Electron density and correlation energy in density functional theory

Ph.D thesis

Erika Bene

supervisor:
Dr. Ágnes Nagy
professor

Department of Theoretical Physics
University of Debrecen

Debrecen, 2002

Contents

Introduction

Density functional theory (DFT) [1-3] provides a quantum-mechanical formalism for the quantitative calculation of the electronic structure of matter. In this method without loss of rigor the electron density can be used as the basic variable, instead of the wave function. In contrast to the application of the many-variable wave function, usage of the electron density is very advantageous because it has only three variables independently of the size of the system under investigation, so the density functional approach is a fundamental and very efficient tool for the calculation of the properties of systems which contain a large number of electrons (molecules, solids, liquids and surfaces, etc.). Density-functional methods are employed for many contemporary calculations done for solids, and increasingly applied to atoms and molecules. The electron density is a non-negative simple function of the three space coordinates. In addition, it is a measurable physical quantity: its Fourier-transform can be readily visualized from diffraction experiments.

Density functional theory has its roots in the papers of Thomas and Fermi [4-6] in the 1920s. They used statistical considerations to describe the charge-clouds of atoms. Their approximation replaces the electron-electron interaction energy by its classical part, the Coulomb potential energy, and takes kinetic energy from the theory of a non-interacting uniform electron gas. Later Dirac [7], Gombás [8], Gáspár [9] and other workers extended the theory of Thomas and Fermi with an exchange energy formula.

The Hohenberg-Kohn theory [10] formally completes the original Thomas-Fermi theory by showing that all ground-state observables of a many-electron system, for example the kinetic, the electron-electron interaction and the external potential energies are functionals of the electron density, and it also provides a variational principle for the total energy functional. The Hohenberg-Kohn theory only states the existence of the functionals, but does not offer a practical guide to their explicit construction.

However, density functional theory yields a computational scheme, the Kohn-Sham equations [11]. These are similar to Hartree-Fock equations, but they include both exchange and correlation effects through a local, density-dependent, one-particle exchange-correlation potential. The Kohn-Sham method offers an important simplification of the many-particle problem. It is in principle an exact theory, however, the exact forms of the exchange-correlation energy and potential functionals are unknown, so in actual calculations approximations have to be used. The simplest and most widely used approximations are the local functionals, in which the exchange-correlation energy density depends on the space coordinates only through the electron density. The local density approximation (LDA) [12]-[16] is based on the theory of the homogeneous interacting electron gas. In the lowest order perturbation theory for a homogeneous electronic system the contribution to the exchange energy density can be obtained, while higher order perturbations lead to terms contributing to the correlation energy density. The generalized gradient approximations (GGAs) [17, 18] contain gradient corrections to the exchange-correlation energy functional.

In the ground-state theory, exchange can be treated exactly via the optimized effective potential (OEP) method [23-26], in which one employs the exact exchange energy expressed in terms of the one-electron spin-orbitals. Only the correlation part of the exchange-correlation energy needs to be approximated in this approach. The central equation in this generation of DFT is still the Kohn-Sham equation, but as a consequence of the orbital dependence of the exchange-correlation energy the calculation of the exchange-correlation potential is somewhat more complicated than in the classical Kohn-Sham scheme. It can be determined by solving an integral equation known as the OEP equation, which is a very difficult task. Krieger, Li and Iafrate (KLI) [27-32] proposed a semi-analytical scheme for solving the OEP integral equation approximately.

In this work Chapter 1 summarizes the basic results of density functional theory: the Hohenberg-Kohn theorems and the constrained-search method of Levy and Lieb, the Kohn-Sham approach, and the OEP and KLI methods.

A well known theorem of quantum mechanics is Kato's theorem [33], from which a relationship involving the values of the density and its derivative at the nuclei was derived [34]. The cusps of the density inform us about the atomic numbers and the position of the nuclei. The integral of the density gives the number of electrons, so from the density the Hamilton operator can be readily obtained. From the Hamiltonian, in principle, every property can be determined, so the density contains all information on the system. This argument [35,36] can only be applied to the Coulomb potential, however, DFT is valid for any local external potential. In addition, Kato's theorem also plays an important role in a density functional approach of excited states [37]. Recently, higher order cusp-relations were derived for the wave function and the electron density of the ground and highly excited states of atoms, ions and molecules [38-40].

In a recent paper March [41] showed for a bare Coulomb potential energy that the total electron density can be calculated if the density of the s-electrons is known, and he gave an explicit formula, which can be considered as the spatial generalization of Kato's theorem. The total density can be determined from the s-density not only for a bare Coulomb field. In a spherically symmetric system one can always determine the total density if the s-density is known [42]. Of course, the relation is not so simple as in the bare Coulomb field. For a non-interacting electron system in a central potential it can be stated, that there exists one-to-one correspondence between the potential and the s-state density. This theorem was proved by Theophilou [43] not only for the angular momentum quantum number $l = 0$ but also for arbitrary l. Theophilou and Gidopoulos [44] proved also the following theorem which may be regarded as the generalization of the aforementioned statement: "For a non-interacting system of N electrons, the part of the density due to the spin-orbitals that transform according to a certain irreducible representation of a group, determines uniquely the ground state." This means, that in a Kohn-Sham system the l-state contribution to the electron density contains all information about the ground-state system. If the l-part of the density is given, in principle it is possible to compute the Kohn-Sham potential and the total electron density. In Chapter 2 this problem is solved in practice by the aid of a numerical method. A cusp-relation for the l-shell contribution to the ground-state electron density is derived in case of central field atoms to get the atomic number from the l-state density. As a numerical demonstration of the theorem of Theophilou calculations are performed for spherically symmetric systems in the exchange-only density functional case [45].

For development of new approximations of the kinetic, exchange and correlation energy functionals, exact relations and criteria that are fulfilled by the exact functionals are of great help. Hierarchies of the equations were derived for the energy functionals [46-48]. These relations are exact. One way of application of these hierarchies is to truncate them. In Chapter 3 hierarchies of equations for the correlation energy and kinetic energy correction functionals are reviewed. Truncation of the hierarchies at different orders leads to explicit relations for the correlation energy and its kinetic component which are expanded in terms of powers of the moments of the electron density [48]. The moment expansion techniques in density functional theory are essential for constructing non-local functionals [49], which are important for the accurate description of systems for which the exchange-correlation hole can be spread over several atomic centers [50,51]. A given density is uniquely determined from an appropriate set of moments. The essence of the problem of moments is the development of complete sets of moments for different families of distribution functions. The moments of the density can be used as the fundamental variables in DFT [52].

Coordinate scaling conditions indicate how various components of the energy change as coordinates in the electron density are scaled uniformly. Such constraints play an important role in the development of density functionals. The connections between the coordinate scaling and the adiabatic connection formulation link the coordinate scaling conditions and accurate functionals [97,54]. In Chapter 3 the dependence of the correlation energy on the adiabatic constant is presented for several atoms and ions. For some two- and four-electron systems the correlation energy and its derivative are compared with the exact results, and with the local density (LDA) and the generalized gradient (GGA) values [55].

Density functional theory was originally developed for the ground state, and it can be applied only for the lowest-energy state in each symmetry class. The symmetry problem in DFT was analyzed in several works [56-58]. The multiplet structure can also be examined using DFT methods [59-62]. Nagy [63] generalized the KLI method for calculating the multiplet energies. In Chapter 4 the OEP method and the KLI approximation generalized to treat the lowest-lying multiplets are reviewed. Generalized KLI calculations with the Colle-Salvetti correlation (KLICS) [64,65] for the p^2 electron configuration of some atoms are presented [66]. Results are compared with the experimental values and those obtained by the generalized KLI with the local Wigner correlation (KLILW) [72,73].

1 The ground-state problem in density functional theory

This chapter starts with the summary of the Hohenberg-Kohn theory, which was originally formulated for local, spin-independent external potentials. Then the Kohn-Sham theory is reviewed.

The spin-independent version of the optimized effective potential (OEP) method and the Krieger-Li-Iafrate (KLI) approximation are also summarized.

1.1 The Hohenberg-Kohn theory

The ground-state energy E_{GS} and the ground-state wave function Ψ_{GS} of an N-electron system can be found from the variational principle

$$E_{GS} = \min_{\Psi} \langle \Psi | \hat{H} | \Psi \rangle = \langle \Psi_{GS} | \hat{H} | \Psi_{GS} \rangle \ , \tag{1.1}$$

where $\hat{H}$ is the Hamiltonian of the system

$$\hat{H} = \hat{T} + \hat{V}_{ee} + \hat{V}_{ne} \ , \tag{1.2}$$

$\hat{T}$ is the kinetic energy operator

$$\hat{T} = \sum_{i=1}^{N} \left(-\frac{1}{2} \nabla_i^2 \right) \ , \tag{1.3}$$

and

$$\hat{V}_{ee} = \sum_{i<j}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \tag{1.4}$$

is the electron-electron repulsion energy operator, and

$$\hat{V}_{ne} = \sum_{i=1}^{N} v(\mathbf{r}_i) \tag{1.5}$$

is the electron-nucleus attraction energy operator, in which

$$v(\mathbf{r}_i) = -\sum_{\alpha} \frac{Z_\alpha}{|\mathbf{r}_i - \mathbf{R}_\alpha|} \tag{1.6}$$

is the so-called external potential acting on electron i, due to nuclei of charges Z_α. Atomic units are used throughout this work.

The definition of the electron density n generated by the N-electron wave function Ψ is

$$n(\mathbf{r}_1) = N \int |\Psi(\mathbf{x}_1, \mathbf{x}_2, ..\mathbf{x}_N)|^2 ds_1 d\mathbf{x}_2 ... d\mathbf{x}_N \ . \tag{1.7}$$

$\mathbf{x}$ stands for both the coordinates and the spin, $\mathbf{x} = (\mathbf{r}, s)$.

For an N-electron system, the external potential $v(\mathbf{r})$ completely fixes the Hamiltonian, thus N and $v(\mathbf{r})$ determine all properties for the ground state. In the sense of the first Hohenberg-Kohn theorem [10] the electron density is the basic variable. The theorem states, that the external potential $v(\mathbf{r})$ is implicitly determined by the ground-state density $n_{GS}(\mathbf{r})$ within a trivial additive constant. Obviously n_{GS} also determines the total number of particles N:

$$\int n_{GS}(\mathbf{r}) d\mathbf{r} = N \ , \tag{1.8}$$

thus, the knowledge of the electron density determines the entire Hamiltonian operator, the ground-state wave function Ψ_{GS} and all other electronic properties of the system. The external potential $v(\mathbf{r})$ is not restricted to Coulomb potentials. The proof of the theorem is based on the minimum-energy principle for the non-degenerate ground state. Let v and v' be two different external potentials giving the same electron density n_{GS}. We have two Hamiltonians, $\hat{H}$ and $\hat{H}'$ with the different wave functions Ψ_{GS} and Ψ'_{GS}.

$$\begin{aligned} E_{GS} < \langle \Psi'_{GS} | \hat{H} | \Psi'_{GS} \rangle &= \langle \Psi'_{GS} | \hat{H}' | \Psi'_{GS} \rangle + \langle \Psi'_{GS} | \hat{H} - \hat{H}' | \Psi'_{GS} \rangle \qquad (1.9) \\ &= E'_{GS} + \int n_{GS}(\mathbf{r}) [v(\mathbf{r}) - v'(\mathbf{r})] d\mathbf{r} \ , \end{aligned}$$

where E_{GS} and E'_{GS} are the ground-state energies for $\hat{H}$ and $\hat{H}'$. Similarly, using the variational principle for the Hamiltonian $\hat{H}'$ with the trial function Ψ_{GS}, we have

$$\begin{aligned} E'_{GS} < \langle \Psi_{GS} | \hat{H}' | \Psi_{GS} \rangle &= \langle \Psi_{GS} | \hat{H} | \Psi_{GS} \rangle + \langle \Psi_{GS} | \hat{H}' - \hat{H} | \Psi_{GS} \rangle \qquad (1.10) \\ &= E_{GS} + \int n_{GS}(\mathbf{r}) [v'(\mathbf{r}) - v(\mathbf{r})] d\mathbf{r} \ . \end{aligned}$$

Adding Eq. (1.9) and Eq. (1.10) we obtain the contradiction

$$E_{GS} + E'_{GS} < E'_{GS} + E_{GS} \;, \tag{1.11}$$

consequently the external potentials v and v' are not differing by more than a constant:

$$v'(\mathbf{r}) = v(\mathbf{r}) + C \;, \tag{1.12}$$

where C is a constant.

Once the Hamiltonian is known from $n_{GS}(\mathbf{r})$, all ground-state properties can be considered as functionals of the electron density. For a given external potential $v(\mathbf{r})$ the total energy functional can be written as

$$E_v[n] = \int n(\mathbf{r})v(\mathbf{r})d\mathbf{r} + F[n] \;, \tag{1.13}$$

where the functional $F[n]$ is the sum of the kinetic energy functional $T[n]$ and the electron-electron repulsion energy functional $V_{ee}[n]$:

$$F[n] = T[n] + V_{ee}[n] \;. \tag{1.14}$$

The second Hohenberg-Kohn theorem [10] provides the energy variational principle. For any trial density n, such that $n(\mathbf{r}) \geq 0$ and $\int n(\mathbf{r})d\mathbf{r} = N$,

$$E_{GS} \equiv E_v[n_{GS}] \leq E_v[n] \;. \tag{1.15}$$

Using the conventional Rayleigh-Ritz variational principle it is easy to show that the functional $E_v[n]$ attains its minimum when $n(\mathbf{r})$ is the ground-state density and that its minimum value is the ground-state energy. The first Hohenberg-Kohn theorem assures that n determines its own wave function Ψ. For the trial wave function Ψ

$$\langle\Psi|\hat{H}|\Psi\rangle = \int n(\mathbf{r})v(\mathbf{r})d\mathbf{r} + F[n] = E_v[n] \geq E_{GS} \;. \tag{1.16}$$

The functional $F[n]$ is defined only for v-representable densities. A v-representable density is one that is associated with a ground-state wave function of some Hamiltonian with a local external potential.

The variation principle of Hohenberg and Kohn allows the determination of the exact ground-state density and energy of a specified many-particle system. With the subsidiary condition of a specific particle number the variational principle

$$\frac{\delta}{\delta n(\mathbf{r})}\left(E_v[n]-\mu\int n(\mathbf{r})d\mathbf{r}\right)=0 \tag{1.17}$$

leads to the Euler equation

$$\frac{\delta E_v[n]}{\delta n(\mathbf{r})}=\mu\ . \tag{1.18}$$

The Lagrangian multiplier μ is the chemical potential of the system. If the functional $F[n]$ were known, Eq. (1.18) with the particle number N would be an exact equation to obtain the ground-state density and energy.

According to the Hohenberg-Kohn theory there is a one-to-one correspondence between the ground-state electron density $n_{GS}(\mathbf{r})$ and the ground-state wave function Ψ_{GS}. Ψ_{GS} gives $n_{GS}(\mathbf{r})$ by quadrature. But there exists an infinite number of antisymmetric wave functions that all give the same density. How to find the real ground-state wave function? This problem was solved by the constrained-search method by Levy and Lieb [74-76].

According to Levy's constrained-search method the minimization of the total energy of the system can be performed in two steps:

$$E_{GS}=\min_{n}\left\{\min_{\Psi\rightarrow n}\langle\Psi|\hat{H}|\Psi\rangle\right\}\ , \tag{1.19}$$

where $\Psi\rightarrow n$ denotes such Ψ which integrates to the given electron density n. The inner minimization is constrained to all wave functions that give $n(\mathbf{r})$, while the outer minimization is a searching over all the N-representable densities. We say that an electron density is N-representable, if there exists an antisymmetric wave function that yields the given density. It can be proved that the density n is N-representable if

$$n(\mathbf{r})\geq 0\ , \tag{1.20}$$

$$\int n(\mathbf{r})d\mathbf{r}=N\ , \tag{1.21}$$

and

$$\int|\nabla n(\mathbf{r})^{1/2}|^2 d\mathbf{r}<\infty\ . \tag{1.22}$$

Eq. (1.19) can be rewritten as

$$E_{GS} = \min_{n} \left\{ F^{HK}[n] + E_{ext}[n] \right\} = F^{HK}[n_{GS}] + E_{ext}[n_{GS}] \ , \tag{1.23}$$

where the constrained-search definition for the Hohenberg-Kohn density functional $F^{HK}[n]$ is

$$F^{HK}[n] = \min_{\Psi \to n} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle = \langle \Psi^{HK}[n] | \hat{T} + \hat{V}_{ee} | \Psi^{HK}[n] \rangle \ , \tag{1.24}$$

and the external energy functional is

$$E_{ext}[n] = \int v(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} \ . \tag{1.25}$$

The ground-state density $n_{GS}(\mathbf{r})$ corresponds to the ground-state wave function Ψ_{GS}.

Eq. (1.24) gives a new proof for the first theorem of Hohenberg and Kohn, and it is not necessary to suppose the non-degeneracy of the ground state. The original Hohenberg-Kohn minimization requires v-representable densities. The variation (1.23) is the extended definition of $F[n]$ to include also non-v-representable densities, it is over all N-representable densities.

The functional $F^{HK}[n]$ is universal in the sense that it is independent of the external field $v(\mathbf{r})$.

Splitting the result of Eq. (1.24) into the kinetic and interaction energy terms we have

$$F^{HK}[n] = T^{HK}[n] + E_{ee}^{HK}[n] \ , \tag{1.26}$$

where

$$T^{HK}[n] = \langle \Psi^{HK}[n] | \hat{T} | \Psi^{HK}[n] \rangle \ , \tag{1.27}$$

and

$$E_{ee}^{HK}[n] = \langle \Psi^{HK}[n] | \hat{V}_{ee} | \Psi^{HK}[n] \rangle \ . \tag{1.28}$$

The expectation values of $\hat{T}$ and $\hat{V}_{ee}$ can be written in terms of the reduced density matrices:

$$T^{HK}[n] = \int -\frac{1}{2} \nabla_1^2 \varrho(\mathbf{r}_1; \mathbf{r}_2)|_{\mathbf{r}_1 = \mathbf{r}_2 = \mathbf{r}} d\mathbf{r} \ , \tag{1.29}$$

and

$$E_{ee}^{HK}[n] = \int n_2(\mathbf{r},\mathbf{r}')\frac{1}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}' \ , \tag{1.30}$$

where ϱ and n_2 are the first and second order density matrices generated by Ψ^{HK}:

$$\varrho(\mathbf{r}_1;\mathbf{r}_1') = N\int \Psi^{*HK}(\mathbf{x}_1,\mathbf{x}_2,...\mathbf{x}_N)\Psi^{HK}(\mathbf{x}_1',\mathbf{x}_2,...\mathbf{x}_N)ds_1d\mathbf{x}_2,...d\mathbf{x}_N \ , \tag{1.31}$$

and

$$\begin{aligned} n_2(\mathbf{r}_1,\mathbf{r}_2) &= N\int \Psi^{*HK}(\mathbf{x}_1,\mathbf{x}_2,...\mathbf{x}_N) \\ &\cdot \quad \Psi^{HK}(\mathbf{x}_1,\mathbf{x}_2,...\mathbf{x}_N)ds_1ds_2d\mathbf{x}_3,...d\mathbf{x}_N \ . \end{aligned} \tag{1.32}$$

The interaction energy can be divided into its classical and non-classical parts:

$$E_{ee}^{HK}[n] = E_{es}[n] + E_{ncl}^{HK}[n] \ , \tag{1.33}$$

where

$$E_{es}[n] = \frac{1}{2}\int n(\mathbf{r})n(\mathbf{r}')\frac{1}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}' \tag{1.34}$$

is the classical electrostatic energy of the electronic cloud of the density n and

$$E_{ncl}^{HK}[n,h_2] = \frac{1}{2}\int n(\mathbf{r}')h_2(\mathbf{r},\mathbf{r}')\frac{1}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}' \tag{1.35}$$

is the non-classical part of the electron-electron interaction energy, where $h_2(\mathbf{r},\mathbf{r}')$ is the pair-correlation function which is defined by

$$n_2(\mathbf{r},\mathbf{r}') = \frac{1}{2}n(\mathbf{r})n(\mathbf{r}')[1+h_2(\mathbf{r},\mathbf{r}')] \ . \tag{1.36}$$

1.2 The Kohn-Sham approach

The Kohn-Sham model [11] for the description of the interacting electron system introduces a non-interacting system, which has the same electron density as the original system.

