surprising and of central importance that an exact representation of the quantum-mechanical many-particle problem can be constructed solely on the basis of the single-particle density (Hohenberg and Kohn, 1964).

The attempt to use the probability density instead of the wavefunction for molecular systems is almost as old as quantum mechanics (Thomas 1927 and Fermi 1927). In the first attempt within the frame of DFT, the quantum nature of electrons is taken into account only in kinetic energy while nuclear-electron and electron-electron interactions are described in a classical way by Coulomb electrostatic interaction. The fermion nature of electrons is not taken into account. The Thomas-Fermi model uses a very simple functional expression for kinetic energy which is based on the uniform electron gas. In this model, the total ground-state energy of an atom is a functional of the density

$$\begin{aligned} E_{TF}[\rho(\vec{r})] &= T[\rho(\vec{r})] + U_{ext}[\rho(\vec{r})] + U_{ee}[\rho(\vec{r})] = \\ &= \frac{3}{10}(3\pi^2)^{2/3}\int (e\rho)^{5/3}(\vec{r})d\vec{r} - Ze^2\int \frac{\rho(\vec{r})}{\vec{r}}d\vec{r} + \frac{e^2}{2}\iint \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|}d\vec{r}_1 d\vec{r}_2, \end{aligned} \tag{2.14}$$

where $T[\rho(\vec{r})]$ is the kinetic energy, $U_{ext}[\rho(\vec{r})]$ is the external potential and $U_{ee}[\rho(\vec{r})]$ is the energy of the electron-electron repulsion. The model gives good qualitative picture of electronic structure but not the shell structure and single-particle density does not behave exponentially and it predicts all molecules to be unstable toward dissociation into their atoms.

The idea to consider the single-particle density instead of the wavefunction plays a central role in the *Density functional theory*. The next stage for this approach and the whole theory is based on the three remarkable theorems of Pierre Hohenberg and Walter Kohn (Hohenberg and Kohn, 1964).

(HK1) *The local external potential* $U_{ext}(\vec{r})$ *is a unique functional of the electron density* $\rho(\vec{r})$*, apart from a trivial additive constant,* which has modified formulation: *the energy* E_0 *of the ground state is unique functional of the ground state electron density* $\rho(\vec{r})$ (Grodzicki 1999).

In other words, if the electron density $\rho_0(\vec{r})$ of the ground state of a quantum-mechanical many-particle system is known any ground state property can be calculated (Grodzicki 1999). Additionally, it should be mentioned that the energy computed as the expectation value of the Hamiltonian $\hat{H}$ from any guessed wavefunction, ψ_t, is always higher or equal than the energy of the ground state

$$\frac{\int \psi_t^* \hat{H} \psi_t dx}{\int \psi_t^* \psi_t dx} = E_t \geq E_0 = \frac{\int \psi_0^* \hat{H} \psi_0 dx}{\int \psi_0^* \psi_0 dx}. \qquad (2.15)$$

Hence, we have to minimize the functional, $E_t[\psi_t]$, by searching through all acceptable wavefunctions, in order to find the ground state energy and wavefunction. This is a so-called *variational principle*. The proof of the Hohenberg-Kohn theorem is based on a *reductio ad absurdum* argument using this principle.

The DFT analogue of the variational principle is HK2 (second Hohenberg-Kohn theorem), which states that:

$E[\rho(\vec{r})]$ *assumes its minimum value for the correct ground state density* $\rho_0(\vec{r})$*, if the admissible functions* $\rho(\vec{r})$ *are restricted by the condition*

$$N[\rho(\vec{r})] = \int \rho(\vec{r}) d\vec{r} = N. \qquad (2.16)$$

If we define a trial one-electron density $\rho'(\vec{r})$ satisfying conditions $\rho'(\vec{r}) \geq 0$ for all $\vec{r}$ and $\int \rho'(\vec{r}) d\vec{r} = N$ than the HK2 can be formulated as:

(HK2) *The energy calculated from a trial one-electron density* $\rho'(\vec{r})$*, such that* $\rho'(\vec{r}) \geq 0$ *(for all r) and* $\int \rho'(\vec{r}) d\vec{r} = N$*, is always larger than the exact ground-state energy* E_0

$$E[\rho'(\vec{r})] \geq E_0[\rho_0(\vec{r})], \qquad (2.17)$$

and sign of equality is valid exactly when $\rho'(\vec{r})$ *is equal to the exact ground-state one-particle density* $\rho_0(\vec{r})$*.*

In other words, the minimum value of the energy corresponds to the exact ground-state electron density and any approximate density gives higher value of energy.

Assuming differentiability of $E[\rho(\vec{r})]$, the variation of the energy functional gives the Euler-Lagrange equation

$$\frac{\delta E[\rho(\vec{r})]}{\delta \rho(\vec{r})} = \mu, \qquad (2.18)$$

where the Lagrange parameter μ can be interpreted as the chemical potential of the system.

Both theorems are *existence theorems,* which state that the external potential and hence all properties of the many-particle system, are determined by the ground-state electron density distribution. Therefore, they do not provide any concrete form of the functional.

