



Cusp conditions for the energy densities

Ph.D. thesis

by

Zsuzsa Jánosfalvi

supervisor

Dr. Ágnes Nagy

professor

University of Debrecen
Faculty of Sciences
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Cusp-conditions for the energy densities

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Témavezető: Dr. Nagy Ágnes

A doktori szigorlati bizottság:

elnök: Dr.

tagok: Dr.

Dr.

A doktori szigorlat időpontja: 200.....

Az értekezés bírálói:

Dr.

Dr.

Dr.

A bírálóbizottság:

elnök: Dr.

tagok: Dr.

Dr.

Dr.

Dr.

Az értekezés védésének időpontja: 200.....

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Chapter 1

Introduction

The density functional theory begins with articles of Thomas and Fermi [1]-[3] in the 1920s, but it became a complete and accurate theory only with the publications of Kohn, Hohenberg and Sham [4, 5] in the early 1960s. The density functional theory is a remarkable theory because it allows a great simplification by using the 3-variable electron density instead of the N -electron wave function $\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)$ in the Schrödinger equation.

What Thomas and Fermi realized was that statistical considerations can be used to approximate the distribution of electrons in an atom. The assumptions stated by Thomas [1] are that: "Electrons are distributed uniformly in the six-dimensional phase space for the motion of an electron at the rate of two for each h^3 of volume," and that there is an effective potential field that "is itself determined by the nuclear charge and this distribution of electrons." The Thomas-Fermi formula for electron density can be derived from these assumptions.

For an N -electron system, the external potential $v(\mathbf{r})$ completely gives the Hamiltonian; thus N and $v(\mathbf{r})$ determine all properties for the ground states. In place of N and $v(\mathbf{r})$, the first Hohenberg-Kohn theorem [4] makes possible that one uses the electron density $\rho(\mathbf{r})$ as basic variable. It states: *The external potential $v(\mathbf{r})$ is determined, within a trivial additive constant, by the electron density $\rho(\mathbf{r})$.* Since $\rho(\mathbf{r})$ determines the number of electrons N , it follows that $\rho(\mathbf{r})$ also determines the ground-state function Ψ and all other electronic properties of the system. Note that $v(\mathbf{r})$ is not restricted to Coulomb potentials.

The second Hohenberg-Kohn theorem [4] provides the energy variational principle. It reads: *For a trial density $\tilde{\rho}(\mathbf{r})$, such that $\tilde{\rho}(\mathbf{r}) \geq 0$ and $\int \tilde{\rho}(\mathbf{r}) d\mathbf{r} = N$,*

$$E_0 \leq E_v[\tilde{\rho}] \quad (1.1)$$

where $E_v[\tilde{\rho}]$ is the energy functional of the ground state at a given external potential $v(\mathbf{r})$.

The theorem offers, however, neither algorithm nor any guide to the explicit construction of the functional in question. For this purpose one still has this problem in the many-particle systems. The energy functionals that are available to date

for Coulomb systems are essentially obtained from two, not unrelated, lines of argumentation. The first relies on the theory of the homogeneous electron gas as a starting point and exploits the linear response of this systems to inhomogenities. The second, more restricted in scope and extension of the simple density functional models, is based on semiclassical expansions.

One can state, that all the approximated ground state energy functionals available lead to more or less accurate but not exact results, if one determines the ground state density and energy based on the variational principle

$$\frac{\delta}{\delta \varrho(r)} \left(E_v[\varrho] - \mu \int \varrho(r) d^3r \right) = 0 \quad (1.2)$$

expressed in the exact basic theorem. The major reason for these deficiencies is an inappropriate representation of the kinetic energy contribution $T[\varrho]$.

Although one may be willing to accept the deficiencies for many problems of practical interest, this situation cannot be considered satisfactory. Thomas-Fermi and related models constitute a direct approach, whereby one constructs explicit forms for $T[\varrho]$ and $V_{ee}[\varrho]$. This allows a nice simplicity - the equations involve electron density alone. However, there are difficulties in going beyond this crude level of approximation.

The exact Kohn-Sham theorem [5] is more complicated, which invented an ingenious indirect approach to the kinetic energy functional $T[\varrho]$, the Kohn-Sham (KS) method. With this method the density functional theory became a practical tool for rigorous calculations introducing a new quantity the exchange-correlation potential. Using the approach introduced by Kohn and Sham [5] is one able to calculate the ground state properties of many-particle Coulomb systems. The accuracy of the KS calculations can be compared with the results of configuration interaction calculations and/or experiment. The eigenfunctions of Kohn-Sham equations, the KS-orbitals, result in the correct single particle density of the interacting system. The Kohn-Sham scheme makes the density functional theory even more effective by introducing the exchange-correlation potential v_{xc} , which is a one-body potential that in principle includes all many-body effects present in the interacting system. Within the density functional theory, the exchange-correlation potential is defined as the functional derivative of the exchange-correlation functional. According to the theory, this exchange-correlation functional is universal, i.e. it is the same for all systems in which the particles interact via the Coulomb potential (such an atom, a molecule, or a solid).

Unfortunately, the density functional theory does not give clues on how to construct this universal functional. At the very best, there are some sumrules for the exact exchange-correlation functional and potential. Therefore, in practice, approximate functionals are used which include the exchange and correlation effects in the many-body system to some extent. Very often these functionals are derived on semi-empirical grounds, e.g. starting from the expansion of the total energy per particle for the homogeneous electron gas. It turned out that simple local density approximations (LDA) [6]-[10] are surprisingly good for periodic solids. However,

LDA cannot provide the precision that is needed in surface chemistry, quantum chemistry, computation biology, etc.

We may identify three generations of density functional schemes which may be classified according to the level of approximations used for the universal functionals $T_S[\varrho]$ and $E_{xc}[\varrho]$. In what we call the *first generation of density functional theory*, explicit density-dependent functionals are used to approximate both $T_S[\varrho]$ and $E_{xc}[\varrho]$. The simplest approximation of this kind is the Thomas-Fermi model, where $E_{xc}[\varrho]$ is neglected completely and $T_S[\varrho]$ is approximated. For functionals of this type, the Hohenberg-Kohn variational principle (1.2) can be used directly, leading to equations of Thomas-Fermi type. As these equations contain only one basic variable, namely the electron density $\varrho(\mathbf{r})$ of the system, they are readily solved numerically. The results obtained in this way, however, are generally of only moderate accuracy in $T_S[\varrho]$, yielding unacceptable large errors in E_0 .

The *second generation of density functional theory* employs the exact functional for the non-interacting kinetic energy and an approximate density functional for the exchange-correlation energy. This leads to the Kohn-Sham version of density functional theory. In practice, the Hohenberg-Kohn equations have to be solved self-consistently employing approximation but explicit density-dependent functionals for $E_{xc}[\varrho]$. The functional for the non-interacting kinetic energy depends on one-electron orbitals. The resulting scheme is still easy to solve numerically and gives - especially for sophisticated density-gradient-dependent approximations (GGAs) [11, 12] of $E_{xc}[\varrho]$ - excellent results for a wide range of atomic, molecular and solid-state systems.

Finally, in the *third generation of density functional theory*, one employs in addition to the exact expression for T_S , also the exact expression for the exchange energy. Only the correlation part of $E_{xc}[\varrho]$ needs to be approximated in this approach. In contrast to the conventional second-generation Kohn-Sham scheme, the third generation allows for the treatment of explicitly orbital-dependent functionals for E_x next to the non-interacting kinetic energy T_S , giving more flexibility in the construction of such approximations. The central equation in the third generation of density functional theory is still the Kohn-Sham equations. The difference between the second and third generation lies in the level of approximation to the exchange-correlation energy.

The motivation of this work is to give additional conditions to the right approximated functionals. Although the electron density is the basic variable of the density functional theory, rigorous information on its structural properties is scarce. Probably, the most useful relations are the cusp relations [13, 14]. From one of the generalizations of Kato's theorem follows that

$$\left. \frac{\partial \bar{\varrho}(r)}{\partial r} \right|_{r=R_\alpha} = -2Z_\alpha \varrho(r)|_{r=R_\alpha} , \quad (1.3)$$

where $\bar{\varrho}$ is the spherical average of ϱ and the partial derivatives are taken at nuclei R_α , with atomic number Z_α . The integral of the density gives us the number of electrons. The cusps of the density $\varrho(\mathbf{r})$ tell us where the nuclei are and what

the atomic numbers Z_α are. Thus we can readily obtain the Hamiltonian $\hat{H}$ of the system, which includes in principle all information on the system. It is important to emphasize that this state is valid only for systems with Coulomb potential. Kato's theorem holds for excited states, too. Based on the concept of adiabatic connection between interacting and non-interacting systems and Kato's theorem a theory for a single excited state has recently been presented [15]. Higher-order cusp relations [16]-[18] have also been derived.

We have also to notice that Kato's theorem holds true of energy densities as well, which enables us to examine the behaviour of energy density functionals at the place of the nucleus. I derived cusp-conditions for kinetic energy densities (Chapter 3). In Chapter 4 I established a relation between kinetic and exchange energy in the frame of Hartree-Fock theory. Then I derived exact energy expression in the strong interaction limit of density functional theory using the adiabatic connection technique (Chapter 5). The adiabatic connection [19]-[23] provides the link between the real interacting and the fictitious non-interacting system. It has recently been shown [24]-[27], that adiabatic connection has an important role in studying strongly interacting systems within the density functional theory. Further the subspace density of the first excited state for two harmonically interacting electrons with isotropic harmonic confinement is given (Chapter 6). Finally a short summary of the thesis (Chapter 7) is presented.

Density functional theory is applied in a variety of molecular modelling problems. An example is situated in the field of biotechnology such as study of proteins which are essential for the regulation of processes (e.g. bacteriorhodopsin) and the description of damage and repair mechanisms in DNA sequences. As another example, one can mention the pharmacology, where new medicines are designed by means of computer simulation instead of by actually producing the prototype molecules.

Chapter 2

Theoretical background of the ground and excited state in density functional theory

In this chapter a short description is given about the theory of Hohenberg-Kohn [4] and Kohn-Sham [5]. The v - and N -representability problems are discussed with the method of Levy-Lieb constrained search [28]-[30]. Basic concept of Kato's theorem [13] is also given, which was originally formulated for the wave functions of systems with Coulomb external potential. Finally the excited states are briefly reviewed [19, 31, 32]. Atomic units are used in this work.

2.1 The Hohenberg-Kohn theory

Based on the variational principle the ground state wave function Ψ_{exact} and the ground state energy E_{exact} of an N -electron system can be derived

$$E_{exact} = \min_{\Psi} \langle \Psi | \hat{H} | \Psi \rangle, \quad (2.1)$$

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

$$\hat{H} = \hat{T} + \hat{V}_{ee} + \hat{V}, \quad (2.2)$$

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

$$\hat{T} = \sum_{i=1}^N \left(-\frac{1}{2} \nabla_i^2 \right) \quad (2.3)$$

and

$$\hat{V}_{ee} = \sum_{i < j}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \quad (2.4)$$

is the electron-electron interacting energy operator and

$$\hat{V} = \sum_{i=1}^N v(\mathbf{r}_i) \quad (2.5)$$

is the electron-nucleus interacting energy operator, in which

$$v(\mathbf{r}_i) = \sum_{\alpha} \frac{Z_{\alpha}}{|\mathbf{r}_i - \mathbf{R}_{\alpha}|} \quad (2.6)$$

is the external potential. The definition of the electron density $\varrho(\mathbf{r})$ generated by the N -electron wave function Ψ is the following

$$\varrho(\mathbf{r}_1) = N \int |\Psi(\mathbf{x}_1, \mathbf{x}_2 \dots \mathbf{x}_N)|^2 ds_1 d\mathbf{x}_2 \dots d\mathbf{x}_N, \quad (2.7)$$

where $\mathbf{x}$ stands for both the spatial and spin coordinates $\mathbf{x} = (\mathbf{r}, s)$. At given external potential $v(\mathbf{r})$ the Hamiltonian $\hat{H}$ is determined, which means if one knows the electron number N and external potential $v(\mathbf{r})$ of the system then all properties for the ground state can be derived.

2.1.1 The ground-state electron density

The $\varrho(\mathbf{r})$ is the basic variable in the density functional theory instead of N and $v(\mathbf{r})$. So the Hamiltonian $\hat{H}$ and all the ground-state properties are functionals of the electron density $\varrho(\mathbf{r})$. Integration of the electron density $\varrho(\mathbf{r})$ for the whole space gives the electron number N of the system

$$\int \varrho_{exact}(\mathbf{r}) d\mathbf{r} = N, \quad (2.8)$$

therefore N is the functional of the exact ground-state electron density $\varrho_{exact}(\mathbf{r})$. The Hohenberg-Kohn theorem provides the connection between the external potential $v(\mathbf{r})$ and electron density $\varrho_{exact}(\mathbf{r})$. It states, that within a trivial additive constant the external potential $v(\mathbf{r})$ is implicitly determined by the ground-state density $\varrho_{exact}(\mathbf{r})$. The validity of Hohenberg-Kohn theorem is not restricted to Coulomb potential. The proof of this theorem is made by using the minimum energy principle for the non-degenerate ground-state energy. Let us suppose there are two different external potentials $v(\mathbf{r})$ and $v'(\mathbf{r})$ deriving the same ground-state electron density $\varrho_{exact}(\mathbf{r})$. Then we have two different Hamiltonians $\hat{H}$ and $\hat{H}'$, to which the following ground-state wave functions belong Ψ and Ψ' . Then the minimum principle for the ground-state energies E and E' gives

$$\begin{aligned}
E < \langle \Psi' | \hat{H} | \Psi' \rangle &= \langle \Psi' | \hat{H}' | \Psi' \rangle + \langle \Psi' | \hat{H} - \hat{H}' | \Psi' \rangle \\
&= E' + \int \varrho_{exact}(\mathbf{r}) [v(\mathbf{r}) - v'(\mathbf{r})] d\mathbf{r},
\end{aligned} \tag{2.9}$$

and

$$\begin{aligned}
E' < \langle \Psi | \hat{H}' | \Psi \rangle &= \langle \Psi | \hat{H} | \Psi \rangle + \langle \Psi | \hat{H}' - \hat{H} | \Psi \rangle \\
&= E + \int \varrho_{exact}(\mathbf{r}) [v'(\mathbf{r}) - v(\mathbf{r})] d\mathbf{r}.
\end{aligned} \tag{2.10}$$

Adding Eq.(2.9) and Eq.(2.10) we get the contradiction

$$E + E' < E' + E, \tag{2.11}$$

consequently the external potentials are not differing by more than a constant C

$$v'(\mathbf{r}) = v(\mathbf{r}) + C. \tag{2.12}$$

We arrived at that the Hamiltonian $\hat{H}$ is the functional of the ground-state electron density, so all the ground state properties can be derived knowing the ground-state electron density.