Applying the variational principle to solve the ground-state problem of an N-electron non-interacting system in an external potential field $v_s(\mathbf{r})$ we have

$$E^s_{GS} = \min_{\Phi_D} \langle \Phi_D | \hat{T} + \hat{V}_s | \Phi_D \rangle = \langle \Phi^s_{GS} | \hat{T} + \hat{V}_s | \Phi^s_{GS} \rangle \ , \tag{1.37}$$

where

$$\hat{V}_s = \sum_{i=1}^{N} v_s(\mathbf{r}_i) \ . \tag{1.38}$$

The variational function is determinantal because it describes a non-interacting system. Performing the minimization in two steps

$$E^s_{GS} = \min_n \left\{ \min_{\Phi_D \to n} \langle \Phi_D | \hat{T} | \Phi_D \rangle + \int n(\mathbf{r}) v_s(\mathbf{r}) d(\mathbf{r}) \right\} \tag{1.39}$$

is obtained. With the help of the non-interacting kinetic energy functional

$$T_s[n] = \min_{\Phi_D \to n} \langle \Phi_D | \hat{T} | \Phi_D \rangle \tag{1.40}$$

and the external energy functional

$$E^s_{ext}[n] = \int n(\mathbf{r}) v_s(\mathbf{r}) d\mathbf{r} \tag{1.41}$$

we arrive at

$$E^s_{GS} \equiv \min_n E^s[n] = \min_n \{ T_s[n] + E^s_{ext}[n] \} = T_s[n^s_{GS}] + E^s_{ext}[n^s_{GS}] \ . \tag{1.42}$$

The non-interacting ground-state problem may be solved by varying the N spin orbitals $\phi_i(\mathbf{x})$ comprising the determinant wave function Φ_D with the Lagrange-multiplicators ε^s_{ij} and the ortonormalization conditions

$$\int \phi^*_i(\mathbf{x}) \phi_j(\mathbf{x}) = \delta_{ij} \ . \tag{1.43}$$

The variation of the functional

$$\begin{aligned}\Omega[\phi_i] &= \sum_{i=1}^{N}\int v(\mathbf{r})|\phi_i(\mathbf{x})|^2 d\mathbf{x} + \frac{1}{2}\sum_{i=1}^{N}\int \phi_i^*(\mathbf{x})\left[-\frac{1}{2}\nabla^2\right]\phi_i(\mathbf{x})d\mathbf{x} \\ &- \sum_{i=1}^{N}\sum_{j=1}^{N}\varepsilon_{ij}^s\int \phi_i^*(\mathbf{x})\phi_j(\mathbf{x})d\mathbf{x}\end{aligned} \tag{1.44}$$

leads to the equations

$$\hat{h}\phi_i = \sum_{j=1}^{N}\varepsilon_{ij}^s\phi_j \ , \tag{1.45}$$

where

$$\hat{h} = -\frac{1}{2}\nabla^2 + v_s(\mathbf{r}) \ . \tag{1.46}$$

The one-electron Hamiltonian $\hat{h}$ is a Hermitian operator. Hence (ε_{ij}) is a Hermitian matrix, it can be diagonalized by a unitary transformation of the orbitals. The one-electron Schrödinger equations are thus obtained in their canonical form:

$$\left[-\frac{1}{2}\nabla^2 + v_s\right]\phi_i = \varepsilon_i^s\phi_i \ . \tag{1.47}$$

The ground-state wave function Φ_{GS}^s is a Slater determinant built from the N occupied orbitals $\phi_i(\mathbf{x})$. For the ground-state density and kinetic energy we have

$$n_{GS}^s(\mathbf{r}) = \sum_s\sum_{i=1}^{N}|\phi_i(\mathbf{r},s)|^2 \ , \tag{1.48}$$

$$T_s[n_{GS}^s] = \int t_s(\mathbf{r};[n_{GS}^s])d\mathbf{r} \ , \tag{1.49}$$

where the non-interacting kinetic energy density is

$$t_s(\mathbf{r};[n_{GS}^s]) = \frac{1}{2}\sum_s\sum_{i=1}^{N}|\nabla\phi_i(\mathbf{r},s)|^2 \ . \tag{1.50}$$

Now the Kohn-Sham method for solution of the ground-state problem of the original interacting electron system is presented:

Subtracting the non-interacting kinetic energy functional $T^{KS}[n] \equiv T_s[n]$ from the Hohenberg-Kohn kinetic energy functional $T^{HK}[n]$ the Kohn-Sham correlation kinetic energy functional is obtained:

$$T_c^{KS}[n] = T^{HK}[n] - T^{KS}[n] \ . \tag{1.51}$$

The Hohenberg-Kohn functional $F^{HK}[n]$ can be rewritten as

$$F^{HK}[n] = T_s[n] + E_{es}[n] + E_{xc}[n] \tag{1.52}$$

with the exchange-correlation energy functional

$$E_{xc}[n] = T_c^{KS}[n] + E_{ncl}^{HK}[n] \ . \tag{1.53}$$

The exchange-correlation functional defined by the equation above consists of two contributions, a difference between the interacting and non-interacting kinetic energy functionals and the non-classical part of the electron-electron energy functional.

Defining the Kohn-Sham effective potential energy functional

$$V^{KS}[n] = E_{ext}[n] + E_{es}[n] + E_{xc}[n] \ , \tag{1.54}$$

the ground-state total energy of the interacting system can be written in the form

$$E_{GS} \equiv \min_n E[n] = \min_n \left\{ T_s[n] + V^{KS}[n] \right\} = T_s[n_{GS}] + V^{KS}[n_{GS}] \ . \tag{1.55}$$

The variation of the interacting system energy functional $E[n]$ is

$$\delta E[n] = \int \left[\frac{\delta T_s[n]}{\delta n(\mathbf{r})} + \frac{\delta V^{KS}[n]}{\delta n(\mathbf{r})} \right] \delta n(\mathbf{r}) d\mathbf{r} \ , \tag{1.56}$$

and the variation of the non-interacting system energy functional is

$$\delta E^s[n] = \int \left[\frac{\delta T_s[n]}{\delta n(\mathbf{r})} + v_s(\mathbf{r}) \right] \delta n(\mathbf{r}) d\mathbf{r} \ . \tag{1.57}$$

Comparing Eq. (1.56) with Eq. (1.57) it can be seen that the minimization in Eq. (1.55) can be performed using methods developed for handling of the non-interacting problem. The variations $\delta E[n]$ and $\delta E^s[n]$ become equivalent if

$$v_{KS}(\mathbf{r};[n]) \equiv v_s(\mathbf{r}) = \frac{\delta V^{KS}[n]}{\delta n(\mathbf{r})} = v(\mathbf{r}) + v_{es}(\mathbf{r};[n]) + v_{xc}(\mathbf{r};[n]) \ , \quad (1.58)$$

where v_{KS} is the effective Kohn-Sham potential, and v_{es} is the electrostatic potential:

$$v_{es}(\mathbf{r};[n]) = \frac{\delta E_{es}[n]}{\delta n(\mathbf{r})} = \int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' \ , \quad (1.59)$$

and v_{xc} is the Kohn-Sham exchange-correlation potential:

$$v_{xc}(\mathbf{r};[n]) = \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})} \ . \quad (1.60)$$

The ground-state density of the interacting system $n_{GS}(\mathbf{r})$ can be determined from the solutions of the so-called Kohn-Sham equation:

$$\left[-\frac{1}{2}\nabla^2 + v_{KS}\right] \phi_i^{KS} = \varepsilon_i^{KS} \phi_i^{KS} \ . \quad (1.61)$$

The ground-state density is calculated from the Kohn-Sham orbitals $\{\phi_i^{KS}\}$ in a similar way as the density of a non-interacting system can be obtained from the one-electron orbitals:

$$n_{GS}(\mathbf{r}) = \sum_s \sum_{i=1}^{N} |\phi_i^{KS}(\mathbf{r};s)|^2 \ . \quad (1.62)$$

The Kohn-Sham exchange-correlation energy is the sum of the exchange and the correlation energy parts:

$$E_{xc}[n] = E_x[n] + E_c[n] \ , \quad (1.63)$$

where the exchange-only contribution $E_x[n]$ is the non-classical part of the Kohn-Sham electron-electron interaction energy:

$$E_x[n] \equiv E_{ncl}^{KS}[n] = \langle \Phi_D^{KS}[n] | \hat{V}_{ee} | \Phi_D^{KS}[n] \rangle - E_{es}[n] \ , \quad (1.64)$$

where $\Phi_D^{KS}[n]$ is the minimizer in

$$T^{KS}[n] = \min_{\Phi_D \to n} \langle \Phi_D | \hat{T} | \Phi_D \rangle = \langle \Phi_D^{KS}[n] | \hat{T} | \Phi_D^{KS}[n] \rangle \ . \quad (1.65)$$

Defining the exchange potential by

$$v_x(\mathbf{r};[n]) = \frac{\delta E_x[n]}{\delta n(\mathbf{r})} \;, \tag{1.66}$$

the exchange-correlation potential is also partitioned into the exchange and correlation potential contributions:

$$v_{xc}(\mathbf{r};[n]) = v_x(\mathbf{r};[n]) + v_c(\mathbf{r};[n]) \;, \tag{1.67}$$

where the correlation potential is

$$v_c(\mathbf{r};[n]) = \frac{\delta E_c[n]}{\delta n(\mathbf{r})} \;. \tag{1.68}$$

For the correlation energy functional holds

$$E_c[n] \leq 0 \tag{1.69}$$

because the correlation energy can be calculated as

$$E_c[n] = \langle \Psi^{HK}[n] | \hat{T} + \hat{V}_{ee} | \Psi^{HK}[n] \rangle - \langle \Phi_D^{KS}[n] | \hat{T} + \hat{V}_{ee} | \Phi_D^{KS}[n] \rangle \tag{1.70}$$

and $\Psi^{HK}[n]$ is the minimizer of the expectation value $\langle \Psi[n] | \hat{T} + \hat{V}_{ee} | \Psi[n] \rangle$. Eq. (1.70) can be rewritten as

$$\begin{aligned} E_c[n] &= (T^{HK}[n] - T^{KS}[n]) + (E_{ee}^{HK}[n] - E_{ee}^{KS}[n]) \\ &= T_c^{KS}[n] + U_c^{KS}[n] \;. \end{aligned} \tag{1.71}$$

Eq. (1.71) shows, that due to the differences between the Hohenberg-Kohn and Kohn-Sham wave functions, the correlation energy comes from two sources, from the differences in kinetic energies and electron-electron interaction energies. $\Phi_D^{KS}[n]$ is the minimizer of $\langle \Psi[n] | \hat{T} | \Psi[n] \rangle$, so

$$T_c^{KS}[n] = \langle \Psi^{HK}[n] | \hat{T} | \Psi^{HK}[n] \rangle - \langle \Phi_D^{KS}[n] | \hat{T} | \Phi_D^{KS}[n] \rangle \geq 0 \;. \tag{1.72}$$

From Eq. (1.71) and Eq. (1.72) it is obvious that

$$U_c^{KS}[n] \leq 0 \;. \tag{1.73}$$

In the Kohn-Sham theory the interacting system can be described with the one-electron equations of a non-interacting system, in which the electrons move in a common, effective potential field $v_{KS}(\mathbf{r})$. The ground-state density of the non-interacting system is equal to the ground-state density of the original system, and the ground-state energies are equal, too. The interaction of the electrons in the Kohn-Sham model is included in the Kohn-Sham potential v_{KS}. The Kohn-Sham equations are in principle exact, however, there are no explicit expressions known for the exchange-correlation potential and energy as functionals of the electron density, so for calculating in practice one has to apply approximations. The most popular functionals have a form appropriate for slowly varying densities: the local density approximation (LDA)

$$E_{xc}^{LDA}[n] = \int n\varepsilon_{xc}^{unif}(n)d\mathbf{r} \ , \tag{1.74}$$

where $\varepsilon_{xc}^{unif}(n)$ is the exchange-correlation energy per particle of a uniform electron gas, and the generalized gradient approximation (GGA)

$$E_{xc}^{GGA}[n] = \int f(n, \nabla n)d\mathbf{r} \ , \tag{1.75}$$

which improve upon the LDA description of atoms, molecules and solids. In the practical calculations ε_{xc}^{unif} and f must be parametrized analytic functions. $\varepsilon_{xc}^{unif}(n)$ is well established [12-16], but the best choice for $f(n)$ depends on the derivations and formal properties of various GGA's [17-22].

1.3 The optimized effective potential method and the KLI approximation

The starting point of the optimized effective potential (OEP) method [23-26] is the total energy functional

$$\begin{aligned} E^{OEP}[\{\phi_j\}] &= \sum_{i=1}^{N} \int \phi_i^*(\mathbf{x}) \left(-\frac{1}{2}\nabla^2\right) \phi_i(\mathbf{x})d\mathbf{x} \qquad (1.76) \\ &+ \frac{1}{2}\int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}' + \int v(\mathbf{r})n(\mathbf{r})d\mathbf{r} + E_{xc}^{OEP}[\{\phi_j\}] \ , \end{aligned}$$

where, in contrast to ordinary density functional theory, the exchange-correlation energy $E_{xc}^{OEP}[\{\phi_j\}]$ is an explicit functional of the one-electron orbitals $\{\phi_j\}$ and therefore only an implicit functional of the electron density $n(\mathbf{r})$.

The one-electron spin orbitals $\{\phi_j\}$ are eigenfunctions of the one-electron Schrödinger equation with a local effective potential $V(\mathbf{r})$

$$\left(-\frac{1}{2}\nabla^2 + V(\mathbf{r})\right)\phi_j(\mathbf{x}) = \varepsilon_j\phi_j(\mathbf{x}) \tag{1.77}$$

by requiring that $V(\mathbf{r})$ is the optimized one yielding orbitals minimizing the total energy functional $E^{OEP}[\{\phi_j\}]$, that is

$$\frac{\delta E^{OEP}[\{\phi_j\}]}{\delta V(\mathbf{r})} = \sum_{i=1}^{N}\int \frac{\delta E^{OEP}[\{\phi_j\}]}{\delta\phi_i(\mathbf{x}')}\frac{\delta\phi_i(\mathbf{x}')}{\delta V(\mathbf{r})}d\mathbf{x}' + c.c. = 0\ . \tag{1.78}$$

The functional derivative of the one-electron orbital $\phi_i(\mathbf{x})$ with respect to the local effective potential $V(\mathbf{r})$ can be calculated using first-order perturbation theory,

$$\frac{\delta\phi_i(\mathbf{x}')}{\delta V(\mathbf{r})} = \sum_s G_i(\mathbf{x}',\mathbf{x})\phi_i(\mathbf{x})\ , \tag{1.79}$$

$$G_i(\mathbf{x}',\mathbf{x}) = {\sum_{j=1}^{\infty}}' \frac{\phi_j(\mathbf{x}')\phi_j^*(\mathbf{x})}{\varepsilon_j - \varepsilon_i}\ , \tag{1.80}$$

where the prime in the sum indicates that only states with $\varepsilon_j \neq \varepsilon_i$ are summed, and $G_i(\mathbf{x}',\mathbf{x})$ is the Green function of the Kohn-Sham equation projected onto the subspace orthogonal to $\phi_i(\mathbf{x})$. It satisfies the equation

$$\left(-\frac{1}{2}\nabla^2 + V(\mathbf{r}) - \varepsilon_i\right)G_i(\mathbf{x}',\mathbf{x}) = -\delta(\mathbf{x}'-\mathbf{x}) + \phi_i(\mathbf{x}')\phi_i^*(\mathbf{x})\ . \tag{1.81}$$

If we define $\hat{h}_i$ by

$$\frac{\delta E^{OEP}[\{\phi_j\}]}{\delta\phi_i(\mathbf{x})} = \hat{h}_i\phi_i^*(\mathbf{x})\ , \tag{1.82}$$

then

$$\hat{h}_i = -\frac{1}{2}\nabla^2 + v_{es}(\mathbf{r}) + v(\mathbf{r}) + v_{xc,i}(\mathbf{x})\ , \tag{1.83}$$

where the orbital dependent potential $v_{xc,i}(\mathbf{x})$ is

$$v_{xc,i}(\mathbf{x}) = \frac{\delta E_{xc}^{OEP}[\{\phi_j\}]}{\phi_i^* \delta \phi_i} . \tag{1.84}$$

From Eqs. (1.77)-(1.84) an integral equation for the effective exchange-correlation potential

$$V_{xc}(\mathbf{r}) = V(\mathbf{r}) - v_{es}(\mathbf{r}) - v(\mathbf{r}) \tag{1.85}$$

is obtained:

$$\sum_{i=1}^{N} \int \phi_i^*(\mathbf{x}') \left(V_{xc}(\mathbf{r}') - v_{xc,i}(\mathbf{x}')\right) G_i(\mathbf{x}', \mathbf{x}) \phi_i(\mathbf{x}) d\mathbf{x}' + c.c. = 0 . \tag{1.86}$$

The main advantage of the OEP method is that it allows for the exact treatment of the exchange energy. In the exchange-only Kohn-Sham theory the exchange energy functional assumes the same form as the Hartree-Fock exchange energy expression:

$$E_x[\{\phi_j\}] = -\frac{1}{2} \sum_{i,j=1}^{N} \int \frac{\phi_i^*(\mathbf{x})\phi_i(\mathbf{x}')\phi_j^*(\mathbf{x}')\phi_j(\mathbf{x})}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{x} d\mathbf{x}' \tag{1.87}$$

with the $\{\phi_j\}$ being the Kohn-Sham orbitals. The exact exchange potential

$$V_x(\mathbf{r}) = \frac{\delta E_x}{\delta n(\mathbf{r})} \tag{1.88}$$

can be found numerically by employing the OEP method. Writing the full OEP integral equation (1.86) separately for the exchange and correlation potentials the OEP equation for $V_x(\mathbf{r})$ is

$$\sum_{i=1}^{N} \int \phi_i^*(\mathbf{x}') \left(V_x(\mathbf{r}') - v_{x,i}(\mathbf{x}')\right) G_i(\mathbf{x}', \mathbf{x}) \phi_i(\mathbf{x}) d\mathbf{x}' + c.c. = 0 , \tag{1.89}$$

and for any given approximate correlation energy functional $E_c[\{\phi_j\}]$ the correlation potential

$$V_c(\mathbf{r}) = \frac{\delta E_c}{\delta n(\mathbf{r})} \tag{1.90}$$

can be obtained by the solution of the corresponding integral equation

$$\sum_{i=1}^{N}\int \phi_i^*(\mathbf{x}')\left(V_c(\mathbf{r}')-v_{c,i}(\mathbf{x}')\right)G_i(\mathbf{x}',\mathbf{x})\phi_i(\mathbf{x})d\mathbf{x}' + c.c. = 0\ . \tag{1.91}$$

Performing the functional derivative of the exact exchange energy $E_x[\{\phi_j\}]$ with respect to the orbitals one obtains for the exchange part of $v_{xc,i}(\mathbf{x})$:

$$v_{x,i}(\mathbf{x}) = \frac{1}{\phi_i^*(\mathbf{x})}\frac{\delta E_x[\{\phi_j\}]}{\delta\phi_i(\mathbf{x})} = -\frac{1}{2\phi_i^*(\mathbf{x})}\sum_{j=1}^{N}\phi_j^*(\mathbf{x})\int\frac{\phi_i^*(\mathbf{x}')\phi_j(\mathbf{x}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{x}'\ . \tag{1.92}$$

$v_{c,i}(\mathbf{x})$ is the orbital dependent correlation potential

$$v_{c,i}(\mathbf{x}) = \frac{1}{\phi_i^*(\mathbf{x})}\frac{\delta E_c[\{\phi_j\}]}{\delta\phi_i(\mathbf{x})}\ . \tag{1.93}$$

Both the exchange-only OEP and Hartree-Fock approaches are based on the same total energy functional, which contains the exchange energy expression (1.87):

$$\begin{aligned} E[\{\phi_j\}] &= \sum_{i=1}^{N}\int\phi_i^*(\mathbf{x})\left(-\frac{1}{2}\nabla^2\right)\phi_i(\mathbf{x})d\mathbf{x} \qquad (1.94)\\ &+ \frac{1}{2}\int\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}' + \int v(\mathbf{r})n(\mathbf{r})d\mathbf{r}\\ &- \frac{1}{2}\sum_{i,j=1}^{N}\int\frac{\phi_i^*(\mathbf{x})\phi_i(\mathbf{x}')\phi_j^*(\mathbf{x}')\phi_j(\mathbf{x})}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{x}d\mathbf{x}'\ . \end{aligned}$$

While in the Hartree-Fock method this total energy functional is minimized without restriction (expect the ortonormality of the orbitals) leading to a single-particle Schrödinger equation containing a non-local effective potential $\hat{V}_x^{HF}$ via the equation

$$(\hat{V}_x^{HF}\phi_i)(\mathbf{x}) = -\frac{1}{2}\sum_{j=1}^{N}\int\frac{\phi_j^*(\mathbf{x}')\phi_i(\mathbf{x}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{x}'\phi_j(\mathbf{x})\ , \tag{1.95}$$

in the exchange-only OEP scheme the total energy functional (1.94) is minimized under the subsidiary condition that the orbitals arise from a local potential, which is determined by the OEP integral equation (1.86). A consequence [36] of the non-locality of the Hartree-Fock potential is that the occupied Hartree-Fock orbitals all have the same exponential decay

$$\phi_i^{HF}(\mathbf{x}) \longrightarrow e^{-(\sqrt{-2\varepsilon_N^{HF}})|\mathbf{r}|} \ , \quad as \ \ |\mathbf{r}| \to \infty \ \ ; \ \ i \leq N \ . \tag{1.96}$$

ε_N^{HF} is the energy of the highest occupied Hartree-Fock state. The orbitals arising from the OEP method, on the other hand, fall off each with its own orbital energy [67]:

$$\phi_i^{OEP}(\mathbf{x}) \longrightarrow e^{-(\sqrt{-2\varepsilon_i})|\mathbf{r}|} \ , \quad as \ \ |\mathbf{r}| \to \infty \ \ ; \ \ i \leq N \ . \tag{1.97}$$

The results of the OEP and Hartree-Fock calculations for the physical quantities are almost identical [68]. The self-consistent Hartree-Fock solutions yield the lowest possible value of the total energy (1.94), so the ground-state energy obtained from the exhange-only self-consistent OEP scheme is necessarily higher,

$$E_{GS}^{HF} \leq E_{GS}^{OEP} \ , \tag{1.98}$$

however, the difference is very small.