In the next step, a *universal functional*, which describes the kinetic energy of the electrons and interelectronic interaction, is defined as

$$F[\rho(\vec{r})] = \int \Psi^*(\hat{T} + \hat{U}_{ee})\Psi d\,\vec{r}. \qquad (2.19)$$

The universal functional is valid for any number of particles and independent of the external potential. With the help of the universal functional, the energy functional for a given external potential $U_{ext}(\vec{r})$ is defined as

$$E[\rho(\vec{r})] = \int U_{ext}(\vec{r})\rho(\vec{r})d\,\vec{r} + F[\rho(\vec{r})]. \qquad (2.20)$$

A first step to the solution of the concrete functional problem is the third Hohenberg-Kohn theorem:

(HK3) *The total energy of a N-electron system in a local, external potential* $U_{ext}(\vec{r})$ *can be presented in the form*

$$E[\rho(\vec{r})] = \int \rho(\vec{r})U_{ext}(\vec{r})d\,\vec{r} + T[\rho(\vec{r})] + U_{ee}[\rho(\vec{r})] = U_{ext}[\rho(\vec{r})] + F_{HK}[\rho(\vec{r})], \qquad (2.21)$$

where $F_{HK}[\rho(\vec{r})]$ does not depend on $U_{ext}(\vec{r})$, and therefore is a universal functional composed of the kinetic energy $T[\rho(\vec{r})]$ of the electrons and the electron-electron interaction $U_{ee}[\rho(\vec{r})]$. The universal functional $F_{HK}[\rho(\vec{r})]$ has the same form as functional of ρ in all systems, so that, the N-electron problem can be split into a general, system-independent and a system-specific parts.

This problem was solved (Kohn and Sham, 1965) by the suggestion that the universal functional should be

$$F[\rho(\vec{r})] = T_s[\rho(\vec{r})] + J[\rho(\vec{r})] + E_{XC}[\rho(\vec{r})], \qquad (2.22)$$

where

$$T_s[\rho(\vec{r})] = \sum_i^N \int \psi_i(\vec{r}_i)(-\frac{\hbar^2}{2m_e}\nabla^2)\psi_i(\vec{r}_i)d\vec{r}_i \qquad (2.23)$$

is the kinetic energy of noninteracting electrons,

$$J[\rho(\vec{r})] = \frac{1}{2}\iint \frac{e^2\rho(\vec{r}_i)\rho(\vec{r}_j)d\vec{r}_i d\vec{r}_j}{|\vec{r}_i - \vec{r}_j|} \qquad (2.24)$$

is the classical electrostatic energy arising from the interaction between two charge densities, and

$$E_{XC}[\rho(\vec{r})] \equiv (T[\rho(\vec{r})] - T_s[\rho(\vec{r})]) + (U_{ee}[\rho(\vec{r})] - J[\rho(\vec{r})]) \qquad (2.25)$$

is the so-called *exchange-correlation energy*. In equation (2.25), T is the exact kinetic energy of the interacting system, T_S is the kinetic energy of the non-interacting system and U_{ee} is the full electron-electron repulsion energy. Hence, the exchange-correlation energy is the part containing all unknown interactions. In addition, it is possible to split the exchange-correlation energy into an exchange and a correlation contribution

$$E_{XC}[\rho(\vec{r})] = E_X[\rho(\vec{r})] + E_C[\rho(\vec{r})] \qquad (2.26)$$

It should be emphasized that usually the exchange contribution is about an order of magnitude larger than the corresponding correlation energy.

Using equations (2.22)-(2.25), the full expression for the total electronic energy within the Kohn-Sham scheme can be written as

$$E[\rho(\vec{r})] = \sum_i^N \int \psi_i(\vec{r}_i)\left(-\frac{\hbar^2}{2m_e}\nabla^2\right)\psi_i(\vec{r}_i)d\vec{r}_i + \frac{e^2}{2}\iint \frac{\rho(\vec{r}_i)\rho(\vec{r}_j)d\vec{r}_i d\vec{r}_j}{|\vec{r}_i - \vec{r}_j|} + E_{XC}[\rho(\vec{r})] + U_{ext}[\rho(\vec{r})]. \qquad (2.27)$$

The corresponding one-electron equations are denoted as *Kohn-Sham equations*

$$\left[-\frac{\hbar^2}{2m_e}\nabla^2 + V_{ext}[\rho(\vec{r}_i)] + \int \frac{e^2\rho(\vec{r}_j)d^3\vec{r}_j}{|\vec{r}_i - \vec{r}_j|} + V_{XC}(\vec{r}_i)\right]\psi_i(\vec{r}_i) = \varepsilon_i\psi_i(\vec{r}_i) \qquad (2.28)$$

where the MOs $\psi_i(\vec{r}_i)$ are called *Kohn-Sham (KS) orbitals* and V_{XC} is the *exchange-correlation functional* which is the functional derivative of the exchange-correlation energy with respect to $\rho(\vec{r})$

$$V_{XC}(\vec{r}_i) = \frac{\delta E_{XC}[\rho(\vec{r})]}{\delta\rho(\vec{r})}. \qquad (2.29)$$

In the calculations the one-electron density is defined as

$$\rho(\vec{r}_i) = \sum_k n_k |\psi_k(\vec{r}_i)|^2, \qquad (2.30)$$

where n_k is the occupation number of k^{th} molecular orbital, $\psi_k(\vec{r})$.

The knowledge of the ground-state density function $\rho_0(\vec{r})$ and the exchange-correlation energy functional $E_{XC}[\rho_0(\vec{r})]$ gives the exact energy. However, neither the exchange-correlation functional nor the exchange-correlation energy are known up to now. Therefore, a number of different approximations and strategies to the Kohn-Sham theory have been proposed to solve the equations.

The simplest approximation for solving the Kohn-Sham equations is the *Local Density Approximation* (LDA). The idea of the LDA consists in identifying the density locally as that of the *uniform electron gas*. Firstly, it is possible to present the exchange correlations energy in the following simple form

$$E_{xc}^{LDA}[\rho(\vec{r})] = \int \rho(\vec{r})\varepsilon_{xc}^{LDA}(\rho(\vec{r}))d\vec{r}. \qquad (2.31)$$