2.1.2 The ground-state energy

One has to find the true ground-state energy. The second Hohenberg-Kohn theorem provides this via energy variational principle. For an arbitrary density $\varrho(\mathbf{r})$, which fulfills the requirements $\varrho(\mathbf{r}) \geq 0$ and $\int \varrho(\mathbf{r}) d\mathbf{r} = N$, gives

$$E_{exact} \equiv E_v[\varrho_{exact}] \leq E_v[\varrho]. \tag{2.13}$$

Using the Rayleigh-Ritz variational principle it can be shown that the functional $E_v[\varrho]$ has the minimum value, which is the exact ground-state energy, when ϱ is precisely the exact ground-state density ϱ_{exact} .

For a given external potential $v(\mathbf{r})$ the total energy functional can be written as

$$E_v[\varrho] = F[\varrho] + \int \varrho(\mathbf{r}) v(\mathbf{r}) d\mathbf{r}, \tag{2.14}$$

where

$$F[\varrho] = T[\varrho] + V_{ee}[\varrho]. \tag{2.15}$$

The Hohenberg-Kohn functional $F[\varrho]$ is the sum of the kinetic energy and electron-electron repulsion energy.

2.1.3 Levy-Lieb constrained-search method

The Hohenberg-Kohn functional is defined for v -representable densities. The v -representability for electron density means that for a given electron number N and external potential $v(\mathbf{r})$ there exists such electron density $\rho(\mathbf{r})$ that this electron density derives the exact ground-state wave functions $\Psi[\rho]$ and ground-state energy $E[\rho]$ of the $\hat{H}$ Hamiltonian. From the exact ground-state wave functions we get the known electron density. Then two questions arise. The first, if there is an appropriate non-negative $\rho(\mathbf{r})$ electron density - which is normalized for N , so $\int \rho(\mathbf{r}) d\mathbf{r} = N$ - then one finds such an external potential to this density, that the given density will be the exact ground-state density or not. In other words, are all the suitable non-negative, normalized functions v -representable densities? The second question is, if not all the non-negative N -normalized functions are v -representable, then the domain of the Hohenberg-Kohn functional $F[\rho]$ can be extended to these densities. These questions lead us to the so-called v -representability problem. The answer to the first one is that not all the appropriate non-negative, N -normalized functions are v -representable. However the domain of the Hohenberg-Kohn functional $F[\rho]$ can be extended to these functions via Levy-Lieb constrained-search method. In the constrained-search formula for $F[\rho_{exact}]$, which is the following expression

$$F[\rho_{exact}] = \min_{\Psi \rightarrow \rho_{exact}} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle , \quad (2.16)$$

is superfluous to require that ρ_{exact} should be a v -representable ground-state density, so long as it is given by an antisymmetric wave function. This allows one to extend the domain of the Hohenberg-Kohn functional $F[\rho_{exact}]$ from v -representable densities to N -representable densities. N -representable density means that there exists such an antisymmetric wave function which yields the given density. Then we can define the Hohenberg-Kohn functional $F[\rho_{exact}]$ for any N -representable density as

$$F[\rho] = \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle . \quad (2.17)$$

The Hohenberg-Kohn functional $F[\rho_{exact}]$ searches all Ψ that yields the given density and then the minimum of the functional itself is derived. It can be seen from Eqs (2.16) and (2.17) that

$$F[\rho_{exact}] = \min_{\rho} F[\rho] . \quad (2.18)$$

Using the constrained-search formula the minimization of the ground-state energy can be done in two steps

$$\begin{aligned}
E_{exact} &= \min_{\varrho} \left\{ \min_{\Psi \rightarrow \varrho} \left[\langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle + \int v(\mathbf{r}) \varrho(\mathbf{r}) d\mathbf{r} \right] \right\} \\
&= \min_{\varrho} \left\{ F[\varrho] + \int v(\mathbf{r}) \varrho(\mathbf{r}) d\mathbf{r} \right\} \\
&= \min_{\varrho} E[\varrho].
\end{aligned} \tag{2.19}$$

The first minimization in the brackets is constrained to those wave functions which yield the given ground-state density ϱ and finally, the second minimization is for all ground-state densities. Hence the Levy-Lieb constrained-search method, the variation is over all N -representable densities, which resolves the v -representability problem in the original Hohenberg-Kohn approach.

2.1.4 Euler-equation

With the additional condition of the given particle number of the system the variational principle includes the μ Lagrange multipliers

$$\frac{\delta}{\delta \varrho(\mathbf{r})} \left(E_v[\varrho] - \mu \int \varrho(\mathbf{r}) d\mathbf{r} \right) = 0 \tag{2.20}$$

and gives the Euler equation

$$\frac{\delta E_v[\varrho]}{\delta \varrho(\mathbf{r})} = \mu. \tag{2.21}$$

The μ Lagrange multipliers turned out to be the chemical potential of the system. If the Hohenberg-Kohn functional $F[\varrho]$ were known, then the exact equation Eq. (2.21) with the N particle number of the system could be used to derive the exact ground-state density and energy.

2.2 The Kohn-Sham theory

The ground-state energy of a many-electron system can be obtained as the minimum of the energy functional $E_v[\varrho]$ in Eq. (2.14). The exact ground-state density, which minimizes the energy functional, satisfies the Euler-equation Eq.(2.21). The lack of knowledge of the kinetic energy $T[\varrho]$ and the non-classical part of electron-electron interaction $V_{ee}[\varrho]$ as the functionals of electron density requires use of approximations. Making drastic assumptions, for example, as it is in the Thomas-Fermi model, we get nice simplicity but it becomes less accurate. Kohn and Sham applied an indirect approach to the kinetic energy functional $T[\varrho]$ introducing a new quantity, the exchange-correlation energy E_{xc} , with which they developed a practical tool for rigorous calculations in density functional theory.

2.2.1 The Kohn-Sham equations

The exact expression for the ground-state kinetic energy of any *interacting* system is

$$T = \sum_{i=1}^{\infty} \lambda_i \langle \xi_i | -\frac{1}{2} \nabla^2 | \xi_i \rangle \quad (2.22)$$

where ξ_i are natural spin orbitals and λ_i are occupation numbers. The kinetic energy T is the functional of the electron density ϱ

$$\varrho(\mathbf{r}) = \sum_{i=1}^{\infty} \lambda_i \sum_s |\xi_i(\mathbf{r}, s)|^2. \quad (2.23)$$

Kohn and Sham invented to handle the kinetic energy and the electron density belonging to a *non-interacting* N -electron system

$$T_s[\varrho] = \sum_{i=1}^N \langle \varphi_i | -\frac{1}{2} \nabla_i^2 | \varphi_i \rangle \quad (2.24)$$

and

$$\varrho(\mathbf{r}) = \sum_{i=1}^N \sum_s |\varphi_i(\mathbf{r}, s)|^2. \quad (2.25)$$

As we discussed earlier, any non-negative, continuous and normalized density ϱ is N -representable and it can be given as in Eq. (2.25). Because of the definition of the kinetic energy functional $T_s[\varrho]$ we need electron orbitals. So how one could have a unique decomposition of electron density ϱ of an *interacting* system in terms of orbitals to get the kinetic energy functional $T_s[\varrho]$. Idea of Kohn and Sham was to associate to the N -electron interacting system a *non-interacting reference system* for which the ground-state electron density is exactly ϱ . The Hamiltonian and its exact ground-state function of this reference system are the following

$$\hat{H}_s = \sum_{i=1}^N \left(-\frac{1}{2} \nabla_i^2 \right) + \sum_{i=1}^N v_s(\mathbf{r}_i) \quad (2.26)$$

$$\Psi_s = \frac{1}{\sqrt{N!}} \det[\varphi_1 \varphi_2 \cdots \varphi_N], \quad (2.27)$$

where the φ_i are the lowest N eigenstates of the one-electron Hamiltonian $\hat{h}_s$

$$\hat{h}_s \varphi_i = \left[-\frac{1}{2} \nabla_i^2 + v_s(\mathbf{r}) \right] \varphi_i = \epsilon_i \varphi_i \quad (2.28)$$

and the kinetic energy functional is

$$\begin{aligned}
T_s[\varrho] &= \langle \Psi_s | \sum_{i=1}^N \left(-\frac{1}{2} \nabla_i^2 \right) | \Psi_s \rangle \\
&= \sum_{i=1}^N \langle \varphi_i | -\frac{1}{2} \nabla_i^2 | \varphi_i \rangle .
\end{aligned} \tag{2.29}$$

The defined kinetic energy $T_s[\varrho]$ does not equal the exact kinetic energy functional $T[\varrho]$. The clever idea of Kohn and Sham was building the Hamiltonian of the interacting system in such a way that the $T_s[\varrho]$ becomes the kinetic energy component of this new Hamiltonian. The difference $T[\varrho] - T_s[\varrho]$ is included in the exchange-correlation energy. Then the Hohenberg-Kohn functional can be rewritten in the following way defining a new quantity, the so-called exchange-correlation energy $E_{xc}[\varrho]$

$$F[\varrho] = T_s[\varrho] + J[\varrho] + E_{xc}[\varrho] \tag{2.30}$$

where

$$E_{xc}[\varrho] = T[\varrho] - T_s[\varrho] + V_{ee}[\varrho] - J[\varrho] \tag{2.31}$$

and the potentials are

$$V_{ee} = \int \int \frac{1}{|\mathbf{r} - \mathbf{r}'|} \varrho_2(\mathbf{r}, \mathbf{r}') d\mathbf{r} d\mathbf{r}' \tag{2.32}$$

and

$$J = \frac{1}{2} \int \int \frac{\varrho(\mathbf{r}) \varrho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' . \tag{2.33}$$

where $\varrho_2(\mathbf{r}, \mathbf{r}')$ is the pair density-matrix defined by

$$\varrho_2(\mathbf{r}, \mathbf{r}') = \frac{N(N-1)}{2} \int \dots \int \Psi_s^* \Psi_s ds_1 ds_2 d\mathbf{x}_3 \dots d\mathbf{x}_N . \tag{2.34}$$

Then the electron density can be derived from the pair density $\varrho(\mathbf{r}, \mathbf{r}')$ in the following way

$$\varrho(\mathbf{r}) = \frac{2}{N-1} \int \varrho(\mathbf{r}, \mathbf{r}') d\mathbf{r}' . \tag{2.35}$$

The exchange-correlation energy $E_{xc}[\varrho]$ includes the difference between the interacting and non-interacting kinetic energy plus the non-classical term of the electron-electron interaction. Finally the Hamiltonian can be constructed with the appropriate external potential, which is the Kohn-Sham effective potential defined by

$$\begin{aligned}
v_{eff}(\mathbf{r}) &= v(\mathbf{r}) + \frac{\delta J[\varrho]}{\delta \varrho(\mathbf{r})} + \frac{\delta E_{xc}[\varrho]}{\delta \varrho(\mathbf{r})} \\
&= v(\mathbf{r}) + \int \frac{\varrho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{xc}(\mathbf{r})
\end{aligned} \tag{2.36}$$

and

$$v_{xc}(\mathbf{r}) := \frac{\delta E_{xc}[\varrho]}{\delta \varrho(\mathbf{r})} . \quad (2.37)$$

With the constrain for the electron number of the system

$$N = \int \varrho(\mathbf{r}) d\mathbf{r} \quad (2.38)$$

and setting

$$\varrho(\mathbf{r}) = \sum_{i=1}^N \sum_s |\varphi_i(\mathbf{r}, s)|^2 \quad (2.39)$$

the one-electron equations are

$$\varepsilon_i \varphi_i = \left[-\frac{1}{2} \nabla_i^2 + v_{eff}(\mathbf{r}) \right] \varphi_i . \quad (2.40)$$

The Eqs(2.36), (2.37), (2.39) and (2.40) are the Kohn-Sham equations. The effective potential v_{eff} depends on $\varrho(\mathbf{r})$ via exchange-correlation potential Eq.(2.37); hence Eqs (2.36), (2.40) and (2.39) must be solved self-consistently. This technique requires an initial guessed electron density $\varrho(\mathbf{r})$, with which one constructs the effective potential $v_{eff}(\mathbf{r})$ through Eq.(2.36). Then finds a new $\varrho(\mathbf{r})$ from Eqs (2.40) and (2.39).

2.3 Kato's theorem

Exact relations can be used either to discover analytical properties of a functional or to estimate the error of an approximation for an exact but unknown functional. For the latter, one of the most useful relations in density functional theory is the Kato's theorem for electron density. The original theorem was derived by Kato [13] for the wave functions for an N -electron system with Coulomb external potential

$$\left. \frac{\partial \bar{\Psi}(r)}{\partial r} \right|_{r=R_\alpha} = -Z_\alpha \bar{\Psi}(r)|_{r=R_\alpha} . \quad (2.41)$$

where the partial derivatives are taken at the nucleus α at its coordinate R_α . The symbol bar over the eigenfunction Ψ denotes the spherical average of Ψ at constant r around the nucleus α .