The OEP method correctly reproduces the discontinuity properties [28,30,67] required for the exact exchange-correlation potential [69-71]. A number of other rigorous statements on the optimized effective exchange and correlation potentials of finite systems can be derived [67]. An important property is that

$$\int \phi_N^*(\mathbf{x}) v_{x,N}(\mathbf{x}) \phi_N(\mathbf{x}) d\mathbf{x} = \int \phi_N^*(\mathbf{x}) V_x(\mathbf{r}) \phi_N(\mathbf{x}) d\mathbf{x} \tag{1.99}$$

is satisfied for $v_{x,N}(\mathbf{x})$ belonging to the exact exchange energy functional (1.87). Likewise,

$$\int \phi_N^*(\mathbf{x}) v_{c,N}(\mathbf{x}) \phi_N(\mathbf{x}) d\mathbf{x} = \int \phi_N^*(\mathbf{x}) V_c(\mathbf{r}) \phi_N(\mathbf{x}) d\mathbf{x} \tag{1.100}$$

is satisfied for any approximate correlation energy functional leading to asymptotically bounded functions

$$v_{c,i}(\mathbf{x}) \longrightarrow const. \ , \ \ as \ \ |\mathbf{r}| \to \infty \ ; \ \ i \leq N \ . \tag{1.101}$$

The consequence of these statements is the asymptotic behaviour of the exchange and correlation potential. $V_x(\mathbf{r})$ and $v_{x,N}(\mathbf{x})$ approach each other exponentially fast for $|\mathbf{r}| \rightarrow \infty$. The asymptotic form of $v_{x,N}(\mathbf{x})$ is $-\frac{1}{|\mathbf{r}|}$. This implies that

$$V_x(\mathbf{x}) \longrightarrow -\frac{1}{|\mathbf{r}|} \ , \ \ as \ \ |\mathbf{r}| \rightarrow \infty \ . \tag{1.102}$$

The difference between $V_c(\mathbf{r})$ and $v_{c,N}(\mathbf{x})$ decays exponentially as well, so the way of testing the asymptotic behaviour of $V_c(\mathbf{r})$ for a given approximate orbital functional $E_c[\{\phi_j\}]$ is that one only determines how $v_{c,N}(\mathbf{x})$ falls off.

Since there is no known analytic solution of V_{xc} depending explicitly on the set of the single-particle orbitals $\{\phi_j\}$, in order to use the OEP method one needs to solve the full integral equation (1.86) numerically, which is a very demanding task because of various numerical problems. It has been achieved so far only for spherically symmetric systems [32,110], for complex systems like molecules, where the potential lacks spherical symmetry, no systematic method has yet been devised to solve Eq. (1.86). However, Krieger, Li and Iafrate [27-32] proposed a highly accurate approximation [KLI] for the effective exchange-correlation potential $V_{xc}(\mathbf{r})$, which reduces the complexity of the original OEP equation significantly, and at the same time keeps many of the essential properties of the OEP method unchanged. With the help of the definition

$$\psi_i^*(\mathbf{x}) := \int \phi_i^*(\mathbf{x}') \left(V_{xc}(\mathbf{r}') - v_{xc,i}(\mathbf{x}')\right) G_i(\mathbf{x}', \mathbf{x}) d\mathbf{x}' \tag{1.103}$$

performing some algebra one arrives at the exact transformation of Eq. (1.86)

$$V_{xc}(\mathbf{r}) = \sum_s \sum_{i=1}^{N} \frac{|\phi_i(\mathbf{x})|^2}{2n(\mathbf{r})} \left(u_{xc,i}(\mathbf{x}) + \overline{V}_{xc,i} - \overline{v}_{xc,i}\right) + c.c. \ , \tag{1.104}$$

where

$$u_{xc,i}(\mathbf{x}) = v_{xc,i}(\mathbf{x}) - \frac{1}{|\phi_i(\mathbf{x})|^2} \nabla \left(\psi_i^*(\mathbf{x}) \nabla \psi_i(\mathbf{x})\right) \ , \tag{1.105}$$

$\overline{V}_{xc,i}$ and $\overline{v}_{xc,i}$ denote the expectation values of $V_{xc}(\mathbf{r})$ and $v_{xc,i}(\mathbf{x})$ with respect to the orbital $\phi_i(\mathbf{x})$:

$$\overline{V}_{xc,i} = \int \phi_i^*(\mathbf{x}) V_{xc}(\mathbf{r}) \phi_i(\mathbf{x}) d\mathbf{x} \ , \tag{1.106}$$

$$\overline{v}_{xc,i} = \int \phi_i^*(\mathbf{x}) v_{xc,i}(\mathbf{x}) \phi_i(\mathbf{x}) d\mathbf{x} \; . \tag{1.107}$$

Eq. (1.104) may serve as a starting point for constructing accurate approximations of $V_{xc}(\mathbf{r})$. The simplest one can be obtained by neglecting the terms involving $\psi_i(\mathbf{x})$. This approximation leads to an analytic expression similar to the Slater construction for $V_{xc}(\mathbf{r})$:

$$V_{xc}^{KLI}(\mathbf{r}) = V_{xc}^{S}(\mathbf{r}) + \sum_s \sum_{i=1}^{N} \frac{|\phi_i(\mathbf{x})|^2}{2n(\mathbf{r})} \left(\overline{V}_{xc,i}^{KLI} - \overline{v}_{xc,i} \right) + c.c. \; , \tag{1.108}$$

where

$$V_{xc}^{S}(\mathbf{r}) = \sum_s \sum_{i=1}^{N} \frac{|\phi_i(\mathbf{x})|^2 v_{xc,i}(\mathbf{x})}{2n(\mathbf{r})} \tag{1.109}$$

is a Slater-type potential.

The rigorous properties of the full OEP are preserved by the KLI approximation [67]:

$$\overline{v}_{x,N} = \overline{V}_{x,N}^{KLI} \; , \tag{1.110}$$

and

$$\overline{v}_{c,N} = \overline{V}_{c,N}^{KLI} \; , \tag{1.111}$$

if $\{v_{c,j}(\mathbf{x})\}$ are asymptotically bounded. The KLI exchange-only potential $V_x^{KLI}(\mathbf{r})$ and $v_{x,N}(\mathbf{x})$ approach each other exponentially fast for $|\mathbf{r}| \rightarrow \infty$ with the same exponential function as for the full OEP, so $V_x^{KLI}(\mathbf{r})$ decays as

$$V_x^{KLI}(\mathbf{r}) \longrightarrow -\frac{1}{|\mathbf{r}|} \; , \;\; as \;\; |\mathbf{r}| \rightarrow \infty \; . \tag{1.112}$$

The difference of $V_{xc}^{KLI}(\mathbf{r})$ from the Slater approximation is due to the second term in Eq. (1.108), which enables the KLI potential $V_{xc}^{KLI}(\mathbf{r})$ to preserve the property of integer discontinuity. The solution of Eq. (1.108) is unique up to an additive constant, which can be determined by the requirement of the correct asymptotic behaviour of $V_{xc}^{KLI}(\mathbf{r})$. The exact relationship

$$\overline{v}_{xc,N} = \overline{V}_{xc,N} \tag{1.113}$$

ensures that $V_{xc}^{KLI}(\mathbf{r})$ goes to zero as r approaches infinity.

In contrast to the exact OEP integral equation, the KLI equation (1.108) can be solved explicitly for $V_{xc}^{KLI}(\mathbf{r})$ in terms of the orbitals $\{\phi_j\}$. Multiplication with $|\phi_j(\mathbf{x})|^2$ and integration over space lead to

$$\overline{V}_{xc,j}^{KLI} = \overline{V}_{xc,j}^{S} + \sum_{i=1}^{N-1} A_{ji} \left(\overline{V}_{xc,i}^{KLI} - \frac{1}{2}(\overline{v}_{xc,i} + \overline{v}_{xc,i}^{*}) \right) \; , \tag{1.114}$$

where

$$\overline{V}_{xc,j}^{S} = \int \frac{|\phi_j(\mathbf{x})|^2}{2n(\mathbf{r})} \sum_{i=1}^{N} |\phi_i(\mathbf{x})|^2 \frac{1}{2} \left(v_{xc,i}(\mathbf{x}) + v_{xc,i}^{*}(\mathbf{x}) \right) d\mathbf{x} \; , \tag{1.115}$$

and

$$A_{ji} = \int \frac{|\phi_j(\mathbf{x})|^2 |\phi_i(\mathbf{x})|^2}{2n(\mathbf{r})} d\mathbf{x} \; . \tag{1.116}$$

The orbital corresponding to the highest occupied single-particle energy eigenvalue ε_m has to be excluded from the sum in Eq. (1.114) because of the condition (1.113). The remaining unknown constants $\{(\overline{V}_{xc,j}^{KLI} - \overline{v}_{xc,j})\}$ are determined by solving the linear equations

$$\begin{aligned} \sum_{i=1}^{N-1} (\delta_{ji} - A_{ji}) \left(\overline{V}_{xc,i}^{KLI} - \frac{1}{2}(\overline{v}_{xc,i} + \overline{v}_{xc,i}^{*}) \right) = \\ = \overline{V}_{xc,j}^{S} - \frac{1}{2} \left(\overline{v}_{xc,i} + \overline{v}_{xc,i}^{*}) \right) \; ; \quad j = 1, ... N-1 \; . \end{aligned} \tag{1.117}$$

Substitution of the results into Eq. (1.108) yields an explicitly orbital-dependent functional.

2 Determination of the total electron density from its l-shell contribution

A theorem of Theophilou and Gidopoulos [44] states that in the case of a non-interacting system of N electrons, the part of the density belonging to the spin orbitals which transform according to a certain irreducible representation of a group, determines uniquely the ground state.

The consequence of this theorem is that for non-interacting systems in central potentials, the n_l part of the density corresponding to orbitals of certain l angular momentum quantum number, specifies uniquely the potential apart from an additive constant [43].

This statement can be easily proved. Let's consider a non-interacting electron-system in a central potential $v(r)$. If the l-shell density n_l is given, and it is v-representable, the number N_l of the l-shell electrons can be computed by integrating n_l over space,

$$N_l = \int n_l(\mathbf{r}) d\mathbf{r} \ . \tag{2.1}$$

Applying the minimum principle for the N_l electron functional $\langle \Phi | \hat{H} | \Phi \rangle$, where

$$\hat{H} = \sum_{i=1}^{N_l} \left[\frac{-\nabla_i^2}{2} + v(r_i) \right] \ , \tag{2.2}$$

and the Slater-determinant $|\Phi\rangle$ is constructed solely from spin orbitals belonging to the subspace characterized by the angular momentum quantum number l, one can obtain the inequalities

$$\langle \Phi_0 | \hat{T} | \Phi_0 \rangle + \langle \Phi_0 | \hat{V} | \Phi_0 \rangle < \langle \Phi_0' | \hat{T} | \Phi_0' \rangle + \langle \Phi_0' | \hat{V} | \Phi_0' \rangle \tag{2.3}$$

$$\langle \Phi_0' | \hat{T} | \Phi_0' \rangle + \langle \Phi_0' | \hat{V}' | \Phi_0' \rangle < \langle \Phi_0 | \hat{T} | \Phi_0 \rangle + \langle \Phi_0 | \hat{V}' | \Phi_0 \rangle \ , \tag{2.4}$$

where $\hat{T} = \sum_{i=1}^{N_l} \frac{\nabla_i^2}{2}$, $\hat{V} = \sum_{i=1}^{N_l} v(r_i)$, $\hat{V}' = \sum_{i=1}^{N_l} v'(r_i)$, v and v' are different external potentials, $|\Phi_0\rangle$ and $|\Phi_0'\rangle$ are the ground state Slater-determinants belonging to the potentials v and v', respectively. Using the equalities

$$\langle\Phi_0|\hat{V}|\Phi_0\rangle = \int n_l v d\mathbf{r} \tag{2.5}$$

$$\langle\Phi_0|\hat{V}'|\Phi_0\rangle = \int n_l v' d\mathbf{r} \tag{2.6}$$

$$\langle\Phi_0'|\hat{V}|\Phi_0'\rangle = \int n_l' v d\mathbf{r} \tag{2.7}$$

$$\langle\Phi_0'|\hat{V}'|\Phi_0'\rangle = \int n_l' v' d\mathbf{r} \tag{2.8}$$

Eqs. (2.3) and (2.4) lead to the inequality

$$\int \left[n_l'(\mathbf{r}) - n_l(\mathbf{r}\right] \left[v(r) - v'(r)\right] d\mathbf{r} > 0 \tag{2.9}$$

therefore, there is a single external potential which corresponds to the given n_l, i.e. there exists one-to-one correspondence between the potential and the l-part of the density.

Using the Kohn-Sham method for handling of the many-electron problem, it can be stated that in a spherically symmetric system the Kohn-Sham l-density uniqely determines the Kohn-Sham potential and the ground-state.

If n_l is the electron density of the s-shells i.e. $n_l = n_0$, as it was shown in a recent paper [41] for a bare Coulomb field $-\frac{Z}{r}$, an explicit connection holds between the total electron density n for an arbitrary number of atomic closed shells and its s-state density part:

$$\overline{n}(r) = 2Z \int_r^\infty n_0(r) dr \ , \tag{2.10}$$

where $\overline{n}(r)$ is the total electron density averaged over the spherical coordinates ϑ and φ.

$$\overline{n}(r) = \frac{1}{4\pi} \int n(r, \vartheta, \varphi) sin\vartheta d\vartheta d\varphi \ . \tag{2.11}$$

Eq. (2.10) can also be transformed into the form

$$\frac{\partial \overline{n}(r)}{\partial r} = -2Zn_0(r) \; . \tag{2.12}$$

This relation is the spatial generalization of Kato's theorem [33,34]

$$\left(\frac{\partial \overline{n}(r)}{\partial r}\right)_{(r=0)} = -2Z\overline{n}(r)(r=0) \; . \tag{2.13}$$

Eq. (2.10) says that knowing the atomic number Z, the total electron density can be determined from the s-electron density. However, the total electron density can be calculated from n_0 not only for a bare Coulomb potential, but also for the Kohn-Sham potential of central-field atoms.

In agreement with the theorem of Theophilou, one can say that the Kohn-Sham potential is a functional of the s-density. Although, the explicit functional form of the Kohn-Sham potential is unknown, it can be calculated numerically from n_0.

The atomic number Z can be determined applying Kato's theorem in a form appropriate for the s-density

$$\left(\frac{\partial n_0}{\partial r}\right)_{(r=0)} = -2Zn_0(r=0) \; . \tag{2.14}$$

The asymptotic behaviour of the Kohn-Sham potential is described by the expression

$$v_{KS}(r) = -\frac{Z-N+1}{r}, \; as \;\; r \to \infty \; , \tag{2.15}$$

from which the total number of electrons N can be computed if the atomic number is known.

Consequently, in the knowledge of both v_{KS} and Z, the total electron density n can be found by solving the Kohn-Sham equations for N electrons. Since both Z and v_{KS} can be computed from n_0, it can be stated that it is possible to calculate the total electron density if the Kohn-Sham s-electron density is given [42].

In this chapter the determination of the total electron density of closed-shell atoms from the l-shell part of the density n_l is described in the case of an arbitrary angular momentum quantum number l [45]. In Section 2.1 the Dawson-March transformation [77,78] is used to obtain potential-phase relation in terms of n_l for two- and three- l-level spherically symmetric systems. In Section 2.2 a numerical, iterative method is proposed to determine the Kohn-Sham potential from n_l for atoms and ions with several electrons. In Section 2.3 it is showed that the cusp-relation Eq. (2.14) can be generalized for the p-, d-, etc. electron densities. Finally, in Section 2.4 the construction of the total density from its n_l contribution is discussed, and exchange-only calculations are presented.

2.1 Two- and three- l-level spherically symmetric systems

In the case of one l-shell systems, from the Kohn-Sham equation

$$\left(-\frac{\nabla^2}{2} + v_{KS}(r)\right)\varphi(\mathbf{r}) = \varepsilon\varphi(\mathbf{r}) \tag{2.16}$$

the Kohn-Sham potential can be trivially constructed at the points r, where $\varphi \neq 0$:

$$v_{KS}(r) = \frac{1}{2n_l^{1/2}}\nabla^2 n_l^{1/2} + \varepsilon \ , \tag{2.17}$$

where

$${}_l = \omega|\varphi|^2 \ , \tag{2.18}$$

and ω is the occupation number of the orbital φ. The one-electron energy ε can be determined from the asymptotic decay of n_l

$$n_l \sim \exp\left\{-2(2|\varepsilon|)^{1/2} r\right\} \ . \tag{2.19}$$

If n_l is obtained from two l-shells, i.e.

$$n_l = \omega_1|\varphi_1|^2 + \omega_2|\varphi_2|^2 \ , \tag{2.20}$$

where ω_1 and ω_2 are the occupation numbers, the Kohn-Sham potential can be formed by using the Dawson-March transformation [77,78]:

$$P_1 = \frac{1}{\sqrt{\omega_1}} \varrho_l^{1/2} \cos\theta \tag{2.21}$$

$$P_2 = \frac{1}{\sqrt{\omega_2}} \varrho_l^{1/2} \sin\theta \ , \tag{2.22}$$

where P_1 and P_2 are the radial wave functions, and ϱ_l is the radial l-shell electron density

$$\varrho_l = 4r^2\pi\overline{n}_l \ . \tag{2.23}$$

Eqs. (2.21), (2.22) and the radial Kohn-Sham equations

$$P_i'' + 2\left(\varepsilon_i - v_{KS} - \frac{l(l+1)}{2r^2}\right) P_i = 0 \ , \quad i = 1,2 \tag{2.24}$$

lead to the relation between ϱ_l and the phase function $\theta(r)$:

$$\theta'' + \frac{\varrho_l'}{\varrho_l}\theta' = 2\xi\sin(2\theta) \ , \tag{2.25}$$

where

$$\xi = \frac{\varepsilon_1 - \varepsilon_2}{2} \ . \tag{2.26}$$

The Kohn-Sham potential takes the form

$$v_{KS} = \frac{1}{4}\frac{\varrho_l''}{\varrho_l} - \frac{1}{8}\left(\frac{\varrho_l'}{\varrho_l}\right)^2 - \frac{1}{2}(\theta')^2 + \xi\cos(2\theta) - \frac{l(l+1)}{2r^2} + \beta \ , \tag{2.27}$$

where

$$\beta = \frac{\varepsilon_1 + \varepsilon_2}{2} \ . \tag{2.28}$$

From Eq. (2.25) the phase θ can be determined from ϱ_l using the normalization and orthogonality conditions

$$\int \varrho_l \cos^2\theta dr = \omega_1 \ , \tag{2.29}$$

$$\int \varrho_l \sin^2\theta dr = \omega_2 \tag{2.30}$$

and

$$\int \varrho_l \sin^2(2\theta) dr = 0 \ , \tag{2.31}$$

then Eq. (2.27) gives v_{KS}.

If three l-shells are taken, the phase functions θ and ϕ are introduced [77,78]:

$$\begin{aligned} P_1 &= \frac{1}{\sqrt{\omega_1}} \varrho_l^{1/2} \sin\theta \cos\phi \ , && (2.32) \\ P_2 &= \frac{1}{\sqrt{\omega_2}} \varrho_l^{1/2} \sin\theta \sin\phi && (2.33) \\ & && (2.34) \end{aligned}$$

and

$$P_3 = \frac{1}{\sqrt{\omega_3}} \varrho_l^{1/2} \cos\theta \ . \tag{2.35}$$

From the Kohn-Sham equations one obtains coupled differential equation for the phases θ and ϕ:

$$\phi'' + \left(\frac{\varrho_l'}{\varrho_l} + 2\theta' \cot\theta \right) \phi' - 2\xi \sin(2\phi) = 0 \ , \tag{2.36}$$

$$\theta'' + \frac{\varrho_l'}{\varrho_l} \theta' - \sin(2\theta) \left[\frac{1}{2} (\phi')^2 + 2\xi \sin^2\phi + \varepsilon_3 - \varepsilon_1 \right] = 0 \ , \tag{2.37}$$

and

$$\xi = \frac{\varepsilon_1 - \varepsilon_2}{2} \ . \tag{2.38}$$

The potential-phase relation can be obtained by combining the radial Kohn-Sham equations with Eq. (2.32)-(2.35):

$$v_{KS} = \frac{1}{4} \frac{\varrho_l''}{\varrho_l} - \frac{1}{8} \left(\frac{\varrho_l'}{\varrho_l} \right)^2 - \frac{1}{2} (\theta')^2 - 2\xi \cos^2\theta - f \ , \tag{2.39}$$

where

$$f = \sin^2\theta[2\xi\sin^2\phi + 1/2(\phi')^2] + \frac{l(l+1)}{2r^2} + \varepsilon_1 \,. \tag{2.40}$$

If ϱ_l is known Eqs. (2.36) and (2.37) can be solved and the Kohn-Sham potential can be calculated, then in the knowledge of the electron number the solutions of the Kohn-Sham equations yield all the occupied wave functions and the total electron density can be calculated.

The uppermost eigenvalue in Eqs. (2.27) and (2.39) can be determined from Eq. (2.19).

2.2 Determination of the Kohn-Sham potential from n_l with several l-shells

Recently, there has been a considerable interest to construct the Kohn-Sham potential in the knowledge of the total electron density [79-85]. In a recent paper Nagy [86] has also proposed a numerical, iterative method that can be modified to calculate the Kohn-Sham potential if the l-shell density n_l is known. The process goes as follows:

In the ith iteration the Kohn-Sham equations

$$\left[-\frac{1}{2}\nabla^2 + v_{KS}^{(i)}(r)\right]\varphi_j(\mathbf{r}) = \varepsilon_j\varphi_j(\mathbf{r}) \tag{2.41}$$

are solved self-consistently. φ_j denotes the jth occupied l-shell orbital. (Because of the uniqueness of the potential one can start from any properly chosen potential $v_{ks}^{(0)}$ in the 0th iteration.) Then the obtained l-state density

$$n_l^{(i)} = \sum_j \omega_j\varphi_j^2 \tag{2.42}$$

is compared with the known density n_l. If the difference is larger than an appropriatelly chosen small constant, another potential is constructed using the potential $v_{KS}^{(i)}$ and the density $n_l^{(i)}$:

$$v_{KS}^{(i+1)} = v_{KS}^{(i)}\left[\frac{n_l}{n_l^{(i)}}\gamma + (1-\gamma)\right] , \tag{2.43}$$

then the Kohn-Sham equations are solved again and so on. (γ is a damping factor to speed the convergence.)

2.3 "Cusp-relation" for the l-shell contribution

Between the atomic number Z and the l-shell density n_l the following relation holds:

$$\left(\frac{\sigma_l'}{\sigma_l}\right)_{(r=0)} = -\frac{2Z}{l+1}\ , \tag{2.44}$$

where σ_l is defined as

$$\sigma_l = \frac{\overline{n}_l}{r^{2l}}\ . \tag{2.45}$$

In the case of $l = 0$, Eq. (2.44) and (2.45) lead to the equation for the s-density Eq. (2.14), which follows directly from Kato's theorem.

To derive Eq. (2.44) let's expand the radial wave functions and the Kohn-Sham potential in a power series in r at $r = 0$:

$$R_i = c_i(r^l + \frac{d_i}{c_i} r^{l+1} + ...) \tag{2.46}$$

and

$$v_{KS} = -\frac{Z}{r} + A + Br + ...\ . \tag{2.47}$$

Substitution of Eqs. (2.46) and (2.47) into the radial Kohn-Sham equation

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR_i}{dr}\right) - \frac{l(l+1)}{r^2}R_i + 2(\varepsilon_i - v_{KS})R_i = 0 \tag{2.48}$$

leads to the result

$$\frac{d_i}{c_i} = -\frac{Z}{l+1}\ . \tag{2.49}$$

On the other hand, substituting the

$$n_l = \sum_i w_i R_i^2 \tag{2.50}$$

l-state density written in terms of the radial wave functions into the definition of σ_l (Eq. (2.45)) one finds that

$$\frac{\sigma_l'}{\sigma_l} = \frac{2(r\sum_i w_i R_i R_i' - l\sum_i w_i R_i^2)}{r\sum_i w_i R_i^2}\ . \tag{2.51}$$

Putting the expansion (2.46) and the relation (2.49) into Eq. (2.51), it can be readily verified that the right hand side of Eq. (2.51) tends to $-\frac{2Z}{l+1}$ as r tends to zero, thus Eq. (2.44) is obtained.

2.4 Exchange-only calculation of the total electron density

According to the theorem of Theophilou [43], the l-shell part of the electron density n_l uniquely determines the potential. Since the theorem is valid for any non-interacting system, using the Kohn-Sham method to treat the many electron problem it can be stated that in a spherically symmetric system the Kohn-Sham l-state density uniquely determines the Kohn-Sham potential.

On the other hand, the atomic number can be computed from Eq. (2.44), and from the asymptotic behaviour of the Kohn-Sham potential (Eq. (2.15)) the total number of electrons can be obtained.

In conclusion we can say that the contribution to the electron density characterized by an arbitrary angular momentum contains all information about the ground-state of closed-shell atoms.

As an illustration of the aforementioned statement exchange-only calculations are performed for several atoms applying the numerical procedure described in Section 2.2 to demonstrate the above reasoning in practice.

In a recent paper [63] Kohn-Sham one-electron orbitals and energies were determined from Hartree-Fock one-electron orbitals [99]. It was shown, that the Kohn-Sham potential leading to the Hartree-Fock density is very close to the exchange-only Kohn-Sham potential, so we can loosy refer to it as the exchange-only case. As a result of this kind of calculation one obtains the exchange-only one-electron energies and orbitals, from which the exchange-only l-shell density can be constructed. Applying this l-state density as an input l-shell density following the procedure described above the exchange-only total electron density can be computed. This method is applied to several atoms and ions with closed shells. Some typical results of these calculations are displayed in the figures. From the s- and p-density contribution the Kohn-Sham potential, the exchange potential and the total electron density are computed for the atoms Ne, Mg, Ar and Kr. For the atom Kr the total density is calculated from the d-density, too.

Fig. 2.1 presents the Kohn-Sham potentials determined from the s-densities. The exchange potentials obtained from the p-densities are plotted in Fig. 2.2. The total densities calculated from the s-densities and the s-densities are displayed in Fig. 2.3, and Fig. 2.4 shows the p-electron densities and the total densities. The total density computed from the d-density and the d-density for Kr can be seen in Fig. 2.5.

The numerical results show that the difference between the Kohn-Sham potential determined from the l-shell density and the exchange-only Kohn-Sham potential (which is determined from the total density) is very small, so the curve of the total density determined from the l-density and the curve of the Hartree-Fock density can be regarded equivalent within computational error. This can be attributed to the manifestation of the uniqueness of the potential, which is stated by the theorem of Theophilou. In principle the l-state part of the density contains all the information that is needed to obtain the total electron density, and the numerical method described above offers a practical way to calculate it from its l-shell contribution.

Fig. 2.1 The Kohn-Sham potential as the function of x calculated from the s-density for Ne, Mg, Ar and Kr. x is defined as $x = (r/\mu)Z^{1/3}$, where Z is the atomic number, $\mu = (1/2)(3\pi/4)^{2/3}$, and r is the radial distance from the nucleus.

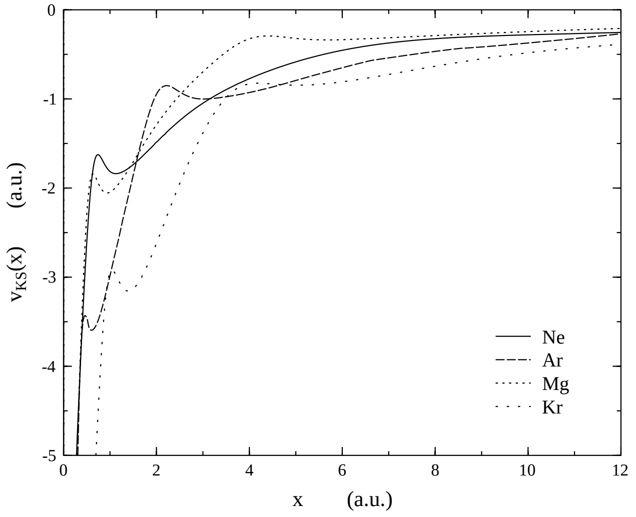


Fig. 2.2 The exchange potentials calculated from the p-densities.

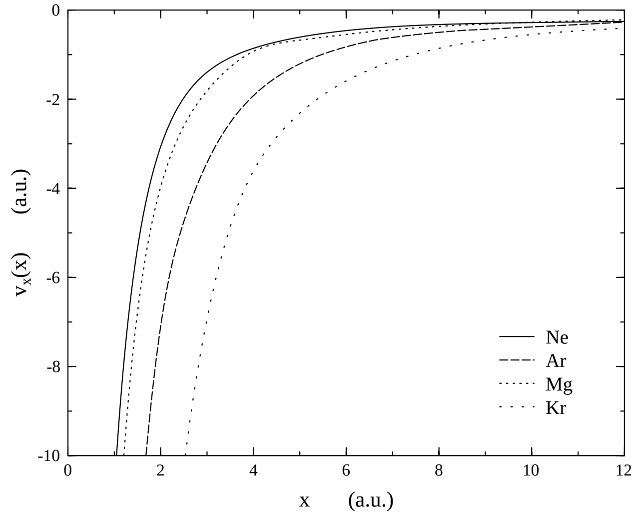


Fig. 2.3 The total radial electron density $\varrho = 4\pi r^2 n$ calculated from the s-density and the radial s-density as the functions of r for Ne, Mg, Ar and Kr.

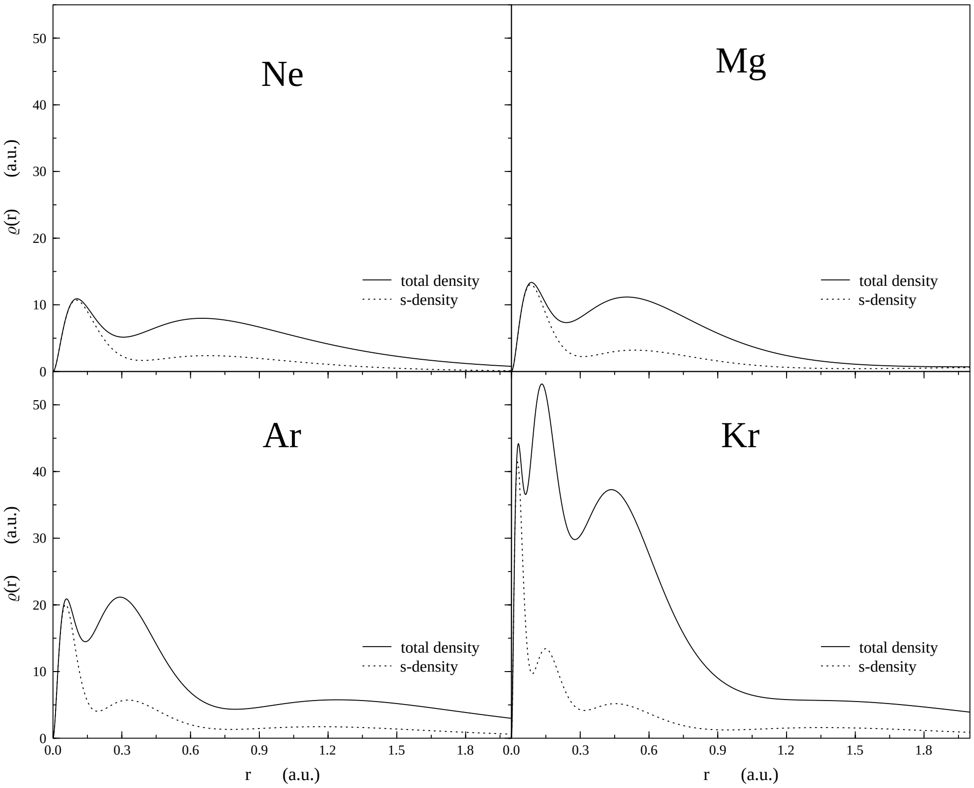


Fig. 2.4 The total densities determined from the *p*-densities and the *p*-densities.

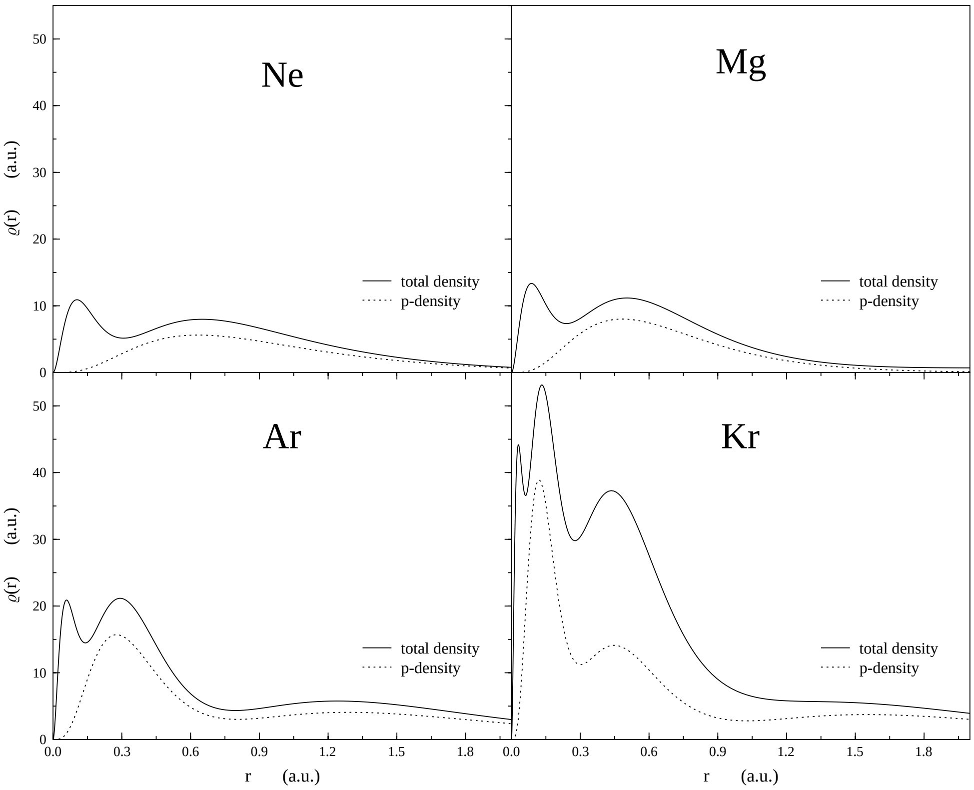
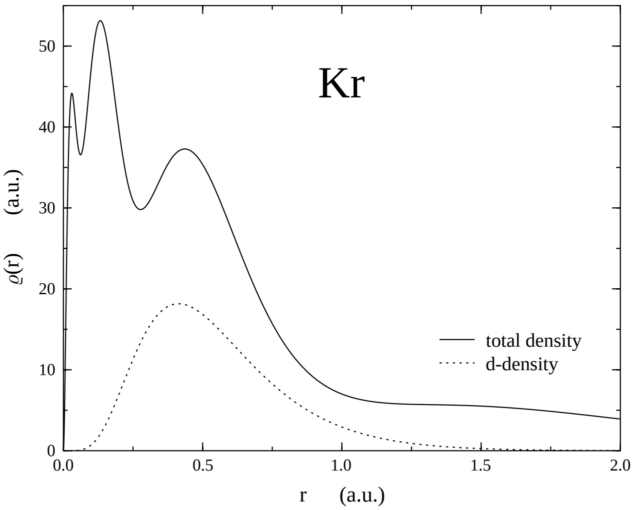


Fig. 2.5 The total density calculated from the *d*-density and the *d*-density for the atom Kr.



3 The correlation energy in terms of density-moments along the adiabatic connection

Exact relations for the functionals play an important role in density functional theory [89], because the functionals are not known exactly and consequently they have to be approximated in the applications. In recent papers [46,47], from coordinate scaling identities, hierarchies of equations were derived for the energy functionals as well as for their Legendre transforms. The hierarchy equations can serve as criteria for improving and constructing approximations. Recently, hierarchies of equations for the correlation energy and the kinetic energy correction functionals were derived [48].

For complete sets of moments there is a one-to-one mapping between the moments and the electron density [52]. All observable properties of the electronic systems can be written as functions of the moments of the density, because all properties of the systems are functionals of the electron density. A set of moments is a complete set, if all perturbations of the electron density can be represented as a change in the moments, i.e. the chain rule

$$\frac{\delta Q[n(\mathbf{r})]}{\delta n(\mathbf{r})} = \sum_k \frac{\partial Q(\{m_k\})}{\partial m_k} \frac{\partial m_k[n(\mathbf{r})]}{\partial n(\mathbf{r})} \tag{3.1}$$

is valid, where $Q[n]$ is a density functional and $\{m_k\}$ are moments of the density. It can be proved [52], that the multipole moments

$$M_{ijk} = \int x^i y^j z^k n(\mathbf{r}) d\mathbf{r} \tag{3.2}$$

are complete for molecular electron densities. One can express any molecular density functional as a function of the moments of the system:

$$Q[n(\mathbf{r})] = Q(\{M_{ijk}\}_{i,j,k=0}^{\infty}) \; . \tag{3.3}$$

Ayers, Lucks and Parr [52] showed, that exact moment functionals typically manifest a non-linear dependence on the moments, and they presented a maximum entropy technique to derive formally exact, arbitrary accurate moment expansions for density functionals.

Exact non-local expressions for density functionals employing moments of the electron density were deduced from the hierarchy equations [48, 90]. Truncating the hierarchies at different orders, one can obtain explicit relations for the correlation energy and for the difference between the interacting and non-interacting kinetic energies in terms of powers of the classical electrostatic moments of the electron density. For neutral atoms with coupling constant $\lambda = 1$, the reasonable accuracy of the two-term linear expansions has already been demonstrated [48]. In this chapter I examine the same expansion along the adiabatic path [55]. In Section 3.1 hierarchies of equations for the correlation energy and kinetic energy correction functionals are reviewed. Truncation of the hierarchies is discussed in Section 3.2. In recent papers, correlation energies have been determined for some two- and four-electron systems along the adiabatic path [91-93]. In Section 3.3 the dependence of the correlation energy on the adiabatic constant is presented for several atoms and ions, and for some two- and four-electron systems the correlation energy and its derivative obtained from the expansion in moments are compared with the exact results, and with the local density (LDA) and the generalized gradient (GGA) values.

3.1 Hierarchies of equations for the correlation energy and for the kinetic energy correction

The adiabatic connection is a fundamental concept in density functional theory [95,96]. The coupling constant path is defined by the Schrödinger equation

$$(\hat{T} + \lambda \hat{V}_{ee} + \hat{V}_{\lambda})\Psi_i^{\lambda} = E_i^{\lambda}\Psi_i^{\lambda} \quad , \tag{3.4}$$

where $\hat{T}$ and $\hat{V}_{ee}$ are the operators for the kinetic energy and the electron-electron energy, respectively. $\lambda = 1$ corresponds to the fully interacting case while $\lambda = 0$ gives the Kohn-Sham system. The potential $\hat{V}_{\lambda}$ is defined by the condition that the electron density is kept fixed along the adiabatic path.

The correlation-energy density functional $E_c^{\lambda}[n]$ at the coupling strength λ is defined as [97]

$$\lambda E_c^{\lambda}[n] = T_c^{\lambda}[n] + \lambda(\langle\Psi^{\lambda}[n]|\hat{V}_{ee}|\Psi^{\lambda}[n]\rangle - \langle\Psi^{\lambda=0}[n]|\hat{V}_{ee}|\Psi^{\lambda=0}[n]\rangle) \quad , \tag{3.5}$$

where $T_c^{\lambda}[n]$ is the kinetic energy correction part:

$$T_c^\lambda[n] = \langle \Psi^\lambda[n] | \hat{T} | \Psi^\lambda[n] \rangle - \langle \Psi^{\lambda=0}[n] | \hat{T} | \Psi^{\lambda=0}[n] \rangle \quad , \tag{3.6}$$

and $\Psi^\lambda[n]$ is the minimizing wave function. The main formulas [97,98], that relate the correlation energy and the kinetic energy correction as functions of the coupling parameter and functionals of the density, arising essentially from scaling arguments, are

$$\lambda \frac{dE_c^\lambda[n]}{d\lambda} = E_c^\lambda[n] + \int n(\mathbf{r})\mathbf{r} \cdot \nabla \frac{\delta E_c^\lambda[n]}{\delta n(\mathbf{r})} d\mathbf{r} \quad , \tag{3.7}$$

$$\lambda \frac{dT_c^\lambda[n]}{d\lambda} = 2T_c^\lambda[n] + \int n(\mathbf{r})\mathbf{r} \cdot \nabla \frac{\delta T_c^\lambda[n]}{\delta n(\mathbf{r})} d\mathbf{r} \quad , \tag{3.8}$$

and

$$T_c^\lambda[n] = -\lambda^2 \frac{dE_c^\lambda[n]}{d\lambda} \quad . \tag{3.9}$$

The K-th functional differentiation of Eq. (3.7) with respect to the density n provides the K-th order equation of the hierarchy for $E_c^\lambda[n]$ [48]:

$$\begin{aligned} \sum_{i=1}^{K} \mathbf{r}_i \nabla_i \frac{\delta^K E_c^\lambda[n]}{\delta n(\mathbf{r}_i)...\delta n(\mathbf{r}_K)} + \int n(\mathbf{r}_{K+1}) \mathbf{r}_{K+1} \nabla_{K+1} \frac{\delta^{K+1} E_c^\lambda[n]}{\delta n(\mathbf{r}_1)...\delta n(\mathbf{r}_{K+1})} d\mathbf{r}_{K+1} \\ = -\frac{\delta^K E_c^\lambda[n]}{\delta n(\mathbf{r}_1)...\delta n(\mathbf{r}_K)} + \lambda \frac{d}{d\lambda} \frac{\delta^K E_c^\lambda[n]}{\delta n(\mathbf{r}_1)...\delta n(\mathbf{r}_K)} \quad . \end{aligned} \tag{3.10}$$

This hierarchy is self-contained in the sense that it contains only the functional derivatives of the correlation energy functional. For $T_c^\lambda[n]$ a similar equation can be derived from Eq. (3.8):

$$\begin{aligned} \sum_{i=1}^{K} \mathbf{r}_i \nabla_i \frac{\delta^K T_c^\lambda[n]}{\delta n(\mathbf{r}_i)...\delta n(\mathbf{r}_K)} + \int n(\mathbf{r}_{K+1}) \mathbf{r}_{K+1} \nabla_{K+1} \frac{\delta^{K+1} T_c^\lambda[n]}{\delta n(\mathbf{r}_1)...\delta n(\mathbf{r}_{K+1})} d\mathbf{r}_{K+1} \\ = -2\frac{\delta^K T_c^\lambda[n]}{\delta n(\mathbf{r}_1)...\delta n(\mathbf{r}_K)} + \lambda \frac{d}{d\lambda} \frac{\delta^K T_c^\lambda[n]}{\delta n(\mathbf{r}_1)...\delta n(\mathbf{r}_K)} \quad . \end{aligned} \tag{3.11}$$

The hierarchies of equations link the Kth functional derivatives to the $(K+1)$th functional derivatives and the electron density.