It is well known that there exist cups relations for the electron density [13, 14, 16, 18],[33]-[35]. From Kato's theorem follows [13] that

$$\left. \frac{\partial \bar{\varrho}(r)}{\partial r} \right|_{r=R_\alpha} = -2Z_\alpha \bar{\varrho}(r)|_{r=R_\alpha} , \quad (2.42)$$

where

$$\varrho(\mathbf{r}) = \int |\Psi(\mathbf{x}_1, \dots, \mathbf{x}_N)|^2 ds d\mathbf{x}_2 \dots d\mathbf{x}_N, \quad (2.43)$$

where $x : \mathbf{r}, s$ stands for both spatial and spin coordinates, $\bar{\varrho}$ is the spherical average of ϱ and the partial derivatives are taken at nuclei R_α , with atomic number Z_α . The integral of the density gives us the number of electrons: $N = \int \varrho(\mathbf{r}) d\mathbf{r}$ and the cusps of the density $\varrho(\mathbf{r})$ tell us where the nuclei are and what the atomic numbers Z_α are. Thus we can readily obtain the Hamiltonian $\hat{H}$ of the system, which includes in principle all information on the system. It is important to emphasize that this condition is valid for systems with Coulomb potential, only. Considerable recent attention has been devoted to the Kato-Steiner cusp condition [36, 37].

Kato's theorem holds for excited states, too. Based on the concept of adiabatic connection between interacting and non-interacting systems and Kato's theorem a theory for a single excited state has recently been presented [15].

There is a special case when the system has no s -electrons. The simplest example is the $2p$ orbital of the excited hydrogen atom. Although in this case Kato's theorem remains valid, it does not give us the atomic number Z_α , because the derivative of the spherical average of the wave function is zero and the value of the wave function is also zero at the nucleus. The cusp relations for this systems has already been generalized [38]. After spherically integrating the electron density $\varrho(r)$:

$$\bar{\varrho} = \sum_{nl'm'} \lambda_n R_{nl'm'}^2, \quad (2.44)$$

where $R_{nl'm'}$ are the spherical harmonics and introducing the quantity

$$\eta_l(r) := \frac{\bar{\varrho}(r)}{r^{2l}}, \quad (2.45)$$

where l is the smallest integer for which η_l is not zero at $r = 0$:

$$\left. \frac{\partial \eta_l(r)}{\partial r} \right|_{r=R_\alpha} = -2 \frac{Z_\alpha}{l+1} \eta_l(r)|_{r=R_\alpha}. \quad (2.46)$$

In the following chapter I derived cusp relations for the non-interacting kinetic energy densities.

2.4 Excited states

The ground-state density can be used as the basic variable in density functional theory. The schemes developed by Hohenberg, Kohn and Sham are restricted to ground states. It is of interest to generalize these schemes for excited states. The first rigorous generalization for excited states was given by Theophilou [32]. For degenerate case, the theory of ensembles of excited states was proposed by Gross et al. [39]. The drawback of this ensemble theory is that the treatment of highly excited states becomes quite complicated. Therefore there is growing

interest in theories for a single excited states [15], [40]-[42]. These theories can be variational and nonvariational as well. An outline of them is given below. There is an alternative theory that is the time-dependent density functional theory [43]-[45], in which transition energies are obtained from the poles of dynamic linear response properties. A nonvariational theory based on Kato's theorem [15, 40] for a single excited state is also reviewed.

2.4.1 Variational theory for a degenerate single excited state

Let us define the N -electron Hamiltonian $\hat{H}$ in the form

$$\hat{H}_v = \hat{T} + \hat{V}_{ee} + \sum_{k=1}^N v(\mathbf{r}_k) , \quad (2.47)$$

and the solutions of the Schrödinger equation are

$$\hat{H}|\Psi_\gamma^i\rangle = E^i|\Psi_\gamma^i\rangle \quad (\gamma = 1, 2, \dots, g_i) , \quad (2.48)$$

where $\hat{T}$, $\hat{V}_{ee}$ and v are the kinetic energy operator, the electron-electron repulsion operator and the external operator, respectively. The g_i is the degeneracy. Only one index i is used to denote the symmetry both in spin and ordinary space. The subspace S_i is used instead of one wave function to describe an individual excited state. The subspace S_i is spanned by a set of wave functions Ψ_γ^i . Then the density matrix $\hat{D}^i$ in subspace S_i can be defined as

$$\hat{D}^i = \sum_{\gamma=1}^{g_i} \eta_\gamma^i |\Psi_\gamma^i\rangle \langle \Psi_\gamma^i| , \quad (2.49)$$

with the conditions

$$1 = \sum_{\gamma=1}^{g_i} \eta_\gamma^i \quad (2.50)$$

and

$$\eta_\gamma^i \geq 0 . \quad (2.51)$$

The symbol η_γ^i denotes the weighting factors. Any set of weighting factors η_γ^i can be used in principle. The only requirement is to satisfy the Eqs (2.50) and (2.51). The subspace density is given

$$n_i = N \sum_{\gamma=1}^{g_i} \eta_\gamma^i \int |\Psi_\gamma^i|^2 ds_1 d\mathbf{x}_2 \dots d\mathbf{x}_N , \quad (2.52)$$

where $\mathbf{x}$ includes the space- and spin-coordinate. The superscript i refers to the wave functions Ψ_γ^i belonging to the subspace S_i , from which the subspace density matrix $\hat{D}^i$ and the subspace density n_i are constructed. If the weighting factors η_γ^i

are all equal then the subspace density transforms according to the first row of the character table.

If one uses the matrix representation of the transformation then, by definition, the sum of diagonal elements of the matrix is the character. The character table gives the characters of all symmetry transformations of a given system in the irreducible representation. The irreducible representation is the simplest matrix representation of a transformation. In general, the character table gives the transformation properties of x , y and z -axis.

For example, if the weighting factors are all equal and the system has spherical symmetry, as it is for atoms, then the subspace density will be spherically symmetric, which is the symmetry property of the external potential, as well.

Define the universal functional in the following way

$$F[n_i, n_0] = \min_{S \rightarrow n_i} \sum_{\gamma=1}^{g_i} \eta_\gamma \langle \Psi_\gamma | \hat{T} + \hat{V}_{ee} | \Psi_\gamma \rangle , \quad (2.53)$$

and with the density matrix it is written as

$$F[n_i, n_0] = \min_{S \rightarrow n_i} \text{tr} \{ \hat{D}(\hat{T} + \hat{V}_{ee}) \} . \quad (2.54)$$

The n_0 is a ground-subspace density and n_i is a trial excited state density, which we discuss now. As it can be seen from Eqs(2.53) and (2.54), the universal functionals are bifunctionals in the sense that they are functionals of both the ground and the i th excited state densities. All the subspaces S_{i-1} corresponding to the first $i-1$ excited states of the Hamiltonian $\hat{H}_v = \hat{T} + \hat{V}_{ee} + \sum_{k=1}^N v(\mathbf{r}_k)$ are supposed to be orthogonal to the subspace S_i . It should be emphasized that the ground-state density of subspaces S_{i-1} is the fixed density n_0 . Thus the total energy of the i th excited state E_i can be given as

$$E_i = \min_{S_i} \sum_{\gamma=1}^{g_i} \eta_\gamma \langle \Psi_\gamma^i | \hat{H}_v | \Psi_\gamma^i \rangle \quad (2.55)$$

$$= \min_{n_i} \left\{ \min_{S_i \rightarrow n_i} \sum_{\gamma=1}^{g_i} \eta_\gamma \langle \Psi_\gamma^i | \hat{H}_v | \Psi_\gamma^i \rangle \right\} \quad (2.56)$$

$$= \min_{n_i} \left\{ F[n_i, n_0] + \int n_i(\mathbf{r}) v(\mathbf{r}) d\mathbf{r} \right\} , \quad (2.57)$$

and in density matrix formalism it will be

$$E_i = \min_{S_i} \left\{ \text{tr} \left\{ \hat{D}^i \hat{H}_v \right\} \right\} = \min_{n_i} \left\{ \min_{S_i \rightarrow n_i} \text{tr} \left\{ \hat{D}^i \hat{H}_v \right\} \right\} . \quad (2.58)$$

We wish to approximate the bifunctional $F[n_i, n_0]$, so let us construct the Hamiltonian

$$\hat{H}^{i,\alpha} = \hat{T} + \alpha \hat{V}_{ee} + \sum_{k=1}^N v_\alpha^i(\mathbf{r}_k) , \quad (2.59)$$

where the potential $v_\alpha^i(\mathbf{r}_k; [n_i, n_0])$ is defined in a way that the subspace density n_i remains independent of the adiabatic coupling constant α and therefore the ground state density of the Hamiltonian $\hat{H}^{i,\alpha}$ becomes closest to the exact ground state density n_0 in a least square sense. When the value of the adiabatic coupling constant equals to zero, $\alpha = 0$, we get to the noninteracting system.

The noninteracting Kohn-Sham Hamiltonian is defined in the following way

$$\hat{H}_w^i = \hat{H}^{i,\alpha=0} = \hat{T} + \sum_{j=1}^N w^i([n_i, n_0]; \mathbf{r}_j) . \quad (2.60)$$

The noninteracting Hamiltonian $\hat{H}_w^i$ and the $w^i([n_i, n_0]; \mathbf{r}_j)$ Kohn-Sham-like potential both depend on i , which means they are not the same for different excited states. The Kohn-Sham-like equations have the form

$$\hat{H}^{i,0}|\Psi_\gamma^{i,0}\rangle = E^{i,0}|\Psi_\gamma^{i,0}\rangle \quad (\gamma = 1, 2, \dots, g_i) , \quad (2.61)$$

where the noninteracting density matrix $\hat{D}_s^i$ can be expressed by the wave functions $\Psi_\gamma^{i,0}$ as

$$\hat{D}_s^i = \sum_{\gamma=1}^{g_i} \eta_\gamma |\Psi_\gamma^{i,0}\rangle \langle \Psi_\gamma^{i,0}|, \quad (2.62)$$

and the noninteracting kinetic energy becomes

$$T_s[n_i, n_0] = \text{tr} \left\{ \hat{D}_s^i \hat{T} \right\} \quad (2.63)$$

and variationally it is

$$T_s[n_i, n_0] = \min_{S_i \rightarrow n_i} \text{tr} \left\{ \hat{D}_s^i \hat{T} \right\} = \text{tr} \left\{ \hat{D}_s^i[n_i, n_0] \hat{T} \right\} , \quad (2.64)$$

where each subspace S_i is orthogonal to all subspaces S_{m-1} belonging to the first $m-1$ excited states of the Kohn-Sham Hamiltonian $\hat{H}_w^i$. The subspace density of the m th excited state of the Hamiltonian $\hat{H}_w^i$ will be n_i . The noninteracting excited-state density matrix $\hat{D}_s^i[n_i, n_0]$ of the Hamiltonian $\hat{H}_w^i$ is pretty that one whose subspace density is exactly n_i . The minimum principle for noninteracting kinetic energy gives

$$T_s[n_i, n_0] + \int n_i(\mathbf{r}) w^i([n_i, n_0]; \mathbf{r}) d\mathbf{r} \quad (2.65)$$

$$= \min_n \left\{ T_s[n, n_0] + \int n(\mathbf{r}) w^i([n, n_0]; \mathbf{r}) d\mathbf{r} \right\} , \quad (2.66)$$

and we get to the Euler equation

$$\mu_i = w^i([n_i, n_0]; \mathbf{r}) + \left. \frac{\delta T_s[n_i, n_0]}{\delta n} \right|_{n=n_i} , \quad (2.67)$$

where μ_i are the Lagrange parameters. The Kohn-Sham potential has the form

$$w^i(\mathbf{r}) = v(\mathbf{r}) + \left. \frac{\delta G[n_i, n_0]}{\delta n} \right|_{n=n_i}, \quad (2.68)$$

where the functional $G[n_i, n_0]$ is defined by the partition of the Hohenberg-Kohn-like functional given below

$$F[n_i, n_0] = T_s[n_i, n_0] + G[n_i, n_0] \quad (2.69)$$

and furthermore

$$G[n_i, n_0] = J[n_i] + E_x[n_i, n_0] + E_c[n_i, n_0], \quad (2.70)$$

can be divided into more parts where $J[n_i]$, $E_x[n_i, n_0]$ and $E_c[n_i, n_0]$ are the Coulomb, exchange and correlation parts of the functional $G[n_i, n_0]$. It is convenient to give the correlation energy as the difference between the interacting and noninteracting electron-electron repulsion energy. In other words,

$$E_c[n_i, n_0] = \text{tr} \left\{ \hat{D}^i \hat{V}_{ee} \right\} - \text{tr} \left\{ \hat{D}_s^i \hat{V}_{ee} \right\}. \quad (2.71)$$

Finally, the Kohn-Sham potential can be given as

$$w^i(\mathbf{r}) = v(\mathbf{r}) + v_J^i(\mathbf{r}) + v_{xc}^i(\mathbf{r}), \quad (2.72)$$

where $v(\mathbf{r})$, $v_J^i(\mathbf{r})$ and $v_{xc}^i(\mathbf{r})$ are the external, Coulomb and exchange-correlation potentials, respectively.

2.4.2 Variational theory for a non degenerate single excited state

A similar theory for non degenerate excited states can be derived immediately using the expressions given above. Only difference is that because of non degeneracy use of electron density is sufficient instead of density matrices.

2.4.3 Nonvariational theory for a single excited state

As it is already described in the previous subsection, the Kato's theorem gives a relation for the behaviour of the electron density at the nuclei. From Eq.(2.42) it follows that the electron density determines the Hamiltonian for a system with Coulomb external potential. The cusps of the electron density give the atomic numbers Z_α and the positions of the nuclei R_α . The integral of the electron density equals to the number of electrons N .