3.2 Truncation of the hierarchy of equations and expansions in moments

Truncation of the K-th equation of the hierarchy (3.10), i.e. neglecting the $(K+1)$-th variation of the correlation energy, leads to the equation

$$\sum_{i=1}^{K} \mathbf{r}_i \nabla_i \frac{\delta^K E_c^\lambda[n]}{\delta n(\mathbf{r}_i)...\delta n(\mathbf{r}_K)} = -\frac{\delta^K E_c^\lambda[n]}{\delta n(\mathbf{r}_1)...\delta n(\mathbf{r}_K)} + \lambda \frac{d}{d\lambda} \frac{\delta^K E_c^\lambda[n]}{\delta n(\mathbf{r}_1)...\delta n(\mathbf{r}_K)} . \tag{3.12}$$

In a spherically symmetric case Eq. (3.12) has the following solution:

$$E_c^\lambda[n] = \sum_{k=1}^{K} \frac{1}{k} \left[\sum_i A_{ki} \lambda^{kc_i+1} \left(\int r^{c_i} n dr \right)^k \right] . \tag{3.13}$$

Also, the K-th order truncated equation for $T_c^\lambda[n]$ leads to:

$$T_c^\lambda[n] = -\sum_{k=1}^{K} \sum_i \left(c_i + \frac{1}{k} \right) A_{ki} \lambda^{kc_i+2} \left(\int r^{c_i} n dr \right)^k , \tag{3.14}$$

where c_i are arbitrary real numbers. The A_{ki} coefficients, which can be functions of the electron number N, can be determined by numerical fitting. For a non-spherically symmetric system Eqs. (3.13) and (3.14) take the form:

$$E_c^\lambda[n] = \sum_{k=1}^{K} \frac{1}{k} \left[\sum_{\alpha\beta\gamma} A_{k\alpha\beta\gamma} \lambda^{k(c_\alpha+c_\beta+c_\gamma)+1} M_{\alpha\beta\gamma}^k \right] , \tag{3.15}$$

and

$$T_c^\lambda[n] = -\sum_{k=1}^{K} \sum_{\alpha\beta\gamma} \left(c_\alpha + c_\beta + c_\gamma + \frac{1}{k} \right) A_{k\alpha\beta\gamma} \lambda^{k(c_\alpha+c_\beta+c_\gamma)+2} M_{\alpha\beta\gamma}^k , \tag{3.16}$$

where

$$M_{\alpha\beta\gamma} = \int x^{c_\alpha} y^{c_\beta} z^{c_\gamma} n(\mathbf{r}) d\mathbf{r} \tag{3.17}$$

are the classical electrostatic moments of the density. Taking appropriate number of terms in the sum, one can obtain a good approximation to the correlation energy and its kinetic component. The simplest possible form, the linear expansion in the moments is the only one which is size consistent, and homogeneous of degree one in the density [100,101]. It has recently been demonstrated [48] that for $\lambda = 1$ the following two-term universal expansions fit the neutral atoms remarkably well:

$$E_c[n] = C_0 lnZ \int ndr + C_1 Z \int rndr \quad , \tag{3.18}$$

and

$$T_c[n] = -C_0 lnZ \int ndr - 2C_1 Z \int rndr \quad , \tag{3.19}$$

where $C_0 = -0.01657$ and $C_1 = 0.00040$ (in a.u.). Ions can also be represented with these expressions fairly good.

3.3 Correlation energies along the adiabatic path

The adiabatic connection is a concept of great importance. The Kohn-Sham equations and the Kohn-Sham potential are defined by this principle. It is not known much about the dependence of the functionals on the coupling constant. Three recent papers [91-93] addressed this problem: the correlation energy has been calculated along the adiabatic path for two- and four-electron systems.

According to Eqs. (3.13) and (3.14), the coupling constant dependence of E_c^λ and T_c^λ corresponding to the fitted density-moment formulas (3.18) and (3.19) are:

$$E_c^\lambda = \lambda C_0 lnZ \int ndr + \lambda^2 C_1 Z \int rndr \quad , \tag{3.20}$$

and

$$T_c^\lambda = -\lambda^2 C_0 lnZ \int ndr - 2\lambda^3 C_1 Z \int rndr \quad . \tag{3.21}$$

Eqs. (3.20) and (3.21) provide simple expressions for the λ-dependence of the correlation energy and the kinetic energy correction. They can be easily calculated as the density is fixed along the adiabatic path. In our calculations Hartree-Fock densities [99] were used for n. Results are shown in Figs. 3.1 – 3.13.

In Figs. 3.1 – 3.4 E_c^λ is presented for He, Ne^{8+}, Be and Ne^{6+}. For comparison exact, LDA and GGA values are also shown. These data are taken from Ref. [92]. Colonna and Savin [92] found a rational approximant for the correlation energy:

$$E_c^\lambda \approx \frac{a\lambda}{1+b\lambda} \quad . \tag{3.22}$$

In Ref. [92] Eq. (3.5) and Eq. (3.22) are written in different forms. With the notation of Levy and Perdew [97] which is used here, the right hand side of Eq. (3.22) contains λ in the nominator instead of λ^2. The coefficients a and b were determined for the exact, LDA and GGA values. Figs. 3.1 – 3.4 present values obtained using Eq. (3.22), where the coefficients a and b are taken from Ref. [92]. Comparing the density-moment formula (3.20) with the exact, the LDA and the GGA formulas (3.22), we can state the following about the qualitative behaviour of these functions:

In the whole range of the interaction strength the expansion formula gives better results than the LDA. While in the case of the two-electron He and Ne^{8+} the exact and the GGA curves are very close to each other, for the four-electron Be and Ne^{6+} the difference between the exact and the GGA values becomes more significant. For Ne^{6+} the fitted values are between the exact and GGA values, so the curve of the fitted formula is closer to the exact one, than the GGA is. For Be it does not apply, but the curve of the density-moment expression is near that of the GGA method. The difference between the values coming from the expression Eq. (3.20) and the exact data at $\lambda = 1$ are due to the fact that the fitting is performed for several atoms and the agreement between the fitted and the exact results is worse for a system of two- and four-electrons [48]. No calculations have been done for the adiabatic constant dependence of the correlation energy of atoms and ions with number of electrons larger than four, before.

Fig. 3.5 and Fig. 3.6 present E_c^λ and T_c^λ along the adiabatic path for the atoms Li, C, F, Mg, P and Ar. The curves of E_c^λ for small atomic numbers are fairly linear due to the small C_1 coefficient in the second term of the expression (3.20). With increasing atomic number $Z\int rndr$ becomes larger, consequently, when the number of electrons increases the curves deviate from the linear. Similarly, the coupling constant dependence of T_c^λ can be predicted using Eq. (3.21). With increasing atomic number the term containing λ^3 becomes more dominant.

Since GGAs can be divided into exchange and correlation contributions to the energy, one can compare both the exchange and the exchange-correlation energies with more accurate calculations for small systems. Typically, the GGA error is smaller for the exchange-correlation energy than for the exchange energy. This led to suggestions for improving the accuracy of density functionals, by replacing a fraction of the most accurate GGA energies (near $\lambda = 1$) with the exact exchange energy (at $\lambda = 0$). These approximations are the so-called hybrid schemes [102]-[104]. A recent analysis [105] of the behaviour of approximate functionals over the range of the adiabatic curve led to the result that LDA or GGA gives a better approximation for $\partial(\lambda E_c^\lambda)/\partial\lambda$ at the $\lambda = 1$ end of the adiabatic connection, which has a great importance in the construction of non-empirical hybrid schemes (cf. Ref. [105] and references therein). In order to examine the density-moment functional from this point of view, the first derivative of λE_c^λ is considered. In Figs. 3.7-3.10 the ratio between the exact correlation energy derivative $\partial(\lambda E_c^\lambda)/\partial\lambda$ calculated from Eq. (3.22) and that calculated from the density-moment formula (3.20) for He, Ne^{8+}, Be and Ne^{6+} as a function of λ is compared with the ratio of the exact values of $\partial(\lambda E_c^\lambda)/\partial\lambda$ and those calculated from Eq. (3.22) for the LDA and GGA approximations. It can be seen, that all three of the approximating functionals work better at higher λ values. For the positive ions of the He- and Be-series for $\partial(\lambda E_c^\lambda)/\partial\lambda$ reliable data are available [93]. In Ref. [93] there are data for the Harris-Jones correlation energy $\widetilde{E}_c^\lambda$ [94]. However, it was shown [92], that these data are in good agreement with those determined at fixed density. Fig. 3.11 and Fig. 3.12 show the ratio between the exact values of $\partial(\lambda E_c^\lambda)/\partial\lambda$ and those obtained from Eq. (3.20) for the He- and Be-series. While in the He-series the curves are almost straight lines, in the Be-series it is conspicuously visible, that the density-moment approximation is better for $\partial(\lambda E_c^\lambda)/\partial\lambda$ when $\lambda \to 1$. It was conjectured [93] that a significant improvement of the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation [18] over LDA is manifest in the He-series, but in the Be-series the error increases rapidly with growing atomic number. In Fig. 3.13 we show the ratio between the exact $\partial(\lambda E_c^\lambda)/\partial\lambda$ and that of the density-moment approximation at $\lambda = 1$. Although there is a weak linear increase of the error in both series, we can state, that the density-moment expansion is a fairly good approximation also for the Be-series.

Fig. 3.1 The density-moment expansion correlation energy E_c^λ (Eq. (3.20)) in atomic units, as the function of the adiabatic constant λ for He compared with the exact, LDA and GGA values (Eq. (3.22)).

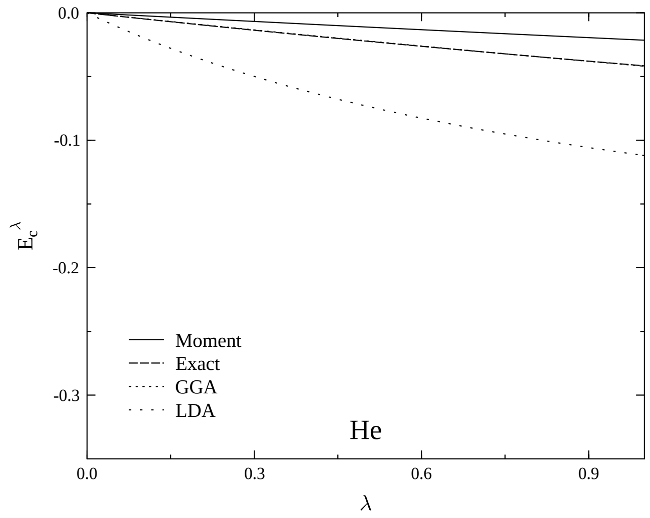


Fig. 3.2 The density-moment expansion correlation energy E_c^λ (Eq. (3.20)) in atomic units, as the function of the adiabatic constant λ for Ne^{8+} compared with the exact, LDA and GGA values (Eq. (3.22)).

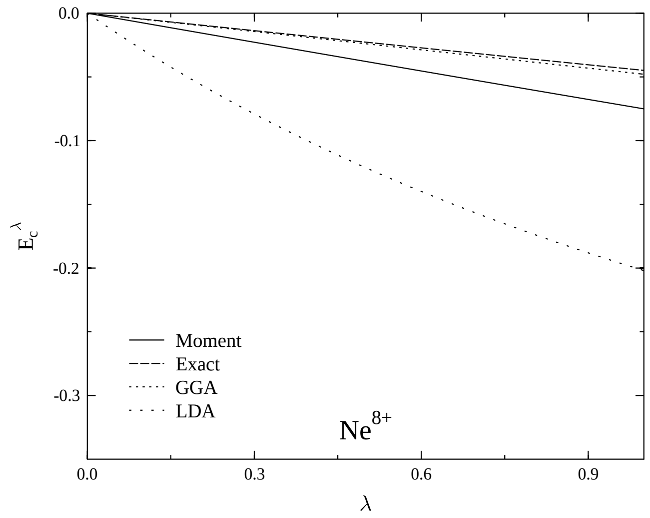


Fig. 3.3 The density-moment expansion correlation energy E_c^λ (Eq. (3.20)) in atomic units, as the function of the adiabatic constant λ for Be compared with the exact, LDA and GGA values (Eq. (3.22)).

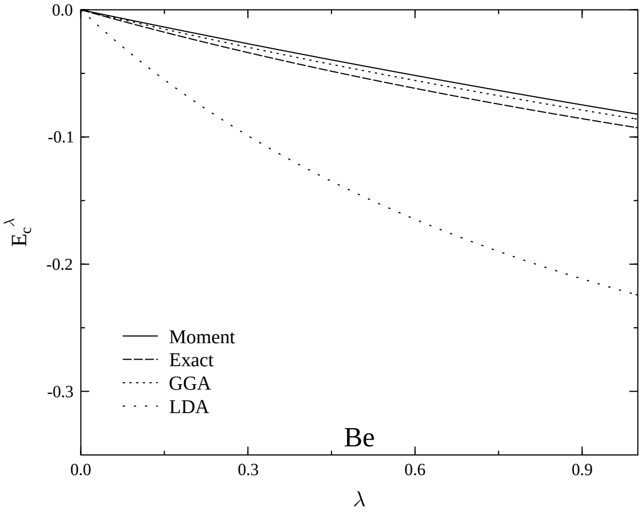


Fig. 3.4 The density-moment expansion correlation energy E_c^λ (Eq. (3.20)) in atomic units, as the function of the adiabatic constant λ for Ne^{6+} compared with the exact, LDA and GGA values (Eq. (3.22)).

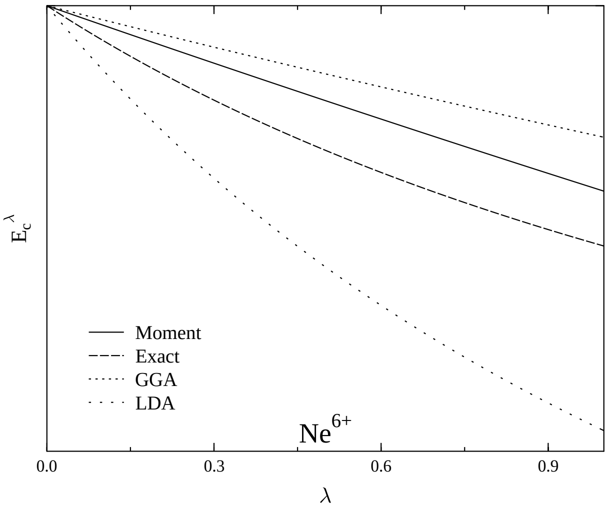


Fig. 3.5 The adiabatic constant dependence of the correlation energy E_c^λ calculated using the density-moment formula (3.20) for the atoms Li, C, F, Mg, P and Ar, in atomic units.

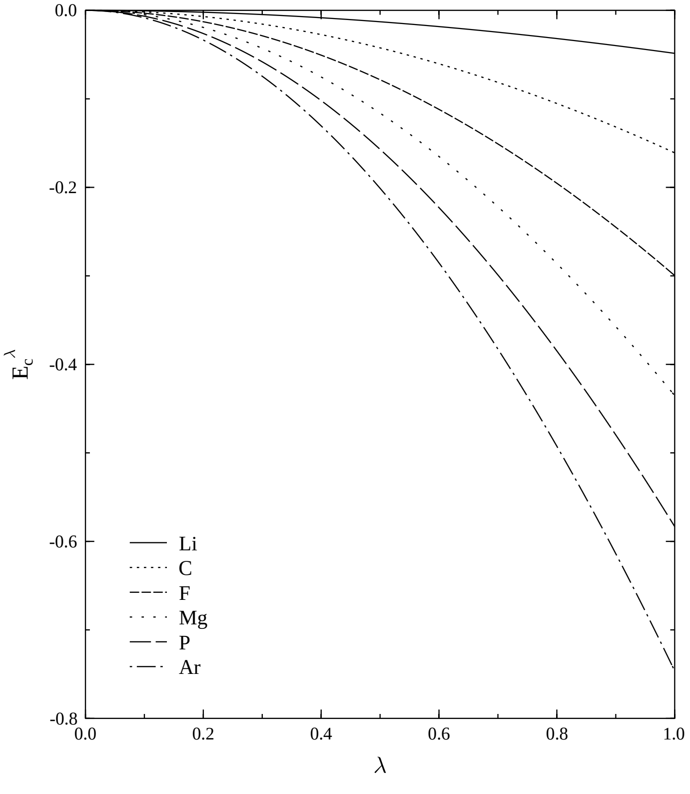


Fig. 3.6 The adiabatic constant dependence of the kinetic energy correction T_c^λ calculated using the density-moment formula (3.21) for the atoms Li, C, F, Mg, P and Ar, in atomic units.

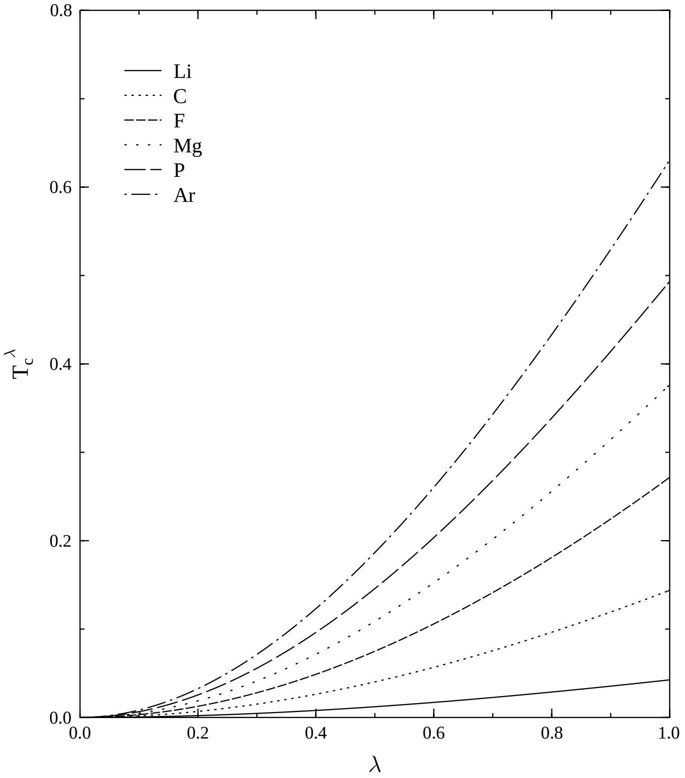


Fig. 3.7 The ratio between the exact correlation energy derivative $\partial(\lambda E_c^\lambda)/\partial\lambda$ calculated from Eq. (3.22) and that calculated from the density-moment formula (3.20) for He as a function of λ, compared with the ratio of the exact values of $\partial(\lambda E_c^\lambda)/\partial\lambda$ and those calculated from LDA and GGA (Eq. (3.22)).

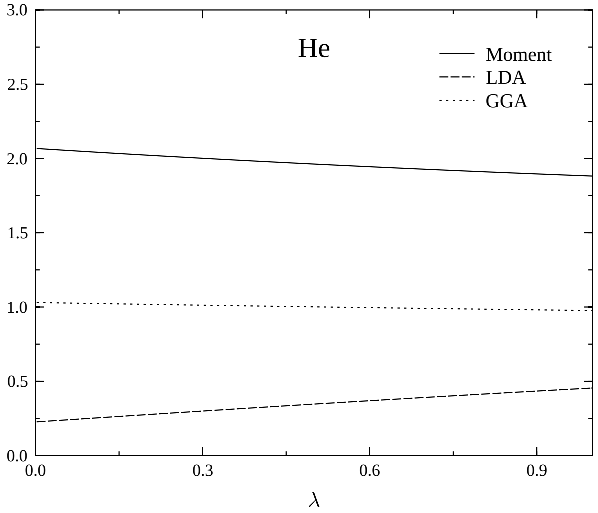


Fig. 3.8 The ratio between the exact correlation energy derivative $\partial(\lambda E_c^\lambda)/\partial\lambda$ calculated from Eq. (3.22) and that calculated from the density-moment formula (3.20) for Ne^{8+} as a function of λ, compared with the ratio of the exact values of $\partial(\lambda E_c^\lambda)/\partial\lambda$ and those calculated from LDA and GGA (Eq. (3.22)).

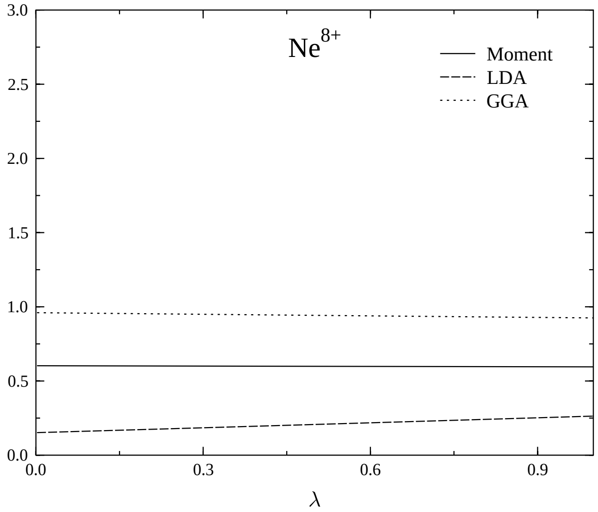


Fig. 3.9 The ratio between the exact correlation energy derivative $\partial(\lambda E_c^\lambda)/\partial\lambda$ calculated from Eq. (3.22) and that calculated from the density-moment formula (3.20) for Be as a function of λ, compared with the ratio of the exact values of $\partial(\lambda E_c^\lambda)/\partial\lambda$ and those calculated from LDA and GGA (Eq. (3.22)).