Kato's theorem is valid for excited states, too. Thus, if the density n_i of the i th excited state is given then the Hamiltonian $\hat{H}$ is also in principle known and its eigen equation

$$\hat{H}\Psi_k = E_k\Psi_k \quad (k = 0, 1, \dots, i, \dots) \quad (2.73)$$

can be solved, where

$$\hat{H} = \hat{T} + \hat{V} + \hat{V}_{ee} \quad (2.74)$$

and in the Hamiltonian the operators are

$$\hat{T} = \sum_{j=1}^N \left(-\frac{1}{2} \nabla_j^2 \right), \quad (2.75)$$

$$\hat{V}_{ee} = \sum_{k=1}^{N-1} \sum_{j=k+1}^N \frac{1}{|\mathbf{r}_k - \mathbf{r}_j|}, \quad (2.76)$$

and

$$\hat{V} = \sum_{k=1}^N \sum_{J=1}^M -\frac{Z_J}{|\mathbf{r}_k - \mathbf{R}_J|} \quad (2.77)$$

the kinetic energy, the electron-electron energy and the electron-nucleon operators.

To give a nonvariational description of excited states, the adiabatic-connection technique will be used in this subsection. Let us suppose the existence of a continuous path between the interacting and noninteracting system. We keep fixed the electron density n_i of the i th excited state along the path

$$\hat{H}_i^\alpha \Psi_k^\alpha = E_k^\alpha \Psi_k^\alpha, \quad (2.78)$$

where

$$\hat{H}_i^\alpha = \hat{T} + \alpha \hat{V}_{ee} + \hat{V}_i^\alpha. \quad (2.79)$$

The fully interacting system is denoted by $\alpha = 1$ while the noninteracting case is given when the coupling constant is zero, $\alpha = 0$

$$\hat{H}_i^0 \Psi_k^0 = E_k^0 \Psi_k^0. \quad (2.80)$$

For the fully interacting case, $\alpha = 1$, the Hamiltonian $\hat{H}_i^1$ is independent of the excited state i . For any other value of the coupling constant α the Hamiltonian depends on the excited state i . Therefore, the noninteracting Hamiltonian $\hat{H}_i^0$ will differ for different excited states. When the system is not degenerated then the electronic state Ψ_k^0 is given by a single Slater-determinant and the Kohn-Sham equations have the form

$$\varepsilon_j^i u_j^i(\mathbf{r}) = \left[-\frac{1}{2} \nabla^2 + v_s^i(\mathbf{r}) \right] u_j^i(\mathbf{r}), \quad (2.81)$$

and the Kohn-Sham potential is

$$v_s^i = v + v_J^i + v_{xc}^i \quad (2.82)$$

the sum of the external, the classic Coulomb and the exchange-correlation potentials.

Chapter 3

Cusp conditions for kinetic energy densities

Though the density functional theory [4],[46]-[48] has become a powerful tool for electronic structure calculations of atoms molecules and solids, the kinetic energy functional is still unknown and even accurate approximations are unavailable. An excellent review of the different approximations has been recently published by Ludena and Karasiev [49]. Contrary to the kinetic energy, the kinetic energy density is not uniquely defined. Still this quantity is applied frequently. So the knowledge on the exact behaviour of the kinetic energy density might be important in several applications. In this chapter we focus on the cusp relations that the kinetic energy density should satisfy, which can be useful in constructing new accurate approximations.

3.1 Cusp relations for the non-interacting kinetic energy densities

There are two natural definitions for non-interacting kinetic energy density:

$$t_1 = \frac{1}{2} \sum_{i=1}^N \lambda_i (\nabla u_i)^2, \quad (3.1)$$

$$t_2 = -\frac{1}{2} \sum_{i=1}^N \lambda_i u_i \nabla^2 u_i, \quad (3.2)$$

where u_i are the eigenfunctions of the Kohn-Sham equations:

$$\left[-\frac{1}{2} \nabla^2 + v_{KS}(\mathbf{r}) \right] u_i = \varepsilon_i u_i. \quad (3.3)$$

Then the electron density is

$$\varrho = \sum_{i=1}^N \lambda_i |u_i|^2. \quad (3.4)$$

The occupation numbers λ_i can be 0 or 1. While both forms, t_2 and t_1 , integrate to the correct total kinetic energy (for finite systems), they differ locally and are related to each other via the expression

$$t_2 = t_1 - \frac{1}{4} \nabla^2 \varrho. \quad (3.5)$$

t_1 resembles in many respects a classical kinetic energy density. On the other hand, t_2 shows positive as well as negative values and becomes infinite at the positions of nuclei.

The Kohn-Sham potential can be written in the form:

$$v_{KS} = -\frac{Z_\alpha}{r} + W, \quad (3.6)$$

where

$$W = v_J + v_{xc} - \sum_{\beta \neq \alpha}^{N_\alpha} \frac{Z_\beta}{|\mathbf{r} - \mathbf{R}_\beta|}. \quad (3.7)$$

v_J and v_{xc} are the Coulomb and exchange-correlation potentials, respectively. As I am interested in the cusp relations at the α th nucleus, I expand the orbitals u_i and the potential W around the nucleus α :

$$u_i = \sum_{lm} a_{nlm} R_{nlm}(r) Y_{lm}(\vartheta, \varphi), \quad (3.8)$$

$$W = A + \sum_{lm} w_{lm}(r) Y_{lm}(\vartheta, \varphi), \quad (3.9)$$

A is a constant, the sum of the Coulomb and exchange-correlation potentials taken at the nucleus α , and Y_{lm} are the spherical harmonics. The expansions of radial functions and the potential have the form:

$$R_{nlm}(r) = c_{nlm} r^l + d_{nlm} r^{l+1} + e_{nlm} r^{l+2} + \dots \quad (3.10)$$

and

$$w_{lm}(r) = B_{lm} r + C_{lm} r^2 + \dots \quad (3.11)$$

Let us define $\chi(r)$ as

$$\chi_{nlm}(r) = \frac{R_{nlm}(r)}{r^l}, \quad (3.12)$$

where l is the smallest integer for which $\chi(r)$ is not zero at $r = 0$.

Let us study first the kinetic energy density t_2 (Eq. 3.2) and take the spherical average

$$\bar{t}_2 = -\frac{1}{2} \sum_{nl'm'} \lambda_n R_{nl'm'} \left[\frac{1}{r} \frac{\partial^2}{\partial r^2} (r R_{nl'm'}) - \frac{l'(l'+1)}{r^2} R_{nl'm'} \right]. \quad (3.13)$$

Using Eq.(3.12) I obtain

$$\bar{t}_2 = -\frac{1}{2} \sum_{nl'm'} \lambda_n \chi_{nl'm'} \left[r^{2l'} \chi_{nl'm'}'' + 2(l'+1)r^{2l'-1} \chi_{nl'm'}' \right], \quad (3.14)$$

where χ' denotes the partial derivative of χ with respect to r . Introducing the definition

$$\tau_{2, l} := \frac{\bar{t}_2}{r^{2l-1}}. \quad (3.15)$$

and taking the limit $r \rightarrow 0$ I am led to:

$$\tau_{2, l}(0) = -(l+1) \sum_{nm} \lambda_n \chi_{nlm}(0) \chi_{nlm}'(0). \quad (3.16)$$

Using the cusp-condition [38] $\chi_{nlm}'(0) = -\frac{Z_\alpha}{l+1} \chi_{nlm}(0)$ at the α th nucleus, I arrive at the cusp relation

$$\tau_{2, l}(0) = Z_\alpha \eta_l(0), \quad (3.17)$$

where

$$\eta_l(0) = \sum_{nm} \lambda_n |\chi_{nlm}(0)|^2. \quad (3.18)$$

The first derivative of $\tau_{2, l}$ at the nucleus α is:

$$\tau_{2, l}'(0) = \sum_{nm} \lambda_n |\chi_{nlm}(0)|^2 \left[\varepsilon_n - A - \frac{2Z_\alpha^2}{l+1} \right]. \quad (3.19)$$

Thus, the kinetic energy cusp relation has the form

$$\frac{\tau'_{2,l}(0)}{\tau_{2,l}(0)} = -\frac{A}{Z_\alpha} - \frac{2Z_\alpha}{l+1} + \frac{1}{Z_\alpha\eta_l(0)} \sum_{nm} \lambda_n |\chi_{nlm}(0)|^2 \varepsilon_n. \quad (3.20)$$

Before turning to the kinetic energy density t_1 (Eq.3.1) the cusp relation for the Laplacian of ϱ has to be determined. Using the definition $\tau_{L,0} = \frac{1}{4}r\nabla^2\bar{\varrho}$ if $l=0$ and $\tau_{L,l} = \frac{1}{4}\frac{\nabla^2\bar{\varrho}}{r^{2l-2}}$ if $l \neq 0$ I can immediately arrive at the cusp relations

$$\tau_{L,0}(0) = -Z_\alpha\eta_0(0) = -Z_\alpha\varrho(0), \quad (3.21)$$

$$\tau'_{L,0}(0) = \frac{3}{4}\eta_0''(0) = \frac{3}{4}\varrho''(0), \quad (3.22)$$

$$\frac{\tau'_{L,0}(0)}{\tau_{L,0}(0)} = -\frac{3\eta_0''(0)}{4Z_\alpha\eta_0(0)} = -\frac{3\varrho''(0)}{4Z_\alpha\varrho(0)}, \quad (3.23)$$

and

$$\tau_{L,l}(0) = \frac{1}{2}l(2l+1)\eta_l(0), \quad (3.24)$$

$$\tau'_{L,l}(0) = -(2l+1)Z_\alpha\eta_l(0), \quad (3.25)$$

$$\frac{\tau'_{L,l}(0)}{\tau_{L,l}(0)} = -\frac{2Z_\alpha}{l}. \quad (3.26)$$

Consider now the kinetic energy density t_1 (Eq.(3.1)) and apply Eq.(3.14). If $l=0$ I obtain

$$t_{1,0}(0) = \frac{Z_\alpha^2}{2}\eta_0(0), \quad (3.27)$$

$$t'_{1,0}(0) = -\frac{2Z_\alpha}{3}(A + Z_\alpha^2)\eta_0(0) + \frac{2Z_\alpha}{3} \sum_{nlm} \lambda_{nlm} \chi_{nlm}^2(0) \varepsilon_n, \quad (3.28)$$

$$\frac{t'_{1,0}(0)}{t_{1,0}(0)} = -\frac{4}{3} \left(\frac{A}{Z_\alpha} + Z_\alpha \right) + \frac{4}{3} \frac{1}{Z_\alpha\eta_0(0)} \sum_{nlm} \lambda_{nlm} \chi_{nlm}^2(0) \varepsilon_n. \quad (3.29)$$

If $l \neq 0$ I define

$$\tau_{1,l} = \frac{\bar{t}_1}{r^{2l-2}}. \quad (3.30)$$

In this case

$$\tau_{1,l}(0) = \frac{1}{2}l(2l+1)\eta_l(0), \quad (3.31)$$

$$\tau'_{1,l}(0) = -2lZ_\alpha\eta_l(0), \quad (3.32)$$

$$\frac{\tau'_{1,l}(0)}{\tau_{1,l}(0)} = -\frac{4Z_\alpha}{2l+1}. \quad (3.33)$$

Expressions (3.20),(3.23),(3.26),(3.29) and (3.33) are the main results of this chapter that will be illustrated by simple examples in the next section.

The cusp relations which I derived in this chapter can be used to obtain information on the atomic number. In the same way as the cusps of the density tell us where the nuclei are and what the atomic numbers are, that is, contain information on the Hamiltonian.

It can be concluded that there are several quantities including local ones, such as electron density and kinetic energy density, which contain information on the external potential, in a certain analogy to the first Hohenberg-Kohn theorem. This knowledge is more limited as it is restricted to Coulombic systems only and it is broader as it is valid on excited states as well.

3.2 Illustrative examples

The cusp relations derived above are now illustrated on a couple of simple examples. Consider first the ground state of the hydrogen atom or hydrogenic ions. After elementary calculation I obtain $\tau_{2,1s} = rt_2 = Z\rho(1 - \frac{Z}{2}r)$, that leads to the cusp relation

$$\tau_{2,1s}(0) = Z\rho(0). \quad (3.34)$$

The derivative of $\tau_{2,1s}$ gives

$$\tau'_{2,1s}(0) = -\frac{5}{2}Z^2\rho(0) \quad (3.35)$$

and

$$\frac{\tau'_{2,1s}(0)}{\tau_{2,1s}(0)} = -\frac{5}{2}Z. \quad (3.36)$$

The results (3.34), (3.35) and (3.36) are in complete agreement with Eqs (3.17), (3.19) and (3.20) as $A = 0$ and the last term in Eq.(3.19) reduces to only one term with $\varepsilon_{1s} = -\frac{Z^2}{2}$. For the Laplacian of the density I obtain $\tau_{L,1s} = Z(Zr - 1)\rho$. It leads to the relations $\tau_{L,1s}(0) = -Z\rho(0)$, $\tau'_{L,1s}(0) = 3Z^2\rho(0)$ and $\frac{\tau'_{L,1s}(0)}{\tau_{L,1s}(0)} = -3Z$ in accord with Eqs (3.21), (3.22) and (3.23). The kinetic energy density t_1 takes the form

$$t_{1,1s} = \tau_{1,1s} = \frac{1}{2}Z^2\rho, \quad (3.37)$$

that is proportional with the density. Then

$$\frac{\tau'_{1,1s}(0)}{\tau_{1,1s}(0)} = \frac{t'_{1,1s}(0)}{t_{1,1s}(0)} = -2Z \quad (3.38)$$

in complete agreement with Eq(3.29). Note that this cusp condition is the same as the one that holds for the density (Eq(2.42)) because of Eq(3.37).

The second example is the $2p$ state of hydrogen atom or hydrogenic ions. In this case

$$\eta_{2p}(r) = \frac{\bar{\varrho}_{2p}}{r^{2l}} = ce^{-Zr}, \quad (3.39)$$

where $l = 1$ and $c = Z^3/24$ is a constant.

$$\tau_{2,2p}(0) = \frac{\bar{t}x_{2,2p}}{r} = Z \left(1 - \frac{Z}{8}r\right) \eta_{2p}. \quad (3.40)$$

Then I obtain the expressions $\tau_{2,2p}(0) = Z\eta_{2p}(0)$, $\tau'_{2,2p}(0) = -9Z^2\eta_{2p}(0)/8$ and $\tau'_{2,2p}(0)/\tau_{2,2p}(0) = -9Z/8$ which are in complete agreement with Eqs (3.17), (3.19) and (3.20) as $A = 0$ and the last term in Eq.(3.19) reduces to only one term with $\varepsilon_{2p} = -Z^2/8$. For the Laplacian of the density I obtain $\tau_{L,2p} = (6 - 6Zr + Z^2r^2)\eta_{2p}/4$. It leads to the relations $\tau_{L,2p}(0) = 3\eta_{2p}(0)/2$, $\tau'_{L,2p}(0) = -3Z\eta_{2p}(0)$ and $\tau'_{L,2p}(0)/\tau_{L,2p}(0) = -2Z$ in accord with Eqs (3.24), (3.25) and (3.26). The kinetic energy density t_1 has the form $\tau_{1,2p} = \bar{t}_{1,2p} = \eta_{2p}(3 - Zr + Z^2r^2/4)/2$. Then I immediately obtain that $\tau_{1,2p}(0) = 3\eta_{2p}(0)/2$, $\tau'_{1,2p}(0) = -2Z\eta_{2p}(0)$ and $\tau'_{1,2p}(0)/\tau_{1,2p}(0) = -4Z/3$ in complete accord with Eqs (3.31), (3.32) and (3.33).

The third example is He -like ions with large atomic number. The first-order density matrix was given by Hall et al. [55]:

$$\gamma(r, r') = \frac{\varrho(r')}{2} \left[\frac{\varrho_0(r)}{\varrho_0(r')} \right]^{1/2} + \frac{\varrho(r)}{2} \left[\frac{\varrho_0(r')}{\varrho_0(r)} \right]^{1/2}, \quad (3.41)$$

where $\varrho_0(r) = Z^3e^{-2Zr}/\pi$ is the bare Coulombic density. After some algebra I am led to the relations

$$\tau_1 = \bar{t}_1 = -\frac{Z}{2} \frac{d\bar{\varrho}}{dr} - \frac{Z^2}{2} \bar{\varrho}, \quad (3.42)$$

$$\tau_1(0) = \frac{Z^2}{2} \varrho(0), \quad (3.43)$$

$$\tau'_1(0) = -\frac{2Z^3}{3} \left(1 + \frac{A - \varepsilon_{1s}}{Z^2}\right) \varrho(0). \quad (3.44)$$

These are in complete agreement with Eqs (3.27), (3.28) and (3.29). For $\tau_{L,0} = \frac{1}{4}r\nabla^2\bar{\varrho}$ the relations (3.21), (3.22) and (3.23) should hold. Then for $\tau_2 = r\bar{t}_2 = r\bar{t}_1 - \tau_{L,0}$ I obtain $\tau_2(0) = Z\varrho(0)$, $\tau'_2(0) = -(2Z^2 - \varepsilon_{1s} + A)\varrho(0)$ and $\tau'_2(0)/\tau_2(0) = (A - \varepsilon_{1s})/Z - 2Z$ in accordance with Eqs (3.17), (3.19) and (3.20).

In summary, I have derived cusp relations for the kinetic energy relations. These are valid for ground and excited states, even highly excited states. The two most frequently used kinetic energy density expressions imply different behaviour at the nuclei.

Chapter 4

Kinetic and exchange energy related non-locally

It is of considerable interest for density functional theory (DFT) to relate the single-particle kinetic energy density to the exchange energy counterpart in the ground state of atoms and molecules. The exchange energy density has been usefully approximated by adding a term involving density gradients to a local density approximation but orbital-free kinetic energy density theory is presently of much poorer quality.

Therefore, in the present chapter I have worked out from Hartree-Fock theory for finite closed shell molecules and clusters an expression for the kinetic energy density in terms of a non-local exchange energy kernel introduced in the early work of March and Santamaria [56, 57]. An illustration of this relation between kinetic and exchange contributions is then presented for two-level systems such as the *Be* atom or *LiH*.

Though the earliest form of DFT proposed by Thomas [1], Fermi [3] and Dirac [58], now known as the local density approximation (LDA) to current DFT, yielded explicit functionals for kinetic energy density $t[\varrho]$ and exchange energy density $\epsilon_x[\varrho]$, namely

$$t^{TFD}[\varrho] = c_k \{\varrho(\mathbf{r})\}^{5/3} : c_k = \frac{6\pi^2}{5} \left(\frac{3}{8\pi} \right)^{2/3} \quad (4.1)$$

and

$$\epsilon_x^{TFD}[\varrho] = -c_x \{\varrho(\mathbf{r})\}^{4/3} : c_x = \frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3}, \quad (4.2)$$

it is the latter that has proved much more useful for recent quantitative versions of DFT, when corrected for density gradients [59, 60]. Therefore, in the Kohn-Sham procedure [5] the single-particle kinetic energy problem is bypassed by returning, as in Hartree self-consistent field theory but without self-interaction correction, to

one-electron Schrödinger equations. Nevertheless, a number of workers in DFT continue to study orbital-free approximations to the single-particle kinetic energy. The present chapter is a contribution in this latter area, and directly connects the exchange and kinetic contributions. However, to do so explicitly, I shall appeal to restricted Hartree-Fock (HF) theory for closed shell systems. This theory is attractive as a result of Möller and Plesset confirms the high quality of its ground-state-electron density $\varrho(\mathbf{r})$, the central tool of DFT.

4.1 Non-local generalizations of kinetic and exchange energy densities

In HF theory, the natural starting point for the direct calculation of kinetic energy density, $t(\mathbf{r})$ say, is the idempotent Dirac density matrix $\gamma(\mathbf{r}, \mathbf{r}')$ defined by

$$\gamma(\mathbf{r}, \mathbf{r}') = \sum_{\text{occupied } i} \Psi_i(\mathbf{r}) \Psi_i^*(\mathbf{r}') \quad (4.3)$$

where $\Psi_i(\mathbf{r})$ denotes the i th HF orbital. Defining the quantity $F(\mathbf{r}, \mathbf{r}')$ by

$$F(\mathbf{r}, \mathbf{r}') = \gamma(\mathbf{r}, \mathbf{r}')^2, \quad (4.4)$$

Dawson and March [61] pointed out that the kinetic energy density $t(\mathbf{r})$ can be written as

$$t(\mathbf{r}) \sim \frac{1}{8} \int \frac{(\nabla_{\mathbf{r}} F(\mathbf{r}, \mathbf{r}'))^2}{F(\mathbf{r}, \mathbf{r}')} d\mathbf{r}', \quad (4.5)$$

which is somewhat reminiscent of the 'inhomogeneity' kinetic energy density proposed by von Weizsäcker [62], namely

$$t_w(\mathbf{r}) = \frac{1}{8} \frac{(\nabla_{\mathbf{r}} \varrho(\mathbf{r}))^2}{\varrho(\mathbf{r})}, \quad (4.6)$$

to which quantity I refer again later in Eq.(4.22) below.

Having written $t(\mathbf{r})$ in terms of $F(\mathbf{r}, \mathbf{r}') = \gamma^2(\mathbf{r}, \mathbf{r}')$ in Eq.(4.5), let us similarly express the exchange energy density $\epsilon_x(\mathbf{r})$ in HF theory. To do so, the Dirac [58] total exchange energy E_x in terms of $\gamma(\mathbf{r}, \mathbf{r}')$ is the natural starting point, namely

$$E_x = -\frac{1}{4} \int \frac{\gamma(\mathbf{r}, \mathbf{r}')^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'. \quad (4.7)$$

Though it is not unique, the definition of the exchange energy density $\epsilon_x(\mathbf{r})$ which I adopt in the following, naturally enough, from Eq.(4.7) as

$$E_x = \int \epsilon_x(\mathbf{r}) d\mathbf{r} \quad (4.8)$$

where

$$\begin{aligned}
\epsilon_x(\mathbf{r}) &= -\frac{1}{4} \int \frac{\gamma(\mathbf{r}, \mathbf{r}')^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \\
&= -\frac{1}{4} \int \frac{F(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' ,
\end{aligned} \tag{4.9}$$

the latter step utilizing the definition (4.4).

March and Santamaria [56, 57] proposed to define non-local kinetic and exchange energy kernels which they denoted respectively by $K(\mathbf{r}, \mathbf{r}')$ and $X(\mathbf{r}, \mathbf{r}')$ such that

$$\tau(\mathbf{r}) = \int K(\mathbf{r}, \mathbf{r}') d\mathbf{r}' , \tag{4.10}$$

where $\tau(\mathbf{r})$ differs from $t(\mathbf{r})$ by an N -dependent-constant only and

$$\epsilon_x(\mathbf{r}) = \int X(\mathbf{r}, \mathbf{r}') d\mathbf{r}' . \tag{4.11}$$

Then the simplest explicit forms for $K(\mathbf{r}, \mathbf{r}')$ and $X(\mathbf{r}, \mathbf{r}')$, which I adopt as definitions below, follow respectively from Eqs(4.5) and (4.9) as

$$K(\mathbf{r}, \mathbf{r}') = \frac{1}{8} \frac{(\nabla_{\mathbf{r}} F(\mathbf{r}, \mathbf{r}'))^2}{F(\mathbf{r}, \mathbf{r}')} \tag{4.12}$$

and

$$X(\mathbf{r}, \mathbf{r}') = -\frac{1}{4} \frac{F(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} . \tag{4.13}$$

Given Eqs(4.12) and (4.13), it is a straightforward matter by using

$$F(\mathbf{r}, \mathbf{r}') = -4X(\mathbf{r}, \mathbf{r}')|\mathbf{r} - \mathbf{r}'| \tag{4.14}$$

in Eq.(4.12), to write the kinetic energy non-local kernel $K(\mathbf{r}, \mathbf{r}')$ solely in terms of its exchange energy counterpart $X(\mathbf{r}, \mathbf{r}')$. Then after some straightforward manipulation, I obtain,

$$K(\mathbf{r}, \mathbf{r}') = -\frac{1}{2} |\mathbf{r} - \mathbf{r}'| \frac{(\nabla_{\mathbf{r}} X)^2}{X} - \nabla_{\mathbf{r}} X \cdot \nabla_{\mathbf{r}} |\mathbf{r} - \mathbf{r}'| - \frac{X}{2|\mathbf{r} - \mathbf{r}'|} (\nabla_{\mathbf{r}} |\mathbf{r} - \mathbf{r}'|)^2 . \tag{4.15}$$

Integrating Eq.(4.15) with respect to $\mathbf{r}'$ we find the HF (normalized) kinetic energy density $\tau(\mathbf{r})$ in terms of the non-local exchange kernel $X(\mathbf{r}, \mathbf{r}')$ as

$$\begin{aligned}
\tau(\mathbf{r}) &= \int K(\mathbf{r}, \mathbf{r}') d\mathbf{r}' = -\frac{1}{2} \int |\mathbf{r} - \mathbf{r}'| \frac{(\nabla_{\mathbf{r}} X(\mathbf{r}, \mathbf{r}'))^2}{X(\mathbf{r}, \mathbf{r}')} d\mathbf{r}' \\
&\quad - \int \nabla_{\mathbf{r}} X(\mathbf{r}, \mathbf{r}') \cdot \nabla_{\mathbf{r}} |\mathbf{r} - \mathbf{r}'| d\mathbf{r}' - \frac{1}{2} \int \frac{(\nabla_{\mathbf{r}} |\mathbf{r} - \mathbf{r}'|)^2}{|\mathbf{r} - \mathbf{r}'|} X(\mathbf{r}, \mathbf{r}') d\mathbf{r}' .
\end{aligned} \tag{4.16}$$

In the last subsection 4.3 of this chapter, I will show that the idempotency of the Dirac density matrix $\gamma(\mathbf{r}, \mathbf{r}')$ can be utilized to rewrite the second term appearing in Eq.(4.16), a Laplacian term $\nabla_{\mathbf{r}}^2 \varrho(\mathbf{r})$ then being introduced into the kinetic energy density.

In subsection 4.2 below I apply Eq.(4.16), valid for an arbitrary number of doubly filled spin-compensated levels in HF theory, to a two-level system such as the Be atom or the diatomic molecule *LiH*.

4.2 Calculation of kinetic energy density for a two-level system

To illustrate the utility of Eq.(4.16), let us calculate $t(r)$ for the Be atom. Then, using the *1s* and *2s* wave functions in terms of the density amplitude $\varrho^{1/2}(r)$ and the phase $\Theta(r)$ we have [61]

$$\Psi_{1s} = \left(\frac{\varrho}{2}\right)^{1/2} \cos\Theta \quad (4.17)$$

and

$$\Psi_{2s} = \left(\frac{\varrho}{2}\right)^{1/2} \sin\Theta . \quad (4.18)$$

Evidently the Dirac density matrix is given by substituting these wave functions into Eq.(4.3), when I obtain the known result

$$\gamma(r, r') = \varrho^{1/2}(r)\varrho^{1/2}(r')\cos(\Theta(r) - \Theta(r')) . \quad (4.19)$$

or from Eq.(4.4):

$$F(r, r') = \varrho(r)\varrho(r')\cos^2(\Theta(r) - \Theta(r')) . \quad (4.20)$$

Substituting therefore Eq.(4.20) into Eq.(4.13), I find the non-local exchange kernel to be

$$X(\mathbf{r}, \mathbf{r}') = -\frac{1}{4} \frac{\varrho(r)\varrho(r')\cos^2(\Theta(r) - \Theta(r'))}{|\mathbf{r} - \mathbf{r}'|} . \quad (4.21)$$

Inserting Eq.(4.21) into Eq.(4.16) I must find the result already in the literature that the total kinetic energy T is given by

$$T = \frac{1}{8} \int \frac{(\nabla\varrho)^2}{\varrho} d\mathbf{r} + \frac{1}{2} \int \varrho(\nabla\Theta)^2 d\mathbf{r} . \quad (4.22)$$

Though the most direct way still of reaching Eq.(4.22) is from $\frac{1}{2} \frac{\partial^2}{\partial \mathbf{r}' \partial \mathbf{r}} \gamma(\mathbf{r}, \mathbf{r}') \Big|_{\mathbf{r}'=\mathbf{r}}$ using Eq.(4.19), from Eq.(4.16) and after allowing for the N -dependent normalization constant relating $\tau(\mathbf{r})$ and $t(\mathbf{r})$ plus idempotency and the pendulum equation [61], the two-level result (4.22) must emerge.