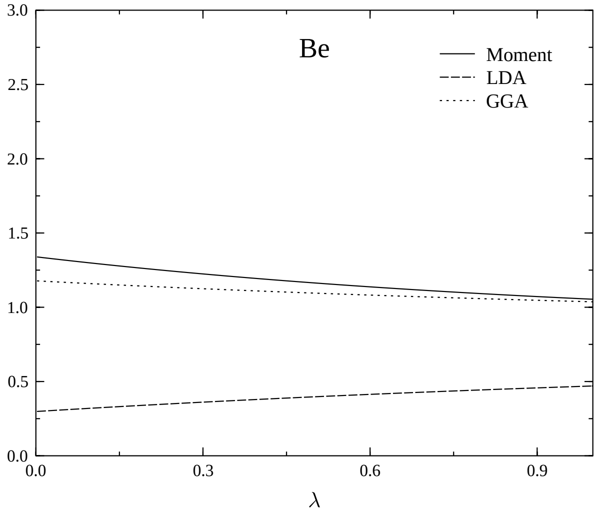


Fig. 3.10 The ratio between the exact correlation energy derivative $\partial(\lambda E_c^\lambda)/\partial\lambda$ calculated from Eq. (3.22) and that calculated from the density-moment formula (3.20) for Ne^{6+} as a function of λ, compared with the ratio of the exact values of $\partial(\lambda E_c^\lambda)/\partial\lambda$ and those calculated from LDA and GGA (Eq. (3.22)).

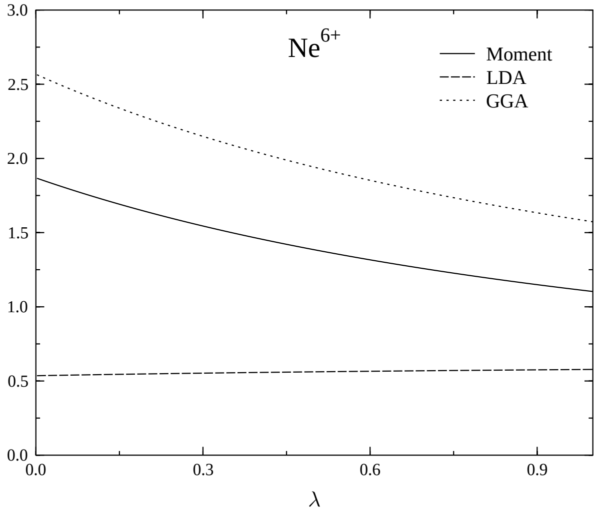


Fig. 3.11 The ratio between the exact values of $\partial(\lambda E_c^\lambda)/\partial\lambda$ and those calculated from the density-moment formula (3.20) for the He-series from He to Ne^{8+} as the function of λ. The exact values of $\partial(\lambda E_c^\lambda)/\partial\lambda$ are taken from Ref. [93]. The curves appear in the order of the nuclear charge. The uppermost curve belongs to He.

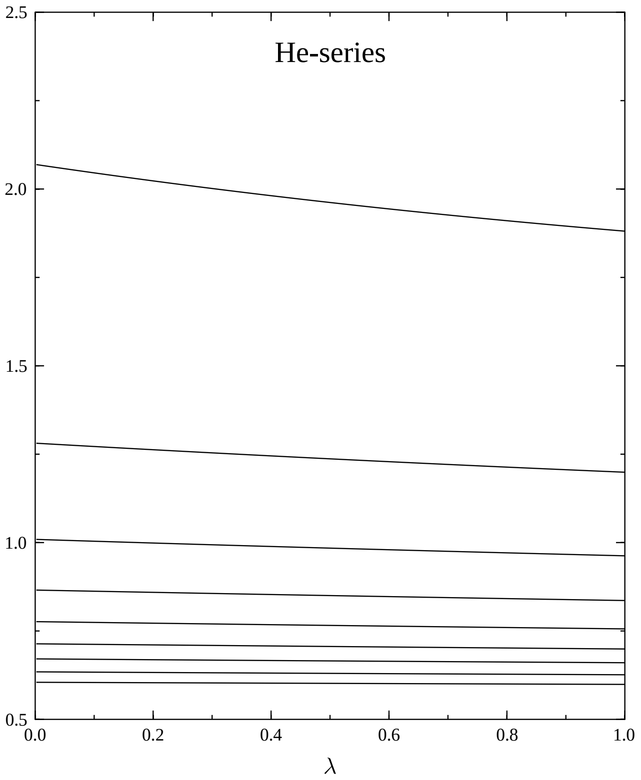


Fig. 3.12 The ratio between the exact values of $\partial(\lambda E_c^\lambda)/\partial\lambda$ and those calculated from the density-moment formula (3.20) for the Be-series from Be to Ne^{6+} as the function of λ. The exact values of $\partial(\lambda E_c^\lambda)/\partial\lambda$ are taken from Ref. [93]. The curves appear in the order of the nuclear charge. The uppermost curve belongs to Ne^{6+}.

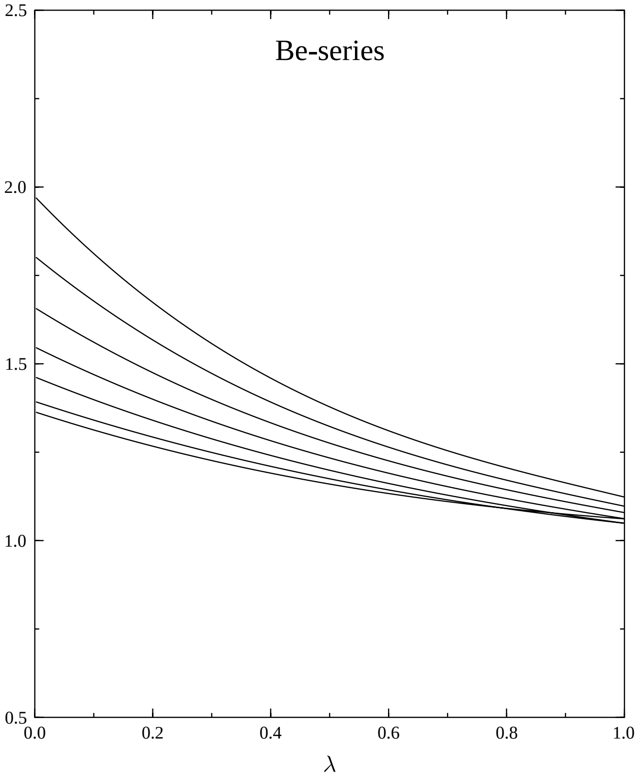
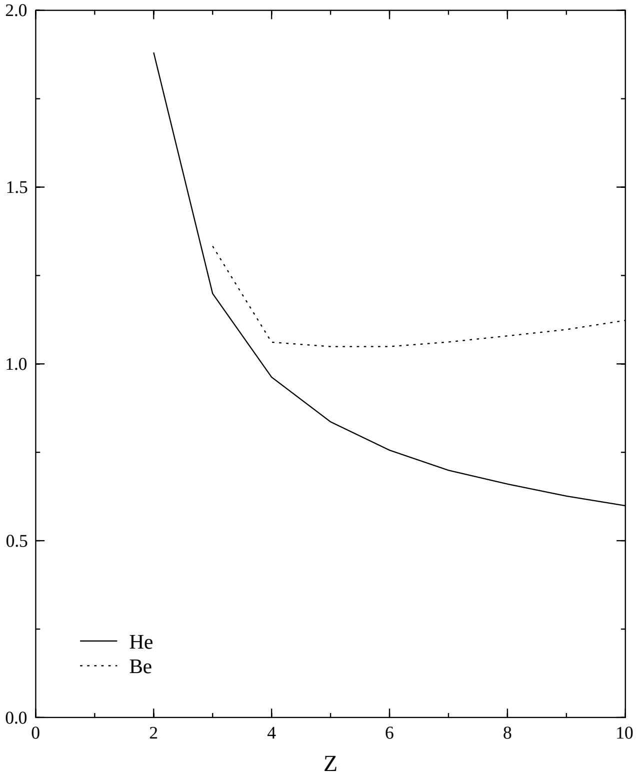


Fig. 3.13 The ratio of the exact values of $\partial(\lambda E_c^\lambda)/\partial\lambda$ and those calculated from the density-moment formula (3.20) at $\lambda = 1$ for the He- and the Be-series, as the function of the atomic number Z. The exact $(\partial(\lambda E_c^\lambda)/\partial\lambda)_{\lambda=1}$ values are taken from Ref. [93].



4 Generalized KLICS approximation for atomic multiplets

Density functional theory can be used to analyse the multiplet structure of atoms and molecules. In a recent paper, a systematic method of treating the lowest-lying multiplets of a given symmetry in the density functional theory has been presented [63]. Nagy previously proposed a method based on the fractionally occupied states [106] to treat the multiplet problem [107], and the exchange potential was determined for ensembles of low-lying multiplets. In the framework of this approach one cannot treat the different multiplets separately as one has to take into account all the multiplets lying under the given multiplet, even if they have different symmetries.

In a recent work, Kohn-Sham equations were derived for atomic multiplets [108]. In order to perform calculations one needs to know the Kohn-Sham potential. In the ground-state theory, exchange can be treated exactly via the optimized effective potential (OEP) method, but it is very difficult to calculate the effective potential because of various numerical problems. The Krieger-Li-Iafrate (KLI) method is an accurate approximate approach to the OEP method. Nagy [63] has introduced the OEP method for the lowest-lying multiplets and used a method proposed earlier [111] to generalize the KLI approximation. It has been shown [63], that the generalized KLI exchange-only potential leads to results as good as the Hartree-Fock results, so the accuracy of the generalized KLI results is about the same as that of the original KLI for the ground state. The exchange-only KLI results are closer to the experimental values than the Hartree-Fock ones, but there is a considerable difference between the KLI results and the experimental values which emphasizes the importance of correlation.

The local Wigner approximation [72] has been applied for the correlation [63] and it has been turned out that inclusion of this simple correlation results in an improvement only in the total energies, whereas the multiplet splitting becomes even worse. In this chapter I perform multiplet calculations for some spherically symmetric systems using the Colle-Salvetti correlation energy functional [64, 65] instead of the local Wigner correlation [66]. The scheme obtained by combining the correlation energy functional of Colle and Salvetti with the KLI exchange energy expression is denoted by KLICS.

In Section 4.1 the Hohenberg-Kohn theorem and the Kohn-Sham equations for multiplets are outlined. In Section 4.2 the OEP method and the generalized KLI approximation for atomic multiplets are summarized, then in Section 4.3 generalized KLICS calculations are presented for the lowest-lying multiplets of some atoms, and these results are compared with the experimental values and the results, which combine the KLI exchange energy with the local Wigner correlation (KLILW).

4.1 The Hohenberg-Kohn theorem and the Kohn-Sham equations for atomic multiplets

The constrained search technique can be applied on "subspace density matrices" constructed from the wave functions of the given multiplet. The space of all antisymmetric wave functions is divided into disjoint subspaces with different symmetries. As the lowest-lying energy level of symmetry Γ is considered, the variational principle is valid. The variation is done over a subspace S^Γ spanned by a set of wave functions of the given symmetry Γ.

For the total energy E_0^Γ, the constrained search formalism can be used as follows:

$$\begin{aligned} E_0^\Gamma &= \min_{S^\Gamma} \sum_{\gamma=1}^{g_\Gamma} w_\gamma \langle \Psi_\gamma^\Gamma | \hat{H} | \Psi_\gamma^\Gamma \rangle \\ &= \min_{n^\Gamma} \left\{ \min_{S^\Gamma \to n^\Gamma} \sum_{\gamma=1}^{g_\Gamma} w_\gamma \langle \Psi_\gamma^\Gamma | \hat{H} | \Psi_\gamma^\Gamma \rangle \right\} \\ &= \min_{n^\Gamma} \left\{ F^\Gamma[n^\Gamma] + \int n^\Gamma(\mathbf{r}) v(\mathbf{r}) d\mathbf{r} \right\} , \end{aligned} \tag{4.1}$$

where the subspace density n^Γ is constructed from wave functions that belong to the subspace S^Γ

$$n^\Gamma = \sum_{\gamma=1}^{g_\Gamma} w_\gamma \int |\Psi_\gamma^\Gamma|^2 ds_1 d\mathbf{x_2} ... d\mathbf{x_N} , \tag{4.2}$$

$$F^\Gamma[n^\Gamma] = \min_{S^\Gamma \to n^\Gamma} \sum_{\gamma=1}^{g_\Gamma} w_\gamma \langle \Psi_\gamma^\Gamma | \hat{T} + \hat{V}_{ee} | \Psi_\gamma^\Gamma \rangle , \tag{4.3}$$

and g_Γ is the degree of degeneracy. The subscript 0 in the energy E_0^Γ emphasizes the fact that only the lowest-lying solution of symmetry Γ is regarded.

The weighting factors $\{w_\gamma\}$ should satisfy the conditions

$$1 = \sum_{\gamma=1}^{g_\Gamma} w_\gamma \tag{4.4}$$

and

$$w_\gamma \geq 0 \; . \tag{4.5}$$

Any set of weighting factors $\{w_\gamma\}$ satisfying Eq. (4.4) and Eq. (4.5) can be used. The symmetry of the density depends on the weighting factors. If the weighting factors $\{w_\gamma\}$ are all equal, the subspace density has the symmetry of the external potential.

The Hohenberg-Kohn theorem can be generalized in the form

$$F^\Gamma[n^\Gamma] + \int n^\Gamma(\mathbf{r}) v(\mathbf{r}) d\mathbf{r} \geq E_0^\Gamma \; . \tag{4.6}$$

In Eq. (4.6) there is an equality if and only if the trial density n^Γ is equal to the true density of the multiplet Γ.

The density matrix in the subspace S^Γ can be defined as

$$\hat{D}^\Gamma = \sum_{\gamma=1}^{g_\Gamma} w_\gamma |\Psi_\gamma^\Gamma\rangle\langle\Psi_\gamma^\Gamma| \; . \tag{4.7}$$

The functional $F^\Gamma[n^\Gamma]$ can be expressed with the density matrix $\hat{D}^\Gamma$ as follows:

$$F^\Gamma[n^\Gamma] = \min_{\hat{D}^\Gamma \to n^\Gamma} tr\{\hat{D}^\Gamma(\hat{T} + \hat{V}_{ee})\} \; . \tag{4.8}$$

The functionals of the Kohn-Sham scheme are defined with the non-interacting density matrices $\hat{D}_s^\Gamma$ [109]. The non-interacting wave functions of symmetry Γ can be written as linear combinations of several Slater determinants Φ_κ:

$$\Psi_{s,\gamma}^\Gamma = \sum_\kappa c_{\gamma,\kappa}^\Gamma \Phi_\kappa \quad (\gamma = 1, 2 \ldots g_\Gamma) \; . \tag{4.9}$$

The non-interacting density matrix is constructed as

$$\hat{D}_s^\Gamma = \sum_{\gamma=1}^{g_\Gamma} w_\gamma |\Psi_{s,\gamma}^\Gamma\rangle\langle\Psi_{s,\gamma}^\Gamma| \; . \tag{4.10}$$

The non-interacting kinetic energy functional as a functional of the non-interacting density matrix is given by

$$T_s^\Gamma[n^\Gamma;\hat{D}_s^\Gamma] = tr\{\hat{D}_s^\Gamma \hat{T}\} \ . \tag{4.11}$$

This is a functional defined over all non-interacting density matrices $\hat{D}_s^\Gamma$ with the density n^Γ. The minimalization of the non-interacting kinetic energy functional (4.11), keeping the density n^Γ fixed, leads to the Kohn-Sham equations, which are rather complicated for an arbitrarily selected set of weighting factors w_γ. For a spherically symmetric case and equal weighting factors the Kohn-Sham equations have a very simple form [108]:

$$-\frac{1}{2}(P_j^\Gamma)'' + \frac{l_j(l_j+1)}{2r^2}P_j^\Gamma + v_{\mathrm{KS}}^\Gamma P_j^\Gamma = \varepsilon_j^\Gamma P_j^\Gamma \ , \tag{4.12}$$

where

$$v_{\mathrm{KS}}^\Gamma(r) = v(r) + \int \frac{n^\Gamma(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\, d\mathbf{r}' + v_{xc}^\Gamma(r;[n^\Gamma]) \ , \tag{4.13}$$

and P_j^Γ -s are the radial wave functions. We have different potentials for different multiplets because the Kohn-Sham potential depends on Γ.

4.2 The OEP method and the KLI approximation for atomic multiplets

The optimized effective potential method which can be applied when the total energy $E^\Gamma[\{\phi_j^\Gamma\}]$ is given as a functional of the one-electron orbitals $\{\phi_j^\Gamma\}$, can be generalized for the lowest lying multiplets. The one-electron equations are

$$\hat{h}^\Gamma \phi_i^\Gamma = (-\frac{1}{2}\nabla^2 + V^\Gamma)\phi_i^\Gamma = \varepsilon_i^\Gamma \phi_i^\Gamma \ , \tag{4.14}$$

where the local effective potential V^Γ is determined by requiring that $E^\Gamma[\{\phi_j^\Gamma\}]$ is minimized for all ϕ_i^Γ obtained from Eq. (4.14). This results in

$$\frac{\delta E^\Gamma}{\delta V^\Gamma} = \sum_i \int \frac{\delta E^\Gamma}{\delta \phi_i^\Gamma(\mathbf{x}')} \frac{\delta \phi_i^\Gamma(\mathbf{x}')}{\delta V^\Gamma(\mathbf{r})} d\mathbf{x}' + c.c. = 0 \ . \tag{4.15}$$

The functional derivative of the one-electron orbital ϕ_i^Γ with respect to the local effective potential V^Γ can be calculated with the help of Green's function:

$$\frac{\delta\phi_i^\Gamma(\mathbf{x}')}{\delta V^\Gamma(\mathbf{r})} = \sum_s G_i^\Gamma(\mathbf{x}',\mathbf{x})\phi_i^\Gamma(\mathbf{x}) \ , \tag{4.16}$$

$$(\hat{h}^\Gamma - \varepsilon_i^\Gamma)G_i^\Gamma(\mathbf{x}',\mathbf{x}) = -\delta(\mathbf{x}'-\mathbf{x}) + \phi_i^\Gamma(\mathbf{x}')\phi_i^{\Gamma *}(\mathbf{x}) \ . \tag{4.17}$$

Using Eqs. (4.14)-(4.17) an integral equation for the effective exchange-correlation potential V_{xc}^Γ can be obtained:

$$\sum_{i=1}^{N} \int \phi_i^{\Gamma *}(\mathbf{x}') \left(V_{xc}^\Gamma(\mathbf{r}') - v_{xc,i}^\Gamma(\mathbf{x}') \right) G_i^\Gamma(\mathbf{x}',\mathbf{x})\phi_i^\Gamma(\mathbf{x}) d\mathbf{x}' + c.c. = 0 \ , \tag{4.18}$$

where the orbital dependent potential is

$$v_{xc,i}^\Gamma(\mathbf{x}) = \frac{\delta E_{xc}^\Gamma[\{\phi_j^\Gamma\}]}{\phi_i^{\Gamma *}\delta\phi_i^\Gamma} \ . \tag{4.19}$$

The effective exchange-correlation potential V_{xc}^Γ can be determined from the effective potential V^Γ:

$$V_{xc}^\Gamma(\mathbf{r}) = V^\Gamma(\mathbf{r}) - v(\mathbf{r}) - v_{es}^\Gamma(\mathbf{r}) \ , \tag{4.20}$$

where v is the external potential and v_{es}^Γ is the classical Coulomb potential.