4.3 Further relations resulting from idempotency of Hartree-Fock Dirac density matrix

Already, in reaching Eqs(4.5) and (4.16), Dawson and March [61] had employed the idempotency of the Dirac density matrix defined in Eq.(4.3). For doubly occupied levels considered throughout this article, this idempotency condition reads

$$\int \frac{\gamma(\mathbf{r}, \mathbf{r}'')}{2} \frac{\gamma(\mathbf{r}'', \mathbf{r}')}{2} d\mathbf{r}'' = \frac{\gamma(\mathbf{r}, \mathbf{r}')}{2} . \quad (4.23)$$

Putting $\mathbf{r}' = \mathbf{r}$, and using the definition (4.4) readily yields

$$\int F(\mathbf{r}, \mathbf{r}') d\mathbf{r}' = 2\varrho(\mathbf{r}) . \quad (4.24)$$

Inserting Eq.(4.14) into Eq.(4.24), I find

$$\int |\mathbf{r} - \mathbf{r}'| X(\mathbf{r}, \mathbf{r}') d\mathbf{r}' = -2\varrho(\mathbf{r}) . \quad (4.25)$$

Taking the gradient with respect to $\mathbf{r}$ of Eq.(4.25) yields

$$\int \nabla_{\mathbf{r}} |\mathbf{r} - \mathbf{r}'| X(\mathbf{r}, \mathbf{r}') d\mathbf{r}' + \int |\mathbf{r} - \mathbf{r}'| \nabla_{\mathbf{r}} X(\mathbf{r}, \mathbf{r}') d\mathbf{r}' = -2\nabla_{\mathbf{r}} \varrho(\mathbf{r}) . \quad (4.26)$$

A further gradient operation on Eq.(4.26) then leads to the result

$$\begin{aligned} & \int \nabla_{\mathbf{r}}^2 |\mathbf{r} - \mathbf{r}'| X(\mathbf{r}, \mathbf{r}') d\mathbf{r}' + 2 \int \nabla_{\mathbf{r}} |\mathbf{r} - \mathbf{r}'| \cdot \nabla_{\mathbf{r}} X(\mathbf{r}, \mathbf{r}') d\mathbf{r}' \\ & + \int |\mathbf{r} - \mathbf{r}'| \nabla_{\mathbf{r}}^2 X(\mathbf{r}, \mathbf{r}') d\mathbf{r}' = -2\nabla_{\mathbf{r}}^2 \varrho(\mathbf{r}) . \end{aligned} \quad (4.27)$$

This identity (4.27) can be used to remove the scalar product term $\nabla_{\mathbf{r}} X \cdot \nabla_{\mathbf{r}} |\mathbf{r} - \mathbf{r}'|$ from Eq.(4.16), which may be helpful in subsequent practical applications.

Eq.(4.16), when combined with Eq.(4.11), sums up the main achievement of this chapter. The kinetic energy density $\tau(\mathbf{r})$ in Eq.(4.16) is determined solely by the exchange energy kernel $X(\mathbf{r}, \mathbf{r}')$, which in turn is related to the exchange energy density $\epsilon_x(\mathbf{r})$ by Eq.(4.11). The relation between $t(\mathbf{r})$ and the exchange kernel $X(\mathbf{r}, \mathbf{r}')$ is fundamentally non-local, in contrast to that in the Thomas-Fermi-Dirac statistical theory valid for large numbers of electrons N , the essential functional content of which has been displayed in Eqs(4.1) and (4.2). Naturally, one can rewrite Eqs(4.1) and (4.2) through the elementary local relation between kinetic energy density $t(\mathbf{r})$ and its exchange counterpart $\epsilon_x(\mathbf{r})$ as

$$t^{TFD}(\mathbf{r}) = const. \{ |\epsilon_x^{TFD}(\mathbf{r})| \}^{5/4} . \quad (4.28)$$

This relation (4.28) is valid only in LDA and must be replaced in HF theory by Eq.(4.16). This must then lead to the correct two-level result (4.22), but I reiterate

that the relation (4.16) between $\tau(\mathbf{r})$ and the non-local exchange kernel $X(\mathbf{r}, \mathbf{r}')$ is valid for an arbitrary number of spin-compensated occupied levels.

Chapter 5

Exact energy expression in the strong-interaction limit of the density functional theory

There have been numerous studies concerning the coupling-constant dependence of the exchange-correlation functional. The success of the so-called hybrid schemes [67] was explained on the grounds of the coupling-constant dependence of the exchange-correlation energy. The adiabatic connection [19], [20]-[23] provides the link between the real interacting and the fictitious non-interacting systems. The key quantities, such as the exchange-correlation energy are defined through adiabatic connection. It has recently been shown [24]-[27] that adiabatic connection has an important role in studying strongly interacting systems within the density functional theory.

To find improved approximations is the aim of much current research. To test new functionals one needs highly accurate density, exchange-correlation energy density or pair-correlation function. These can be obtained from accurate many-body calculations, such as configuration interaction (CI) or quantum Monte Carlo (QMC) methods. There is another way of testing the quality of new functionals: to find out how accurately the trial functionals satisfy exact relations. So exact expressions have even practical importance. They provide a tool of improving functionals. The aim of this paper is to derive such an exact relation.

This chapter is organized as follows: In the following subsection adiabatic connection is summarized. Then the coupling constant dependent approximations for the exchange-correlation energy are reviewed. A subsection is devoted to the derivation of higher-order cusp relations for the wave function and the electron density for arbitrary coupling constant. In the last subsection the main result of

this chapter: a total energy expression in the strong-interaction limit is presented.

5.1 Adiabatic connection

Consider a system of N interacting electrons in a local external potential $v(\mathbf{r})$. The Hamiltonian has the form

$$\hat{H}^\lambda = \hat{T} + \hat{V}_{ee} + V, \quad (5.1)$$

where

$$\hat{T} = \sum_{i=1}^N \left(-\frac{1}{2} \nabla_i^2 \right) \quad (5.2)$$

and

$$\hat{V}_{ee} = \sum_{i < j}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \quad (5.3)$$

are the kinetic energy and the electron-electron energy operators and

$$V = \sum_{i=1}^N v(\mathbf{r}_i). \quad (5.4)$$

Then a coupling constant λ is introduced into the Hamiltonian with the definition

$$\hat{H}^\lambda = \hat{T} + \lambda \hat{V}_{ee} + V^\lambda. \quad (5.5)$$

$$V^\lambda = \sum_{i=1}^N v^\lambda(\mathbf{r}_i) \quad (5.6)$$

is defined by the condition that the density ϱ is fixed along the adiabatic path. $\lambda = 1$ corresponds to the real interacting system, $\lambda = 0$ gives the non-interacting Kohn-Sham system. In this case the Schrödinger equation is

$$\left(\hat{T} + V^{\lambda=0} \right) \Psi^{\lambda=0} = E^{\lambda=0} \Psi^{\lambda=0}, \quad (5.7)$$

where the Kohn-Sham potential $V^{\lambda=0} = \sum_{i=1}^N v_{KS}(\mathbf{r}_i)$ is defined by the condition that the density of the non-interacting and the interacting systems are the same. For a non-degenerate system Eq. (5.7) takes the well-known form:

$$\left(-\frac{1}{2} \nabla^2 + v_{KS} \right) \phi_i = \varepsilon_i \phi_i \quad (5.8)$$

and the density is expressed with the occupied one-electron orbitals ϕ_i as

$$\varrho = \sum_i |\phi_i|^2. \quad (5.9)$$

It has been shown [19, 23] that the exchange-correlation energy can be given as an integral with respect to the coupling constant

$$E_{xc}[\varrho_{\uparrow}, \varrho_{\downarrow}] = \int_0^1 d\lambda W^{\lambda}[\varrho_{\uparrow}, \varrho_{\downarrow}], \quad (5.10)$$

where

$$W^{\lambda}[\varrho_{\uparrow}, \varrho_{\downarrow}] = \langle \Psi^{\lambda} | \hat{V}_{ee} | \Psi^{\lambda} \rangle - J. \quad (5.11)$$

$$J = \frac{1}{2} \int \frac{\varrho(\mathbf{r})\varrho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' \quad (5.12)$$

is the classical Coulomb energy. The density of electrons with spin σ is defined as

$$\varrho_{\sigma}(\mathbf{r}) = N \int |\Psi^{\lambda}(\mathbf{r}\sigma, x_2, \dots, x_N)|^2 dx_2 \dots dx_N. \quad (5.13)$$

The variable x stands for both the spatial $\mathbf{r}$ and spin σ variables. W^{λ} can also be expressed with the pair density

$$\Gamma^{\lambda}(\mathbf{r}, \mathbf{r}') = \frac{1}{2} N(N-1) \int |\Psi^{\lambda}(\mathbf{r}\sigma_1, \mathbf{r}'\sigma_2, x_3, \dots, x_N)|^2 dx_3 \dots dx_N d\sigma_1 d\sigma_2 \quad (5.14)$$

as

$$W^{\lambda}[\varrho_{\uparrow}, \varrho_{\downarrow}] = \int \frac{\Gamma^{\lambda}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' - J. \quad (5.15)$$

The pair density can be written in the form

$$\Gamma^{\lambda}(\mathbf{r}, \mathbf{r}') = \frac{1}{2} \varrho(\mathbf{r}) [\varrho(\mathbf{r}') + \varrho_{xc}^{\lambda}(\mathbf{r}, \mathbf{r}')]. \quad (5.16)$$

Applying Eq. (5.10) the exchange-correlation energy reads as

$$E_{xc}[\varrho_{\uparrow}, \varrho_{\downarrow}] = \frac{1}{2} \int_0^1 d\lambda \int \frac{\varrho(\mathbf{r})\varrho_{xc}^{\lambda}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' \quad (5.17)$$

$\varrho_{xc}^{\lambda}(\mathbf{r}, \mathbf{r}')$ is the density at $\mathbf{r}'$ of the exchange-correlation hole around an electron at $\mathbf{r}$ for coupling strength λ . It can be easily shown that the charge of the exchange-correlation hole is -1:

$$\int \varrho_{xc}^{\lambda}(\mathbf{r}, \mathbf{r}') d\mathbf{r}' = -1. \quad (5.18)$$

The weak interaction limit is $\lambda \rightarrow 0$. For a given shape of the density the weak interaction limit can also be performed at $\lambda = 1$ by uniform density scaling to the high-density limit [68]

$$\varrho(\mathbf{r}) \rightarrow \gamma^3 \varrho(\gamma \mathbf{r}) \text{ and } \gamma \rightarrow \infty. \quad (5.19)$$

In this limit the Kohn-Sham theory is exactly the exchange-only theory and the pair density Γ can be given by a Hartree-Fock like expression

$$\Gamma^\lambda(\mathbf{r}, \mathbf{r}) = \varrho^2(\mathbf{r}) - \varrho_\uparrow^2(\mathbf{r}) - \varrho_\downarrow^2(\mathbf{r}). \quad (5.20)$$

For the fully polarized density, i.e. $\varrho_\uparrow = \varrho$ and $\varrho_\downarrow = 0$ we obtain $\Gamma^\lambda(\mathbf{r}, \mathbf{r}) = 0$, while for the fully unpolarized case, that is for $\varrho_\uparrow = \varrho_\downarrow = \varrho/2$ we arrive at $\Gamma^\lambda(\mathbf{r}, \mathbf{r}) = \varrho^2(\mathbf{r})/2$.

In the weakly correlated case, from the competition between the kinetic energy and the Coulomb repulsion, the kinetic energy dominates. The wave function tends to that of the non-interacting system, which minimizes the kinetic energy for a given density.

Originally the adiabatic connection was defined between $\lambda = 0$ and $\lambda = 1$. However, it is possible to extend the value of λ outside the range of the coupling constant integration of Eq. (5.10). Then the strong-interaction limit is $\lambda \rightarrow \infty$. The density functional measure of the correlation strength of the true wave function ($\lambda = 1$) is defined as $(W_0 - W_1)/(W_0 - W_\infty)$. For independent electrons it is 0, for strictly correlated electrons it gives 1. (Other measures can also be used [69]).

The strong-interaction limit can also be performed in another way: with the low density limit for $\lambda = 1$

$$\varrho(\mathbf{r}) \rightarrow \gamma^3 \varrho(\gamma \mathbf{r}) \text{ and } \gamma \rightarrow 0. \quad (5.21)$$

In this limit the pair-density function at $\mathbf{r} = \mathbf{r}'$, called on-top pair-density, goes to zero:

$$\Gamma^\lambda(\mathbf{r}, \mathbf{r}) \rightarrow 0 \text{ for } \lambda \rightarrow \infty. \quad (5.22)$$

It has been shown [69, 70] that the integral of Γ^λ for any volume fragment Ω of the system

$$\int_\Omega \Gamma^\lambda(\mathbf{r}, \mathbf{r}) d\mathbf{r} d\mathbf{r}' = \langle \hat{N}_\Omega^2 \rangle - \langle \hat{N}_\Omega \rangle^2 \quad (5.23)$$

is the mean square fluctuation of electron number in the volume Ω .

$$\hat{N}_\Omega = \int_\Omega \hat{\varrho} d\mathbf{r} = \int d\mathbf{r} \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i) \quad (5.24)$$

is the particle number operator for the volume Ω . Strong correlation means a strong suppression of electron number fluctuations. When the system is strongly correlated the Coulomb repulsion dominates. The wave function is close to the one which minimizes the Coulomb repulsion for a given density. In this case there is a deep exchange-correlation hole around the electron and the electron number fluctuations are suppressed.

Examples in model or real systems for strong correlations: A uniform electron gas with density $\varrho(\mathbf{r}) = \varrho = \frac{3}{4\pi r_s^3}$ becomes strongly correlated in the low density

limit $r_s \rightarrow \infty$. The electrons avoid one another as much as they can and form a Wigner lattice. H atoms on a lattice are strongly correlated at large lattice constant. In some materials containing transition-metal or rear-earth ions with partially filled narrow d or f Kohn-Sham bands, the d or f electrons localize and the fluctuations of electron numbers are suppressed to minimize the Coulomb repulsion.

It is known that LSD [5, 7] and GGA [12, 60], [71]-[73] cannot describe strongly correlated electrons with realistic densities, because of self-correlation error. Consequently, these methods cannot give a proper description of the Wigner crystallization of the low-density uniform electron gas. Inclusion of self-interaction correction to LSD or LSD+U method [74]-[76] leads to a more reliable description. There is a hope that the recently developed self-interaction free meta-GGA [77]-[84] and hyper-GGA [85, 86] will be able to describe strongly correlated systems reliably.

5.2 Coupling constant dependent approximations for the exchange-correlation energy

In this subsection a summary of the coupling constant dependent approximations is presented. The λ dependence of W and E_c has been studied by several authors [87]-[94]. Knowledge of exact properties of these functionals contributes to find improved approximations (see e.g. [89, 90, 94]). Several exact expressions have already been derived. The key properties for W have the form [68, 95, 96]

$$W_\lambda[\varrho] = \lambda W_1[\varrho_{1/\lambda}], \quad (5.25)$$

$$\varrho_\lambda(\mathbf{r}) = \lambda^3 \varrho(\lambda \mathbf{r}), \quad (5.26)$$

$$W'_\lambda[\varrho] \equiv \frac{dW_\lambda[\varrho]}{d\lambda} < 0 \quad (\lambda \geq 0), \quad (5.27)$$

$$W_0[\varrho] = E_x[\varrho], \quad (5.28)$$

$$W'_0[\varrho] = 2E_c^{GL2}[\varrho], \quad (5.29)$$

$$W_\infty[\varrho] = \lim_{\lambda \rightarrow \infty} W_\lambda[\varrho] \text{ (finite)}. \quad (5.30)$$

E_x is the exchange energy, while E_c^{GL2} denotes the second-order coefficients in the Görling-Levy perturbation theory [95], where the correlation energy is expanded in a series

$$E_{xc}[\varrho] = E_x[\varrho] + \sum_{n=2}^{\infty} E_c^{GLn}[\varrho]. \quad (5.31)$$

It has been shown [25, 27] that

$$W_\lambda[\varrho] \rightarrow W_0[\varrho] + W'_0[\varrho]\lambda \quad (\lambda \rightarrow 0) \quad (5.32)$$

in the weak interaction limit and

$$W_\lambda[\varrho] \rightarrow W_\infty[\varrho] + W'_\infty[\varrho]\lambda^{-1/2} \quad (\lambda \rightarrow \infty) \quad (5.33)$$

in the strong interaction limit.

As $\lambda \rightarrow \infty$ the electrons become strongly correlated. The concept of “strictly correlated electrons” (SCE) [25, 26, 69] has been worked out for them. This model can be solved exactly for one-dimensional systems and three-dimensional two-electron systems with spherically symmetric density $\varrho(r)$. In the latter case the two electrons can be found on opposite sides of the spherical center [25, 26]. The radial distance r_1 of one of the electrons strictly determines that of the other electron, $r_2 = f(r_1)$. The “correlation” function $f(r)$ is uniquely determined by the density $\varrho(r)$. It is interesting to note that the differential equation satisfied by f ,

$$\frac{df(r)}{dr} = -\frac{r^2 \varrho(r)}{f(r)^2 \varrho(f(r))}, \quad (5.34)$$

closely resembles the expression of a local scaling transformation [97]. It has been shown that for a two-electron system

$$W_\infty^{SCE}[\varrho] = 2\pi \int_0^\infty dr \frac{r^2 \varrho(r)}{r + f(r)} - J[\varrho]. \quad (5.35)$$

The generalization for systems having more than two electrons is difficult. Based on the expressions (5.25) - (5.30) a simple interpolation was proposed [25]

$$W_\lambda^{appr} = W_\infty + \frac{W_0 - W_\lambda}{\sqrt{1 + 2X\lambda}}, \quad (5.36)$$

where

$$X = \frac{W'_0}{W_\infty - W_0}. \quad (5.37)$$

Integration of Eq. (5.36) leads to the correlation energy

$$E_c^{appr} = (W_0 - W_\infty) \left[\frac{1}{X} \left(\sqrt{1 + 2X} - 1 \right) - 1 \right]. \quad (5.38)$$

This model functional predicts accurate ground-state correlation energies for real atoms and the two-dimensional uniform electron gas [25].

Though there is no exact expression for the strong interaction or the low density limit, it is supposed that the SCE energy should be close to that of a bcc Wigner crystal [98]-[100]

$$E_{xc}^W = -\frac{0.89593}{r_s} + \frac{1.325}{r_s^{3/2}} + \dots. \quad (5.39)$$

The uniform electron gas expression for $(r_s \rightarrow \infty)$ has the form

$$E_{xc} = -\frac{0.90000}{r_s} + \frac{1.500}{r_s^{3/2}} + \dots. \quad (5.40)$$

The closeness of the energy expressions for the Wigner crystal and the uniform electron gas for $r_s \rightarrow \infty$ was observed long ago [11, 101].

Another model is the point-charge-plus-continuum (PC) model. This is an approximation to the SCE concept and provides simple explicit functionals $W_\infty^{PC}[\varrho]$ and $W_\infty'^{PC}[\varrho]$ for the coefficients in Eqs. (5.33). The interaction strength interpolation (ISI) [27] gives the following model expression:

$$W_\lambda^{ISI} = W_{\infty, ISI} + \frac{X}{\sqrt{1 + \lambda Y} + Z} , \quad (5.41)$$

where

$$X = \frac{xy^2}{z^2} , \quad Y = \frac{x^2y^2}{z^4} , \quad Z = \frac{xy^2}{z^3} - 1 , \quad (5.42)$$

$$x = -2W'_0 , \quad y = W'_\infty , \quad z = W_0 - W_\infty . \quad (5.43)$$

The analytical integration in Eq. (5.10) leads to

$$E_{xc}^{ISI}[\varrho] = W_\infty + \frac{2X}{Y} \left[(1 + Y)^{1/2} - 1 - Z \ln \left(\frac{(1 + Y)^{1/2} + Z}{1 + Z} \right) \right] . \quad (5.44)$$

A combination of the ISI model with the “point-charge-plus-continuum “ (PC) model [25, 27] leads to a new correlation functional. The PC approximations have the form

$$W_\infty^{PC} = \int d\mathbf{r} \left[A\varrho(\mathbf{r})^{4/3} + B \frac{|\nabla\varrho(\mathbf{r})|^2}{\varrho(\mathbf{r})^{4/3}} \right] \quad (5.45)$$

and

$$W_\infty'^{PC} = \int d\mathbf{r} \left[C\varrho(\mathbf{r})^{3/2} + D \frac{|\nabla\varrho(\mathbf{r})|^2}{\varrho(\mathbf{r})^{7/6}} \right] . \quad (5.46)$$

A , B , C and D are constants. Functionals of the form (5.45) and (5.46) can be considered exact for the uniform electron gas. The atomization energies calculated in the ISI model [27] are remarkably accurate: the error is 2.8% of the mean experimental atomization energies.

5.3 Higher-order cusp relations for the wave function and the electron density for arbitrary coupling constant

The aim of this subsection is to derive a new exact relation. To achieve this goal first Kato’s theorem [13, 33, 34, 63] is generalized for arbitrary value of λ . The original theorem states that for an eigenfunction Ψ of the Hamiltonian H for an N -electron system

$$\left. \frac{\partial \bar{\Psi}}{\partial r} \right|_{r=R_\alpha} = -Z_\alpha \Psi|_{r=R_\alpha} , \quad (5.47)$$

where the partial derivatives are taken at the nuclei α and $\bar{\Psi}$ is the average value of Ψ taken over the sphere $r = \text{constant}$ around the nucleus α , for fixed values of the remaining electron coordinates. Steiner [33] derived the corresponding theorem for the electron density

$$Z_\alpha = -\frac{1}{2\rho(r)} \left. \frac{\partial \rho(r)}{\partial r} \right|_{r=R_\alpha} . \quad (5.48)$$

The cusp condition for wave functions were generalized by Roothaan and Kelly [102] and Pack and Brown [38]. Further references can be found in [16]-[18],[51, 52]. Recently this theorem has been generalized for highly excited states for $\lambda = 0$ and $\lambda = 1$ [18]. Now an extension for any value of λ follows.

The total Hamiltonian (5.1) can be written as a sum

$$\hat{H}^\lambda = \hat{H}_1 + \hat{F}^\lambda + \hat{G}^\lambda, \quad (5.49)$$

where

$$\hat{H}_1 = -\frac{1}{2}\nabla_1^2 - \frac{Z_\alpha}{r_1}, \quad (5.50)$$

$$\hat{F}^\lambda = -\sum_{\beta \neq \alpha}^M \frac{Z_\beta}{|\mathbf{r}_1 - \mathbf{R}_\beta|} + \tilde{v}^\lambda(\mathbf{r}_1) + \lambda \sum_{j=2}^N \frac{1}{|\mathbf{r}_1 - \mathbf{r}_j|} \quad (5.51)$$

and

$$\hat{G}^\lambda = -\sum_{i=2}^N \left(\sum_{\beta \neq \alpha}^M \frac{Z_\beta}{|\mathbf{r}_i - \mathbf{R}_\beta|} + \tilde{v}^\lambda(\mathbf{r}_i) \right) + \lambda \sum_{i=2}^N \sum_{j \neq i}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \quad (5.52)$$

$$-\frac{1}{2} \sum_{i=2}^N \nabla_i^2 - \sum_{j \neq 1}^N \frac{Z_\alpha}{r_j}. \quad (5.53)$$

The external potential V^λ which is defined to ensure the density being fixed is written as a sum of the true external potential and the remaining term $\tilde{V}^\lambda = \sum_{i=1}^N \tilde{v}^\lambda(\mathbf{r}_i)$:

$$V^\lambda = \sum_{\beta=1}^M \frac{Z_\beta}{|\mathbf{r}_i - \mathbf{R}_\beta|} + \tilde{V}^\lambda. \quad (5.54)$$

In the following the origin of the coordinate system is placed at the nucleus α . To study the wave function in the vicinity of the nucleus α consider the case where $|\mathbf{r}_1| = r_1$ is small. Taking into account the expansions

$$\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} = \sum_{l,m} \frac{4\pi}{2l+1} \frac{r_1^l}{r_2^{l+1}} Y_{lm}^*(\Omega_1) Y_{lm}(\Omega_2) \quad (5.55)$$

and

$$\tilde{v}^\lambda = \sum_{l,m} r_1^l \tilde{v}_{lm}^\lambda Y_{lm}^*(\Omega_1), \quad (5.56)$$

F^λ has the form

$$F^\lambda = \sum_{l,m} r_1^l F_{lm}^\lambda Y_{lm}^*(\Omega_1) , \quad (5.57)$$

where F_{lm}^λ depend on $\mathbf{r}_2, \dots, \mathbf{r}_N$ but do not depend on $\mathbf{r}_1$

$$F_{lm}^\lambda = -\frac{4\pi}{2l+1} \left[\sum_{\beta \neq \alpha}^M Z_\beta \frac{Y_{lm}(\Omega_\beta)}{R_\beta^{l+1}} - \lambda \sum_{j>1}^N \frac{Y_{lm}(\Omega_j)}{r_j^{l+1}} \right] + \tilde{v}_{lm}^\lambda . \quad (5.58)$$

Y_{lm} are the spherical harmonics. The operator G^λ acts only on $\mathbf{r}_2, \dots, \mathbf{r}_N$.

The antisymmetric wave function Ψ^λ is expanded around the nucleus α

$$\Psi^\lambda = \sum_{l,m} r_1^l \chi_{lm}^\lambda(r_1, X) Y_{lm}(\Omega_1) , \quad (5.59)$$

where X stands for the coordinates $s_1, \mathbf{r}_2, s_2, \dots, \mathbf{r}_N, s_N$. In certain highly excited states the spherical average of the derivative of the wave function can be zero at a nucleus: $\chi_{00}^\lambda(0, X) = 0$. This corresponds to the case where there is no s electrons. So Eq. (5.59) is rewritten in the form

$$\Psi^\lambda = \sum_m r_1^l \chi_{lm}^\lambda(r_1, X) Y_{lm}(\Omega_1) + \sum_{l'>l, m'} r_1^{l'} \chi_{l'm'}^\lambda(r_1, X) Y_{l'm'}(\Omega_1) , \quad (5.60)$$

where l is the smallest integer for which χ_{lm}^λ is not zero. So the expressions, which I derived in the following, are valid not only in the ground state but even in the highly excited states. Then the function χ_{lm}^λ is expanded as

$$\chi_{lm}^\lambda(r, X) = a_{lm}^{(0)\lambda}(X) + a_{lm}^{(1)\lambda}(X)r + a_{lm}^{(2)\lambda}(X)r^2 + a_{lm}^{(3)\lambda}(X)r^3 + \dots \quad (5.61)$$

Substituting expressions (5.60), (5.61) and (5.57) into the Schrödinger equation

$$\hat{H}^\lambda \Psi^\lambda = E^\lambda \Psi^\lambda , \quad (5.62)$$

multiplying it with the spherical harmonics $Y_{lm}^*(\Omega_1)$, integrating on the polar angles Ω_1 and equating the coefficients of r^{l-1} , r^l , r^{l+1} separately to zero, I arrive at the system of equations

$$Z_\alpha a_{lm}^{(0)\lambda}(X) + (l+1) a_{lm}^{(1)\lambda}(X) = 0 , \quad (5.63)$$

$$(2l+3) a_{lm}^{(2)\lambda}(X) + Z_\alpha a_{lm}^{(1)\lambda}(X) - \left(\hat{G}^\lambda + \bar{F}^\lambda - E^\lambda \right) a_{lm}^{(0)\lambda}(X) = 0 , \quad (5.64)$$

where $\bar{F}^\lambda = (4\pi)^{-1/2} F_{00}^\lambda$.