To obtain the effective potential V^Γ for the multiplet Γ the total energy $E^\Gamma[\{\phi_j^\Gamma\}]$ is needed. In a degenerate case we cannot approximate the wave function as a single Slater determinant. In the case of a given electron configuration (in this work calculations are presented for the electron configuration p^2) there exist several Slater determinants, Φ_κ. Constructing an appropriate linear combination of these Slater determinants one can obtain wave functions of symmetry Γ:

$$\tilde{\Psi}_\gamma^\Gamma = \sum_\kappa c_{\gamma,\kappa}^\Gamma \Phi_\kappa \qquad (\gamma = 1, 2, \ldots, g_\Gamma) \ . \tag{4.21}$$

The energy expression for the multiplets is

$$E^\Gamma = \langle \tilde{\Psi}_\gamma^\Gamma | \hat{H} | \tilde{\Psi}_\gamma^\Gamma \rangle \ . \tag{4.22}$$

E^Γ is a functional of the one-electron orbitals $\{\phi_j^\Gamma\}$:

$$E^\Gamma = E^\Gamma[\{\phi_j^\Gamma\}] \ . \tag{4.23}$$

For the special case of atomic multiplets, it is a functional of the radial wave functions $\{P_j^\Gamma\}$:

$$E^\Gamma = E^\Gamma[\{P_j^\Gamma\}] \ . \tag{4.24}$$

It can also be written as

$$E^\Gamma = E_{av} + \sum_j C_j^\Gamma B_j^\Gamma \ , \tag{4.25}$$

where E_{av} is the average energy of the different multiplets corresponding to the given configuration. The second term in the right hand side of Eq. (4.25) is responsible for the multiplet separation. The explicit forms of Eq. (4.25) for the p^2 electron configuration are [112]

$$E(^3P) = E_{av} - \frac{3}{25}F^2(pp) \ , \tag{4.26}$$

$$E(^1D) = E_{av} + \frac{3}{25}F^2(pp) \ , \tag{4.27}$$

and

$$E(^1S) = E_{av} + \frac{12}{25}F^2(pp) \ . \tag{4.28}$$

$F^2(pp)$ is the Slater integral

$$F^2(pp) = \int\int R_{2p}^2(r_1)R_{2p}^2(r_2)\frac{r_<^2}{r_>^3}dr_1dr_2 \ , \tag{4.29}$$

where R_{2p} is the radial wave function of the $2p$ electrons. $r_<$ means r_1 if it is smaller than r_2 and r_2 if it is smaller than r_1, and $r_>$ is the greater of r_1 and r_2.

In the knowledge of the total energy expression, the OEP calculations can be performed solving Eqs. (4.18)-(4.19). However, to find the optimized potential V^Γ is very difficult because of vast numerical problems. Recently, an alternative derivation of the exchange-only KLI approximation has been presented [111], and a generalization of this method has been performed for atomic multiplets [63].

The Kohn-Sham equations of the multiplet Γ are

$$\left(-\frac{1}{2}\frac{d^2}{dr^2} + \frac{l_i(l_i+1)}{r^2} + v^\Gamma_{KS}\right) P^\Gamma_i = \epsilon^\Gamma_i P^\Gamma_i \ . \tag{4.30}$$

The exchange-only Kohn-Sham potential is

$$v^\Gamma_{KS} = v + v^\Gamma_{es} + v^\Gamma_x + w^\Gamma \ , \tag{4.31}$$

where v^Γ_x is the exchange potential and w^Γ is the potential which is responsible for the multiplet separation. The generalization of the KLI method leads to the accurate approximations [63]

$$v^\Gamma_x = v^\Gamma_S + \sum_i (\epsilon^\Gamma_i - \varepsilon^\Gamma_i)|k^\Gamma_i|^2 \tag{4.32}$$

and

$$w^\Gamma = \sum_i (k^\Gamma_i)^2 w^\Gamma_i = \sum_i (k^\Gamma_i)^2 \sum_j C^\Gamma_j \frac{1}{P^\Gamma_i}\frac{dB^\Gamma_j}{dP^\Gamma_i} \ , \tag{4.33}$$

where v^Γ_S is the Slater potential

$$v^\Gamma_S(\mathbf{r}) = -\frac{1}{2}\int d\mathbf{r}' n^\Gamma(\mathbf{r}')|\sum_j k^\Gamma_j(\mathbf{r}')k^\Gamma_j(\mathbf{r})|^2/|\mathbf{r}-\mathbf{r}'| \ . \tag{4.34}$$

The functions k^Γ_i are defined with

$$P^\Gamma_i = \left(\varrho^\Gamma\right)^{\frac{1}{2}} k^\Gamma_i \ , \tag{4.35}$$

where ϱ^Γ is the radial electron subspace density.

$(\epsilon^\Gamma_i - \varepsilon^\Gamma_i)$ are the differences between the Kohn-Sham and the Hartree-Fock one-electron energies:

$$\epsilon^\Gamma_i - \varepsilon^\Gamma_i = \langle\phi_i|v^\Gamma_x|\phi_i\rangle - \langle\phi_i|\hat{v}^{HF}_x|\phi_i\rangle \ , \tag{4.36}$$

where $\hat{v}^{HF}_x$ is the Hartree-Fock exchange potential taken with the density functional orbitals.

4.3 Generalized KLICS calculations

A correlation energy formula due to Colle and Salvetti [64,65] in which the correlation energy density is expressed in terms of the electron density and a Laplacian of the second-order Hartree-Fock density matrix was restated as a formula involving the density and local kinetic energy density [113]:

$$E_c^{CS}[\{\phi_j\}] = -a \int \frac{n + bn^{-2/3}[t_{HF} - 2t_W]e^{-cn^{-1/3}}}{1 + dn^{-1/3}} d\mathbf{r} \ , \tag{4.37}$$

where $a = 0.04918$, $b = 0.132$, $c = 0.2533$, $d = 0.349$, and

$$t_W = \frac{1}{8}\frac{|\nabla n|^2}{n} - \frac{1}{8}\nabla^2 n \tag{4.38}$$

is a local "Weizsacker" kinetic energy density and

$$t_{HF} = \frac{1}{8}\sum_i \frac{|\nabla n_i|^2}{n_i} - \frac{1}{8}\nabla^2 n \tag{4.39}$$

is the local Hartree-Fock kinetic energy density, where $\{n_i\}$ are the electron densities belonging to the one-electron orbitals:

$$n_i(\mathbf{r}) = \sum_s |\phi_i(\mathbf{x})|^2 \ . \tag{4.40}$$

In the multiplet calculations this Colle-Salvetti functional is applied. The correlation energy expression (4.37) is added to the generalized KLI total energy E^Γ, and the Kohn-Sham potential has the form

$$v_{KS}^\Gamma = v + v_{es}^\Gamma + v_x^\Gamma + w^\Gamma + v_c^{CS,\Gamma} \ , \tag{4.41}$$

where the correlation potential $v_c^{CS,\Gamma}$ is the functional derivative of $E_c^{CS,\Gamma}$. $v_c^{CS,\Gamma}$ depends slightly on Γ, as the subspace density n^Γ is somewhat different for different multiplets. The Kohn-Sham equations (4.30) with the Kohn-Sham potential including the Colle-Salvetti correlation potential $v_c^{CS,\Gamma}$ are solved self-consistently. This method is denoted by KLICS.

Table 4.1 presents total energies obtained by the KLICS method for the multiplets ^3P, ^1D and ^1S of the atoms C, O, Si and S. Experimental data

[114] and generalized KLI results with local Wigner correlation (KLILW) [63] are also shown. The local Wigner correlation energy expression is

$$E_c^{LW}[n] = \int \frac{an}{b + r_s} d\mathbf{r} \ , \tag{4.42}$$

where the parameters obtained by Süle and Nagy [73] ($a = -0.02728$ and $b = 0.21882$) are used and r_s is the Wigner-Seitz radius:

$$r_s = (3/4\pi n)^{1/3} \ . \tag{4.43}$$

For comparison, Table 4.1 contains Hartree-Fock [99] and exchange-only KLI values as well.

Comparing the KLICS results with the experimental and the KLILW values we can state that for the atoms Si and S KLICS gives much better results than the KLILW approximation. For the multiplets of the atoms C and O, except the multiplet ^3P, the KLICS values are slightly better than the KLILW results.

Table 4.2 contains multiplet separation. It can be seen that the KLICS results are better than the Hartree-Fock and the KLILW results, but the exchange-only KLI values are closer to the experimental ones. It means that KLICS predicts multiplet splitting poorly, just as KLILW does.

Table 4.1

Total energies for the multiplets ^3P, ^1D and ^1S of the atoms C, O, Si and S calculated with Hartree-Fock (HF), and approximated optimized potential (KLI, KLILW and KLICS) methods (in Ryd).

		C	O	Si	S
^3P	HF	-75.3772	-149.6187	-577.7085	-795.0095
	KLI	-75.3715	-149.6133	-577.6963	-794.9950
	$KLILW$	-75.6854	-150.1231	-578.3987	-796.0861
	$KLICS$	-75.7284	-150.1635	-578.7785	-796.2757
	Exp	-75.6904	-150.1346	-578.7500	-796.2780
^1D	HF	-75.2626	-149.4584	-577.6300	-794.9042
	KLI	-75.2607	-149.4562	-577.6228	-794.8950
	$KLILW$	-75.5720	-149.9644	-578.3177	-795.9834
	$KLICS$	-75.6163	-150.0056	-578.7035	-796.1748
	Exp	-75.5979	-149.9900	-578.6926	-796.1938
^1S	HF	-75.0991	-149.2219	-577.5169	-794.7489
	KLI	-75.1001	-149.2236	-577.5166	-794.7468
	$KLILW$	-75.4071	-149.7292	-578.1996	-795.8312
	$KLICS$	-75.4537	-149.7720	-578.5947	-796.0251
	Exp	-75.4931	-149.8267	-578.6097	-796.0759

Table 4.2

Experimental and calculated energy difference of the term from the ^3P (in Ryd) for the atoms C, O, Si and S. Calculations are with HF, KLI, KLILW and KLICS methods.

		C	O	Si	S
$^3P -^1 D$	HF	0.1146	0.1603	0.0785	0.1053
	KLI	0.1108	0.1571	0.0735	0.1001
	$KLILW$	0.1135	0.1587	0.0810	0.1027
	$KLICS$	0.1121	0.1579	0.0750	0.1009
	Exp	0.0929	0.1446	0.0574	0.0842
$^3P -^1 S$	HF	0.2782	0.3968	0.1916	0.2606
	KLI	0.2713	0.3896	0.1797	0.2483
	$KLILW$	0.2783	0.3939	0.1991	0.2549
	$KLICS$	0.2747	0.3915	0.1838	0.2506
	Exp	0.1973	0.3079	0.1403	0.2021

Summary of results and conclusions

In density functional theory (DFT) [1-3] the basic quantity is the electron density. All properties of a many-electron system can be considered as functionals of the density. Another important quantity is the correlation energy functional. It's explicit form is unknown, so every statement in connection with the correlation energy may be useful to develop good approximations.

In the thesis I discussed the determination of the total electron density from the l-shell contribution to the electron density, then along the adiabatic connection I tested the density-moment expansion formula given by Liu, Nagy and Parr [48], finally I performed KLI calculations [63] with the Colle-Salvetti correlation energy formula [64,65] for atomic multiplets. The progress I made in these three subjects of DFT can be summarized as follows:

I. According to the theorem of Theophilou [43,44], the l-shell part of the electron density n_l uniquely determines the external potential. This theorem is valid for any non-interacting system, so using the Kohn-Sham method to treat the many-electron problem it can be stated that in a spherically symmetric system the Kohn-Sham l-state density uniquely determines the Kohn-Sham potential.

- I used the Dawson-March transformation [77,78] to obtain potential-phase relation in terms of n_l for two- and three- l-level spherically symmetric systems.

- I modified a numerical, iterative procedure worked out by Nagy [86] to calculate the Kohn-Sham potential from n_l for atoms and ions with several electrons.

- I derived a cusp-relation, from which the atomic number can be computed in the knowledge of n_l at the nucleus. From the asymptotic behaviour of the Kohn-Sham potential the total number of electrons can be obtained. So the l-state part of the density contains all the information that is needed to get the total electron density.

- To demonstrate the above statement in practice I performed exchange-only calculations, in which I computed the Kohn-Sham potential, the exchange potential, and the total electron density from the l-shell density n_l.

II. The adiabatic connection is a fundamental concept in DFT [95,96]. It provides a direct link between calculations using the Kohn-Sham Hamiltonian and those using the exact one. From scaling relations formulas can be derived, which relate the correlation energy and the kinetic energy correction as functions of the coupling parameter and functionals of the electron density [97,98]. The functional differentiations of these formulas lead to the hierarchies of equations, which can serve as criteria for improving and constructing approximations. Arising from the truncation of the hierarchy equations a universal formula in terms of the moments of the electron density was developed for the correlation energy and kinetic correction functionals [48]. In this work I examined the same expansions along the adiabatic path.

- I presented the correlation energy E_c^λ and the correlation kinetic energy T_c^λ along the adiabatic path for several atoms. The curves of $E_c^\lambda = \lambda C_0 lnZ \int ndr + \lambda^2 C_1 Z \int rndr$ for systems with small atomic numbers are fairly linear due to the small coefficient C_1 in the second term of the expression. With increasing atomic number the second term becomes larger, consequently, when the number of electrons increases the curves deviate from the linear. For the coupling constant dependence of $T_c^\lambda = -\lambda^2 C_0 lnZ \int ndr - 2\lambda^3 C_1 Z \int rndr$ it can be stated that with increasing atomic number the term containing λ^3 becomes more dominant.

- Comparing the density-moment adiabatic connection curve of the correlation energy with the exact, LDA and GGA curves, it can be stated that there is a good agreement between the density-moment results and those of Colonna and Savin [92].

- I found that in the whole range of the interaction strength the density-moment expansion formula gives better results than the LDA.

- The adiabatic coupling can be used to produce density functionals. In recent years non-empirical hybrid schemes were constructed based on the adiabatic connection [102-104]. It was pointed out [105] that these hybrids improve on the results of the approximate functionals, when the adiabatic connection is much better approximated at the coupling strength close to 1, than in the range close to 0. I examined this behaviour of the density-moment expansion formula for some two- and four-electron systems. I showed that this approximation works better for large coupling constant values, such as LDA, or GGA.

- It was conjectured [93] that a significant improvement of the PBE approximation [18] over LDA is manifest in the He-series, while in the Be-series the error increases rapidly with growing atomic number. I compared the ratio between the exact $\partial(\lambda E_c^\lambda)/\partial\lambda$ and that of the density-moment approximation at $\lambda = 1$ for the He- and Be-series, and I found that although there is a weak linear increase of the error in both series, the density-moment expansion is a fairly good approximation also for the Be-series.

III. Density functional theory can be used to analyse the multiplet structure. I performed KLI calculations with the Colle-Salvetti correlation (KLICS) for the lowest-lying multiplets of some atoms, and I compared these results with the experimental values, the Hartree-Fock and exchange-only KLI values, and with the results, which combine the KLI exchange with the local Wigner correlation formula (KLILW) [73]. From the results the following conclusions can be drawn:

- The KLICS gives slightly better results than the KLILW approximation.
- For the multiplet separation the KLICS results are better than the Hartree-Fock and the KLILW results, but the exchange-only KLI values are closer to the experimental ones. It means that the KLICS approximation predicts multiplet splitting poorly.

Az értekezés összefoglalása

A sűrűségfunkcionál elmélet [1-3] a kvantummechanikai többtestprobléma megoldására kidolgozott hatékony elmélet. Az elektronsűrűség módszerek során a többelektronos rendszerek jellemzése az elektronsűrűségen, mint alapvető mennyiségen keresztül történik. A Hohenberg-Kohn-elmélet [10] szerint ugyanis az elektronsűrűség, amely egy adott térbeli pontban a térfogategységre eső elektronszámot jelenti, a rendszer alapállapotára vonatkozó összes információt tartalmazza. Az elektronok száma a sűrűség integrálásával áll elő; ugyanakkor az első Hohenberg-Kohn-tétel kimondja, hogy az alapállapoti elektronsűrűségek és a külső potenciálok (például az elektron-mag vonzást leíró Coulomb-potenciálok) között kölcsönösen egyértelmű megfeleltetés létesíthető. Az elektronszám és a külső potenciál ismeretében pedig felírható a rendszer Hamilton-operátora, amely meghatározza az alapállapoti hullámfüggvényt, melynek ismeretében elvben bármely fizikai mennyiség átlagértéke meghatározható. Az alapállapotot jellemző összes mennyiség tehát az elektronsűrűség funkcionáljaként kezelhető.

Az elektronsűrűség alapmennyiségként való értelmezése rendkívül előnyös, hiszen a sűrűség a sokváltozós hullámfüggvénnyel szemben csupán háromváltozós az elektronok számától függetlenül. Ezenkívül az elektronsűrűség megfigyelhető fizikai mennyiség, kísérletileg meghatározható; például röntgenszórással a sűrűség Fourier-transzformáltját lehet mérni.

A második Hohenberg-Kohn-tétel variációs elvet mond ki az energiafunkcionálra: az energia, mint a sűrűség funkcionálja, a rendszer alapállapoti sűrűségénél veszi fel minimális értékét. A Hohenberg-Kohn-tételeket Levy és Lieb általánosította [74-76]. A Levy-féle korlátozott keresési módszer során a Hamilton-operátor átlagértékének minimumát nem a teljes Hilbert-téren keressük, hanem a Hilbert-térnek csak azon részén, melyet kifeszítő hullámfüggvényekhez tartozó sűrűség egy adott, rögzített elektronsűrűséggel egyezik meg.

Az elektronsűrűség a Kohn-Sham-elméletben [11] a Kohn-Sham-egyenletekből határozható meg. A Kohn-Sham-elmélet az eredeti, kölcsönható rendszer helyett egy olyan kölcsönhatásmentes rendszert tekint, amelynek a sűrűsége az eredeti rendszer sűrűségével egyezik meg. Ezen független részecskéket leíró egyelektron-egyenletek a Kohn-Sham-egyenletek, melyekben külső, effektív potenciálként az ún. Kohn-Sham-potenciál szerepel, amely egy lokális, multiplikatív potenciál, s magában foglalja az eredeti rendszer elektronjainak a kölcsönhatását. A Kohn-Sham-potenciál a mag-elektron vonzást és az elektronok egymás közötti taszítását leíró klasszikus Coulomb-potenciálokból, valamint a kicserélődési-korrelációs potenciálból tevődik össze. A kicserélődési-korrelációs potenciál a kicserélődési-korrelációs energia sűrűség szerinti funkcionálderiváltja. A kicserélődési-korrelációs energia két részből áll: a kölcsönható és kölcsönhatásmentes kinetikus energia funkcionálok különbségéből, az ún. korrelációs kinetikus energia funkcionálból, és az elektron-elektron kölcsönhatást leíró energiafunkcionál nem-klasszikus összetevőjéből. A Kohn-Sham-féle kicserélődési-korrelációs energia kicserélődési és korrelációs összetevőkre bontható. Az egyik leggyakoribb felbontás a kicserélődési energiára a Hartree-Fock-féle kifejezést alkalmazza, a Hartree-Fock-pályák helyébe a Kohn-Sham-pályákat helyettesítvén. A kicserélődési-korrelációs energiával analóg módon a kicserélődési-korrelációs potenciál is két tag összegére bontható; a kicserélődési és korrelációs potenciálra, melyek a megfelelő energiatagok sűrűség szerinti funkcionálderiváltjai.

A Kohn-Sham-egyenletekkel a kölcsönható rendszer egzaktul leírható, azonban az elektronsűrűség meghatározásakor mégis közelítésekhez kell folyamodni, mivel a kicserélődési-korrelációs potenciál egzakt funkcionál alakja nem ismert. A legegyszerűbb gyakran használt közelítés a lokális sűrűség közelítés (LDA) [12-16], melyben a kicserélődési-korrelációs energiasűrűség meghatározásának alapjául a homogén elektron gáz statisztikus elmélete szolgál. Az általánosított gradiens közelítésekben (GGA) [19-22] a kicserélődési-korrelációs energiasűrűség nemcsak a sűrűségtől, hanem a sűrűség deriváltjaitól is függ.

A közelítő formulák felállításához, illetve "jóságuk" ellenőrzéséhez rendkívül fontos minden információ, melyet a kicserélődési-korrelációs potenciálról, illetve energiáról nyerhetünk. Így nagy jelentősége van annak is, hogy a Kohn-Sham-egyenletek révén lehetőség adódik az egzakt kicserélődési-korrelációs potenciál elektronsűrűségből történő meghatározására [86], amennyiben az egzakt sűrűség ismert. Ismert Hartree-Fock-sűrűségből pedig az egzakt kicserélődési potenciál határozható meg [87].

Gömbszimmetrikus rendszerek, így zárt héjú atomok és ionok esetében azonban nem szükséges a teljes elektronsűrűség ismerete a kicserélődési-korrelációs potenciál meghatározásához, mert a Theophilou-tételből [43, 44] következően a teljes elektronsűrűség megadásával egyenértékű az ugyanazon adott l mellékkvantumszámhoz tartozó Kohn-Sham-féle egyelektron állapotok teljes n_l sűrűségének ismerete. Ez azt jelenti, hogy az elektronsűrűség n_l része (ahol $l = s, p, d...$) elvben minden információt tartalmaz az alapállapoti rendszerről. A sűrűségfunkcionál elmélet alapjainak rövid áttekintése után a jelen értekezés 2. fejezetében egy eljárást dolgoztam ki arra vonatkozóan, hogy konkrétan hogyan számolható ki a Kohn-Sham-potenciál és a teljes elektronsűrűség az l-pályákhoz tartozó sűrűségből.

A közelítő energia-funkcionálok kifejlesztésében jelentős segítséget nyújtanak a funkcionálokra vonatkozó egzakt összefüggések. Ilyenek a hierarchia-egyenletek is, amelyek az energia-funkcionálok K-adik funkcionálderiváltját kapcsolják össze a $(K+1)$-edik funkcionálderiválttal és az elektronsűrűséggel. Liu, Nagy és Parr [48] a korrelációs energiára és a korrelációs kinetikus energia funkcionálra származtatott hierarchia-egyenleteket, melyek csak a megfelelő energia-funkcionált és annak funkcionálderiváltjait tartalmazzák. A hierarchia-egyenletek K-ad rendű csonkítása, azaz a $(K+1)$-edik funkcionálderiváltat tartalmazó tagok elhanyagolása az elektronsűrűség klaszikus momentumai szerinti sorfejtésekre vezet. A momentumok szerinti sorfejtéseknek jelentős szerepük van a nem-lokális funkcionálok konstruálásában [49]. Belátható [52], hogy a vizsgált rendszer elektronsűrűségét egyértelműen meghatározza a momentumok valamely, alkalmasan megválasztott teljes rendszere, tehát az elektronsűrűség helyett annak momentumai is alapvető mennyiségekként kezelhetők. Liu, Nagy és Parr [48] gömbszimmetrikus rendszerek korrelációs energiájára és korrelációs kinetikus energiájára kéttagú, univerzális, lineáris momentum-formulákat adtak meg, melyekben a sűrűség nulladik és második momentumai előtti együtthatókat numerikus illesztéssel kapták meg. Az értekezés 3. fejezetében ezen kéttagú momentum-formulákat vizsgáltam meg az adiabatikus csatolási paraméter függvényében. Az adiabatikus csatolás az eredeti, kölcsönható rendszer viselkedését a Kohn-Sham-rendszerével köti össze a csatolási paraméteren keresztül.

A sűrűségfunkcionál elmélet eredeti formájában csak az egyes szimmetriaosztályok legalacsonyabb állapotaira alkalmazható. A szimmetria-problémát a sűrűségfunkcionál elméletben sokan vizsgálták [56-58]. Atomok és molekulák multiplett-szerkezetét szintén sikerült már elektronsűrűség módszerekkel elemezni [59-62]. Az alapállapoti rendszerek kicserélődési energiája egzaktul leírható az optimalizált effektív potenciál (OEP) módszer [23- 26] segítségével, melyben az egzakt kicserélődési energia funkcionál az egyelektron-pályákkal van kifejezve és csak a korrelációs energia, mint az egyelektron-pályák funkcionálja szorul közelítésre. A kicserélődési-korrelációs potenciál az OEP módszeren belül egy bonyolult integrálegyenlet numerikus megoldásával határozható meg. Krieger, Li és Iafrate (KLI) [27-32] egy közelítő eljárást javasoltak az OEP integrálegyenlet megoldására. Nagy [63] a KLI- módszert általánosította a legalacsonyabb multiplettek energiájának számolására. A 4. fejezetben a multiplettekre általánosított csak-kicserélődési KLI-módszert a Colle-Salvetti-korrelációs funkcionállal [64,65] egészítettem ki (KLICS).

A következőkben a sűrűségfunkcionál elmélet fentiekben tárgyalt három részterületén elért eredményeimet és a belőlük levonható következtetéseket foglalom össze.

I. A Theophilou-tétel szerint [43,44], gömbszimmetrikus potenciáltérben levő kölcsönhatásmentes elektronrendszer adott l mellékkvantumszámú pályáihoz tartozó elektronsűrűség, n_l, egyértelműen meghatározza a külső potenciált. A többelektronos rendszerek leírására a Kohn-Sham-elméletet alkalmazván megállapítható, hogy gömbszimmetrikus rendszerek esetén a Kohn-Sham n_l sűrűség egyértelműen meghatározza a Kohn-Sham-potenciált.

- Két, illetve három l-pályával rendelkező gömbszimmetrikus rendszerek Kohn-Sham-potenciáljának meghatározására potenciál-fázisfüggvény összefüggést vezettem le a Dawson-March-transzformációt [77,78] alkalmazván. Az összefüggésben szereplő fázisfüggvényekre csatolt differenciálegyenlet rendszert kaptam, amely n_l ismeretében megoldható.

- Többelektronos atomi rendszerek Kohn-Sham-potenciáljának az l mellékkvantumszámú pályákhoz tartozó sűrűségből, n_l-ből történő kiszámítására a Nagy [86] által kidolgozott numerikus, iteratív eljárást módosítottam.

- Sikerült levezetnem egy “cusp”-relációt, amelyből az atomok és ionok rendszáma n_l ismeretében kiszámolható. Ismervén a rendszámot, a Kohn-Sham-potenciál aszimptotikus viselkedéséből az elektronok száma meghatározható. Így tehát az l-pályákhoz tartozó sűrűség az alapállapot leírásához szükséges összes információt tartalmazza, azaz lehetőség adódik a teljes elektronsűrűség n_l sűrűségből történő numerikus kiszámítására.

- Az előző állítás illusztrálására atomokra csak-kicserélődési számításokat végeztem, melyek során az l-pályákhoz tartozó sűrűségből sikerült meghatároznom a Kohn-Sham-potenciált és a teljes elektronsűrűséget.

II. A hierarchia-egyenletek csonkításával nyert Liu-Nagy-Parr-féle kéttagú momentum-formulákat [48] az adiabatikus csatoláson keresztül vizsgáltam.

- Az $E_c^\lambda = \lambda C_0 lnZ \int ndr + \lambda^2 C_1 Z \int rndr$ korrelációs energiát és a $T_c^\lambda = -\lambda^2 C_0 lnZ \int ndr - 2\lambda^3 C_1 Z \int rndr$ korrelációs kinetikus energiát a λ csatolási paraméter függvényében különböző atomokra vizsgálván megállapítható, hogy kis rendszámú atomok esetében az E_c^λ-görbék közel egyenesek a momentum-formula második tagjában szereplő kis C_1 együttható miatt. A rendszám növekedésével a második tag egyre nagyobbá válik, így a görbék egyre jobban eltérnek az egyenestől. A korrelációs kinetikus energia λ-függésére is az jellemző, hogy a második tag egyre dominánsabbá válik a rendszám növekedtével.

- A korrelációs energiára vonatkozó momentum-formula adiabatikus csatolási görbéjét összehasonlítottam az egzakt, az LDA- és a GGA-görbével, melyeket Colonna és Savin [92] kifejezése alapján kaptam. A momentum-formula mindhárom görbével elég jó egyezést mutat.

- A csatolási paraméter egész tartományán a momentum-formula az LDA-nál jobb eredményeket ad.

- Az adiabatikus csatolás igen jelentős szerepet játszik új, nem-lokális sűrűség-funkcionálok konstruálásában. Ez képezi a nem-empirikus hibrid-módszerek kifejlesztésének alapját is [102,104]. Kimutatták [105], hogy a hibrid-módszerek általában javítják a közelítő funkcionálok eredményeit, ha azok a csatolási paraméter függvényében a $\lambda = 1$-hez közeli tartományon lényegesen jobb értékeket adnak, mint a $\lambda = 0$ körül. A momentum-formulát ebből a szempontból is elemeztem. Két- és négyelektronos rendszerekre kimutattam, hogy a momentumos közelítés a csatolási paraméter nagy értékeire jobban működik, mint a $\lambda = 0$ körüli értékekre, ami az LDA- és a GGA-közelítés esetében is tapasztalható.

- Az egyik leggyakrabban használt GGA-módszer, a Perdew-Burke-Ernzerhof (PBE)-féle közelítés [18] a He-sorozatra jobb eredményeket nyújt az LDA-nál [93]. A Be-sorozatra viszont a rendszám növekedésével egyre rosszabb közelítést eredményez. A He- és a Be-sorozatra összehasonlítván a momentum-formulából származó, $\lambda = 1$-nél képzett $\partial(\lambda E_c^\lambda)/\partial\lambda$ derivált, és az egzakt derivált hányadosát azt tapasztaltam, hogy bár mindkét sorozatban a rendszám növekedésével kicsit növekszik a közelítés hibája, a momentum-formula a Be-sorozatra is meglehetősen jó közelítés.

III. Atomok legalacsonyabb multiplett-állapotainak vizsgálatára KLI számolásokat [63] végeztem a Colle-Salvetti- korrelációs funkcionál [64,65] felhasználásával. Az így kapott KLICS multiplett energiákat kísérleti eredményekkel, Hartree-Fock-eredményekkel és csak-kicserélődési KLI értékekkel hasonlítottam össze, valamint a kicserélődési potenciált a lokális Wigner-korrelációs formulával [73] kiegészítő KLI módszer eredményeivel (KLILW). A következőket tapasztaltam:

- A KLICS-módszer valamivel jobb eredményeket ad, mint a KLILW-közelítés.

- A alapállapoti konfigurációból származtatható multiplett-állapotok energiakülönbségeire a KLICS-eredmények a Hartree-Fock- és a KLILW-eredményeknél jobbnak mutatkoznak, de a csak-kicserélődési KLI-értékek közelebb esnek a kísérletileg megfigyelhető értékekhez, mint a KLICS-eredmények, tehát a Colle-Salvetti-korrelációs potenciál alkalmazásával a multiplett-szerkezet nem írható le olyan jól, mint a korreláció figyelembe vétele nélkül.

Acknowledgements

I gratefully thank my supervisor, Dr. Ágnes Nagy for the valuable discussions and her continual support and guidance in both the writing of this thesis and the work which preceded it. I would also like to thank the members of the Department of Theoretical Physics for their steady help and encouragement.

List of publications

Á. Nagy and E. Bene: The total electron density from the s-electron density,
Phys. Rev. A **57**, 3458 (1998).

E. Bene and Á. Nagy: Determination of the total electron density from its l-shell contribution,
J. Mol. Struct. (Theochem) **501-502**, 107 (2000).

E. Bene and Á. Nagy: The correlation energy in terms of density moments along the adiabatic connection in the density functional theory,
Chem. Phys. Lett. **324**, 475 (2000).

E. Bene and Á. Nagy: Generalized KLICS calculations for atomic multiplets,
Acta. Phys. Chem. Debr. **33**, 7 (2000).

Posters

"Correlation Energy in Terms of Density-Moments"
Workshop on Calculation of Material Properties Using Total Energy and Force Methods and Ab-initio Molecular Dynamics (Trieste, Italy, 9-18 August, 1999)
8th International Conference on the Application of Density Functional Theory to Chemistry and Physics (Roma, Italy, 6-10 September, 1999).

"Excitation Energies in Density Functional Theory"
EUCO-CC3 (Budapest, Hungary, 4-8 September, 2000).

"Generalized KLICS Calculations for Atomic Multiplets"
Third Research Workshop and Graduate School on Physics and Chemistry of Quantum Systems (Debrecen, Hungary, 14-18 May, 2001).

Bibliography

1. R. G. Parr and W. Yang, Density-Functional Theory of Atoms and Molecules, (Oxford, University Press, New York, 1989).
2. N. H. March, Electron Density Theory of Atoms and Molecules, (Academic Press, New York, 1989).
3. R. M. Dreizler and E. K. Gross, ed.: Density Functional Theory (Springer-Verlag, Berlin, 1990).
4. L. H. Thomas, Proc. Cambridge Phil. Soc. **23**, 542 (1927).
5. E. Fermi, Rend. Accad. Naz. Linzei **6**, 602 (1927).
6. E. Fermi, Z. Phys. **48**, 73 (1928).
7. P. A. M. Dirac, Proc. Cambridge Phil. Soc. **26**, 376 (1930).
8. P. Gombás, Z. Physik **94**, 473 (1935).
9. R. Gáspár, Acta. Phys. Hung. **3**, 263 (1954).
10. P. Hohenberg and W. Kohn, Phys. Rev. B **136**, 864 (1964).
11. W. Kohn and L. J. Sham, Phys. Rev. A **140**, 1133 (1965).
12. J. C. Slater, Phys. Rev. **81**, 385 (1951).
13. U. von Barth and L. Hedin, J. Phys. C **5**, 1629 (1972).
14. R. Gáspár, Acta. Phys. Hung. **35**, 213 (1974).
15. O. Gunnarsson, B. I. Lundqvist and J. W. Wilkins, Phys. Rev. B **10**, 1319 (1974).
16. S. H. Vosko, L. Wilk and M. Nusair, Can. J. Phys. **58**, 1200 (1980).
17. J. P. Perdew and Y. Wang, Phys. Rev. B **45**, 244 (1992).
18. J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

19. D. C. Langreth and M. J. Mehl, Phys. Rev. **B 28**, 1809 (1983).

20. A. D. Becke, Phys. Rev. **A 38**, 3098 (1988).

21. A. D. Becke, J. Chem. Phys. **96**, 2155 (1992).

22. J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh and C. Fiolhais, Phys. Rev. **B 46** 6671 (1992).

23. R. T. Sharp and G. K. Horton, Phys. Rev. **90**, 317 (1953).

24. J. D. Talman and W. F. Shadwick, Phys. Rev A **14**, 36 (1976).

25. A. Görling and M. Levy, Phys. Rev. A **50**, 196 (1994).

26. T. Grabo and E. K. U. Gross, Chem. Phys. Lett. **240**, 141 (1995).

27. J. B. Krieger, Y. Li and G. J. Iafrate, Phys. Lett. A **146**, 256 (1990).

28. J. B. Krieger, Y. Li and G. J. Iafrate, Phys. Rev. A **45**, 101 (1992).

29. J. B. Krieger, Y. Li and G. J. Iafrate, Phys. Rev. A **46**, 5453 (1992).

30. J. B. Krieger, Y. Li and G. J. Iafrate, Int. J. Quantum. Chem. **41**, 489 (1992).

31. Y. Li, J. B. Krieger and G. J. Iafrate, Chem. Phys. Lett, **191**, 38 (1992).

32. Y. Li, J. B. Krieger and G. J. Iafrate, Phys. Rev. A **47**, 165 (1993).

33. T. Kato, Commun. Pure Appl. Math. **10**, 151 (1957).

34. E. Steiner, J. Chem. Phys. **39**, 2365 (1963).

35. E. B. Wilson, Structural Chemistry and Biology, ed.: A. Rich and N. Davidson (San Francisco, CA: Freeman, 1968).

36. N. C. Handy, Quantum Mechanical Simulation methods for Studying Biological Systems, ed.: D. Bicout and M. Field (Heidelberg: Springer, 1996).

37. Á. Nagy, Int. J. Quantum. Chem. **70**, 681 (1998).

38. Á. Nagy and K. D. Sen, J. Phys. B **33**, 1 (2000).

39. Á. Nagy and K. D. Sen, Chem. Phys. Lett. **332**, 154 (2000).

40. Á. Nagy and K. D. Sen, J. Chem. Phys. **115**, 6300 (2001).

41. N. H. March, Phys. Rev. A **33**, 88 (1986).

42. Á. Nagy and E. Bene, Phys. Rev. A **57**, 3458 (1998).

43. A. K. Theophilou, Phil. Mag. B **69**, 771 (1994).

44. A. K. Theophilou and N. T. Gidopoulos, Int. J. Quantum. Chem. **56**, 333 (1995).

45. E. Bene and Á. Nagy, J. Mol. Struct. **501-502**, 107 (2000).

46. Á. Nagy, Phys. Rev. A **47**, 2715 (1993).

47. Á. Nagy, Phys. Rev. A **52**, 984 (1995).

48. S. Liu, Á. Nagy and R. G. Parr, Phys. Rev. A **59**, 1131 (1999).

49. G. K. L. Chan and N. C. Handy, J. Chem. Phys. **112**, 5639 (2000).

50. Y. Zhang and W. Yang, J. Chem. Phys. **109**, 2604 (1998).

51. O. V. Gritsenko, B. Ensing, P. R. T. Schipper and E. J. Baerends, J. Phys. Chem. A **104**, 8558 (2000).

52. P. W. Ayers, J. B. Lucks and R. G. Parr, Acta. Phys. Chem. Debr. **34-35**, 223 (2002).

53. M. Levy and J. P. Perdew, Phys. Rev. A **32**, 2010 (1985).

54. Y. A. Wang, Phys. Rev. A **56**, 1646 (1997).

55. E. Bene and Á. Nagy, Chem. Phys. Lett. **324**, 475 (2000).

56. O. Gunnarsson and B. I. Lundqvist, Phys. Rev. B **13**, 4274 (1976).

57. J. P. Perdew, A. Savin and K. Burke, Phys. Rev. A **51**, 4531 (1995).

58. A. Görling, Phys. Rev. A **47**, 2783 (1993).

59. P. S. Bagus and B. I. Bennett, Int. J. Quantum. Chem. **9**, 143 (1975).

60. U. von Barth, Phys. Rev. A **20**, 1693 (1979).

61. C. Jamorski, M. E. Casida and D. R. Salahub, J. Chem. Phys. **104**, 5134 (1995).

62. M. Petersilka, U. J. Grossman and E. U. K. Gross, Phys. Rev. Lett. **76**, 1212 (1998).

63. Á. Nagy, J. Phys. B **32**, 2841 (1999).

64. R. Colle and D. Salvetti, Theoret. Chim. Acta **37**, 329 (1975).

65. R. Colle and D. Salvetti, Theoret. Chim. Acta **53**, 55 (1979).

66. E. Bene and Á. Nagy, Acta. Phys. Chem. Debr. **33**, 7 (2000).

67. T. Grabo, T. Kreibich, S. Kurth and E. K. U. Gross in: Strong Coulomb Correlations in Electronic Structure: Beyond the Local Density Approximation, ed: V. I. Anisimov (Gordon Breach, Tokyo, 1998).

68. N. C. Handy, M. T. Marron and H. J. Silverstone, Phys. Rev. **180**, 45 (1969).

69. J. P. Perdew, R. G. Parr, M. Levy and J. L. Balduz, Phys. Rev. Lett. **49**, 1691 (1982).

70. M. Schlüter and L. J. Sham, Phys. Rev. Lett. **51**, 1888 (1983).

71. M. Schlüter and L. J. Sham, Phys. Rev. B **32**, 3883 (1985).

72. E. P. Wigner, Trans. Faraday Soc. **34**, 678 (1938).

73. P. Süle and Á. Nagy, Acta Phys. Chem. Debr. **29**, 31 (1994).

74. M. Levy, Proc. Natl. Acad. Sci. USA **76**, 6002 (1979).

75. M. Levy, Phys. Rev. A **26**, 1200 (1982).

76. E. H. Lieb, Int. J. Quantum. Chem. **24**, 243 (1982).

77. K. A. Dawson and N. H. March, J. Chem. Phys. **81**, 5850 (1984).

78. Á. Nagy and N.H. March, Phys. Rev. A **39**, 5512 (1989).

79. F. Aryasetiawan and M. J. Stott, Phys. Rev. B **38**, 2974 (1988).

80. J. Chen and M. J. Stott, Phys. Rev. A **44**, 2816 (1991).

81. J. Chen, R. O. Esquivel and M. J. Stott, Phil. Mag. B **69**, 1001 (1994).

82. A. Görling, Phys. Rev. A **46**, 3753 (1992).

83. A. Görling, Phys. Rev. A **51**, 4501 (1995).

84. Q. Zhao and R. G. Parr, J. Chem. Phys. **98**, 543 (1993).

85. R. G. Parr, Phil. Mag. B **69**, 737 (1994).

86. Á. Nagy, Phil. Mag. B **69**, 779 (1994).

87. Á. Nagy, J. Phys. B **26**, 43 (1993).

88. E. Clementi and A. Roetti, At. Data Nucl. Data Tables **14**, 177 (1974).

89. Á. Nagy, Phys. Reports **298**, 1 (1998).

90. Á. Nagy, S. Liu and R. G. Parr, Phys. Rev. A **59**, 3349 (1999).

91. D. Joubert and G. Srivastava, J. Chem. Phys. **109**, 5212 (1998).

92. F. Colonna and A. Savin, J. Chem. Phys. **110**, 2828 (1999).

93. A. Savin, F. Colonna, and J. Teuler, in Electronic Density Functional Theory: *Recent Progress and New Directions*, Edited by Dobson *et al.*, Plenum Press, New York 1998.

94. J. Harris and R. O. Jones, J. Phys. F **4**, 1170 (1974).

95. D. Langreth and J. Perdew, Solid State Comm. **17**, 1425 (1975).

96. O. Gunnarsson and B. Lundquist, Phys. Rev. **13**, 4274 (1976).

97. M. Levy and J. P. Perdew, Phys. Rev. **A 32**, 2010 (1985).

98. S. Liu and R. G. Parr, Phys. Rev. A **53**, 2211 (1996).

99. E. Clementi and A. Roetti, At. Data Nucl. Data Tables **14**, 177 (1974).

100. R. G. Parr and S. Liu, Chem. Phys. Lett. **276**, 164 (1997).

101. S. Liu and R. G. Parr, Chem. Phys. Lett. **278**, 341 (1997).

102. A. D. Becke, J. Chem. Phys. **98**, 1372 (1993).

103. V. Barone, Chem. Phys. Lett. **226**, 392 (1994).

104. K. Burke, M. Ernzerhof and J. P. Perdew, Chem. Phys. Lett. **265**, 115 (1997).

105. K. Burke, J. P. Perdew, and M. Ernzerhof, in Electronic Density Functional Theory: *Recent Progress and New Directions*, Edited by Dobson *et al.*, Plenum Press, New York, 1998.

106. E. K. U. Gross, L. N. Oliveira and W. Kohn, Phys. Rev. **A 37**, 2805, 2809, 2821 (1988).

107. Á. Nagy, Int. J. Quantum. Chem. S. **29**, 297 (1995).

108. Á. Nagy, Phys. Rev. A **57**, 1672 (1998).

109. N. Hadjisavvas and A. K. Theophilou, Phys. Rev. A **30**, 2183 (1984).

110. E. Engel and S. H. Vosko, Phys. Rev. A **47**, 2800 (1993).

111. Á. Nagy, Phys. Rev. A **55**, 3465 (1997).

112. J.C. Slater, Quantum Theory of Atomic Structure vol 1 (New York: McGraw-Hill) (1960).

113. C. Lee, W. Yang and R. G. Parr, Phys. Rev. B **37**, 785, (1988).

114. C. E. Moore, Atomic Energy Levels (NBS Circular No 467) (Washington, Dc: US Govt. Printing Office.