Combining these equations I am led to the relations for the terms $a_{l,m}^\lambda$

$$a_{lm}^{(1)\lambda}(X) = -\frac{Z_\alpha}{l+1} a_{lm}^{(0)\lambda}(X) , \quad (5.65)$$

$$a_{lm}^{(2)\lambda}(X) = \frac{1}{2l+3} \left[\frac{Z_\alpha^2}{l+1} + \hat{G}^\lambda + \bar{F}^\lambda - E^\lambda \right] a_{lm}^{(0)\lambda}(X) . \quad (5.66)$$

For $l = 0$ and $\lambda = 0$ the relations of Rassolov and Chipman [103] can be recovered.

The spherical average of the electron density can be obtained by integrating $|\Psi^\lambda|^2$ for all coordinates but r

$$\bar{\varrho}(r) = \sum_m r^{2l} \widetilde{(\chi_{lm}^\lambda)^2} + \sum_{\substack{l', m' \\ l' > l}} r^{2l'} \widetilde{(\chi_{l'm'}^\lambda)^2} , \quad (5.67)$$

where $\widetilde{(\chi_{lm}^\lambda)^2}$ is obtained after integrating $(\chi_{lm}^\lambda)^2$ for all the coordinates X

$$\widetilde{(\chi_{lm}^\lambda)^2} = \int (\chi_{lm}^\lambda)^2 dX . \quad (5.68)$$

To include even the highly excited states I introduced the function $\eta_l(r)$ instead of $\bar{\varrho}(r)$ with the definition

$$\eta_l(r) = \frac{\bar{\varrho}(r)}{r^{2l}} . \quad (5.69)$$

From Eqs. (5.67) and (5.69) follows that

$$\eta_l(r) = \sum_m \widetilde{(\chi_{lm}^\lambda)^2} + \sum_{\substack{l', m' \\ l' > l}} r^{2(l'-l)} \widetilde{(\chi_{l'm'}^\lambda)^2} . \quad (5.70)$$

Taking $\eta_l(r)$ at the nucleus α

$$\eta_l(0) = \sum_m \widetilde{(\chi_{lm}^\lambda)^2}(0) = \int [a_{lm}^{(0)\lambda}]^2 dX . \quad (5.71)$$

Differentiating Eq. (5.70) with respect to r and making use of Eq. (5.65) I arrive at the cusp relation for $\eta_l(r)$

$$\eta'_l(0) = -2 \frac{Z_\alpha}{l+1} \eta_l(0) . \quad (5.72)$$

The second derivative can be given by

$$\begin{aligned} \eta''_l(0) &= 2 \left[\frac{1}{2l+3} \left[\left(\frac{Z_\alpha^2}{(l+1)^2} (4l+5) - 2E^\lambda \right) \eta_l(0) \right. \right. \\ &\quad \left. \left. + 2 \left(F_l^\lambda(0) + G_l^\lambda(0) \right) \right] + \eta_{l+1}(0) \right] , \end{aligned} \quad (5.73)$$

where

$$F_l^\lambda(0) = N \sum_m \int a_{lm}^{(0)\lambda} \bar{F}^\lambda a_{lm}^{(0)\lambda} dX , \quad (5.74)$$

$$G_l^\lambda(0) = N \sum_m \int a_{lm}^{(0)\lambda} \hat{G}^\lambda a_{lm}^{(0)\lambda} dX . \quad (5.75)$$

(These relations have already been derived [18] for $\lambda = 1$.) This expression for the second derivative is the main relation that is going to be applied in the strong-interaction limit in the next section.

5.4 Total energy expression in the strong-interaction limit

First I emphasize that the density and consequently η_l and their derivatives are the same for any value of λ . Taking arbitrary two values of λ the total energy difference can be written as

$$E^{\lambda_2} - E^{\lambda_1} = \frac{F_l^{\lambda_2}(0) - F_l^{\lambda_1}(0) + G_l^{\lambda_2}(0) - G_l^{\lambda_1}(0)}{\eta_l(0)}. \quad (5.76)$$

For the ground state and low excited states $l = 0$ and $\eta_l(0) = \varrho(0)$.

To consider the strong-interaction limit $\lambda \rightarrow \infty$ the Schrödinger equation

$$\left(\hat{T} + \lambda \hat{V}_{ee} + V^\lambda \right) \Psi^\lambda = E^\lambda \Psi^\lambda \quad (5.77)$$

is rewritten as

$$\left(\frac{1}{\lambda} \hat{T} + \hat{V}_{ee} + \frac{1}{\lambda} \sum_{\beta} \frac{Z_{\beta}}{|\mathbf{r}_i - \mathbf{R}_{\beta}|} + \frac{1}{\lambda} \tilde{V}^\lambda \right) \Psi^\lambda = \frac{E^\lambda}{\lambda} \Psi^\lambda. \quad (5.78)$$

If $\lambda \rightarrow \infty$ Eq. (5.78) reduces to

$$\left(\hat{V}_{ee} + \frac{1}{\lambda} \tilde{V}^\lambda \right) \Psi^\lambda = \frac{E^\lambda}{\lambda} \Psi^\lambda, \quad (5.79)$$

consequently for $\lambda \gg 1$

$$\tilde{V}^\lambda = \lambda U = \lambda \sum_{i=1}^N u(\mathbf{r}_i) \quad (5.80)$$

and

$$\tilde{v}_{lm}^\lambda = \lambda u_{lm}(\mathbf{r}_i). \quad (5.81)$$

Then from (5.73) follows that

$$\lim_{\lambda \rightarrow \infty} \frac{E^\lambda}{\lambda} = \frac{N}{\eta_l(0)} \sum_m \int |a_{lm}^{(0)\infty}|^2 (F^\infty + G^\infty) dX, \quad (5.82)$$

where

$$F^\infty = \sqrt{4\pi} \left(\sum_{j=2}^N \frac{1}{r_j} + u_{00} \right) \quad (5.83)$$

and

$$G^\infty = \sum_{j=2}^N \left(\sum_{i=3}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + u(\mathbf{r}_j) \right). \quad (5.84)$$

For the ground state and low excited states $l = 0$ and $\eta_l(0) = \varrho(0)$, therefore

$$\lim_{\lambda \rightarrow \infty} \frac{E^\lambda}{\lambda} = \frac{N}{\varrho(0)} \int |a_{00}^{(0)\infty}|^2 (F^\infty + G^\infty) dX. \quad (5.85)$$

This final equation (5.85) is an exact relation that contains only the first term in the wave function expansion around the given nucleus and parts of the electron-electron interaction and external potential operators. Notice that one should obtain the same relation for any nucleus. One can see from Eq. (5.78) that the $1/r$ terms in the kinetic and the true external terms that cancel each other at a nucleus α both are divided by λ , therefore there is an exact cancellation at any value of λ . If $\lambda \rightarrow \infty$ both the kinetic and the true external terms are negligible.

There are exact relations for the functionals themselves, see e. g. Eqs. (5.25)-(5.30). Other expressions are formalized for average values of certain quantities, such as the total energy or certain parts of the energy. A well-known relation of the latter type is the virial theorem. The exact expression derived in this paper belongs to the latter category.

Chapter 6

Subspace density of the first excited state for two harmonically interacting electrons with isotropic harmonic confinement

There is a growing interest in studying excited states within the density functional theory. Several theories [4, 19] [32]-[41] have been worked out. In all of them the exact form of the functional is unknown. (It is not surprising as it is unknown even in the ground state.) Hohenberg and Kohn [4] proved in 1964 that the ground state of a system is uniquely determined by the ground-state density. A further development of the density functional theory was given by Kohn and Sham [5]. They showed that it is possible to determine the exact one-particle properties of a many-electron system by using a set of Schrödinger -type equations, in which the exchange operator is approximated by a local potential. These theories are restricted to the description of the ground state of a system. The generalization of the KS-theory for excited states was not straightforward. The main difference was that subspace had to be considered instead of eigenstates. Either it can be the lowest-energy states of each symmetry [19]. Later it was shown rigorously that the density can be used as a basic variable for describing excited states by Theophilou [32]. There is correspondence between the subspace and the sum of the densities of lowest eigenstates, which spanned the given subspace instead of between an eigenstate and its density. Fritsche [108] and Englisch et al. [109] also provided formalisms for excited states. A more general treatment was given by Gross et al. [39]. Nagy and Nagy et al. did several calculations using this method [110]-[116].

The main object of this chapter is to demonstrate certain properties of the

subspace density of the first excited state for two harmonically interacting electrons with antiparallel spins and isotropic harmonic confinement. (In the Letter of March et al. [117] ground-state properties were presented.) This system, also known as Moshinsky model, has the Hamiltonian

$$H = \frac{1}{2}(-\nabla_1^2 + r_1^2) + \frac{1}{2}(-\nabla_2^2 + r_2^2) + \frac{1}{2}Kr_{12}^2, \quad (6.1)$$

where

$$\mathbf{r}_{12} = \mathbf{r}_1 - \mathbf{r}_2. \quad (6.2)$$

The first and the third term are the kinetic energies of the electrons. The second and the fourth term are the external (harmonic) potentials and the last term is the interparticle interaction between electrons. After introducing relative (Eq.(6.2)) and centre of mass coordinates

$$\mathbf{R} = \frac{1}{2}(\mathbf{r}_1 + \mathbf{r}_2) \quad (6.3)$$

the Schrödinger equation can be separated leading to the equations

$$\left(-\frac{1}{2}\nabla_R^2 + 2R^2\right)\Psi^{CM} = E^{CM}\Psi^{CM} \quad (6.4)$$

and

$$\frac{1}{2}\left(-\nabla_{r_{12}}^2 + \frac{1}{2}\left(\frac{1}{2} + K\right)r_{12}^2\right)\Psi^{RM} = E^{RM}\Psi^{RM}. \quad (6.5)$$

The total energy has the form:

$$E = n^{CM} + \frac{3}{2} + (n^{RM} + \frac{3}{2})(1 + 2K)^{1/2}, \quad (6.6)$$

where n^{CM} and n^{RM} are the quantum numbers. In the first excited state $n^{CM} = 1$ and $n^{RM} = 0$ as for $K > 0$ $(1 + 2K)^{1/2} > 1$. Introducing the notation

$$\alpha = \frac{1}{2}\left(1 + (1 + 2K)^{1/2}\right), \quad (6.7)$$

the total energy of the first excited state is

$$E_1 = 3\alpha + 1. \quad (6.8)$$

The spatial part of the wave function

$$\Psi^{(1)} = \Psi_1^{CM(1)}\Psi_0^{RM} \quad (6.9)$$

has to be multiplied by the antisymmetric spin state $\alpha(1)\beta(2) - \alpha(2)\beta(1)$. The interelectronic part of the wave function has the ground-state form

$$\Psi_0^{RM} = \pi^{-3/4} \left(\frac{2\alpha - 1}{2}\right)^{3/4} \exp\left(-\frac{2\alpha - 1}{4}r_{12}^2\right). \quad (6.10)$$

The CM part of the Schrödinger equation has a three-fold degeneracy with wave functions

$$\Psi_1^{CM(1)} = 2X \left(\frac{2}{\pi} \right)^{3/4} e^{-R^2} \quad (6.11)$$

and $\Psi_1^{CM(2)}$ and $\Psi_1^{CM(3)}$ are the same expressions having Y and Z respectively, instead of X , the coordinates of $\mathbf{R}$.

The pair density function is the diagonal element of the second-order density matrix. The subspace pair density function can be obtained by the average: [118]

$$n_1(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{3} \left(|\Psi^{(1)}|^2 + |\Psi^{(2)}|^2 + |\Psi^{(3)}|^2 \right), \quad (6.12)$$

where

$$\Psi^{(i)} = \Psi_1^{CM(i)} \Psi_0^{RM}. \quad (6.13)$$

Its value at coincidence, $\mathbf{r}_1 = \mathbf{r}_2 = \mathbf{r}$ is

$$n_1(\mathbf{r}, \mathbf{r}) = \frac{4}{3} \left(\frac{2\alpha - 1}{\pi^2} \right)^{3/2} r^2 e^{-2r^2}. \quad (6.14)$$

With the notation

$$\Gamma(\mathbf{r}, \mathbf{r}) = \frac{n_1(\mathbf{r}, \mathbf{r})}{r^2} \quad (6.15)$$

at $\mathbf{r} = 0$

$$\Gamma_1(0, 0) = \frac{4}{3} \left(\frac{2\alpha - 1}{\pi^2} \right)^{3/2}. \quad (6.16)$$

Using this relation with Eq. (6.8) the total energy can be expressed as

$$E_1 = \frac{5}{2} \left(1 + a\pi^2 [\Gamma_1(0, 0)]^{2/3} \right), \quad (6.17)$$

where $a = \frac{1}{5} \frac{3^{5/3}}{2^{4/3}}$. It is worth comparing this remarkable expression with the corresponding ground-state relation

$$E_0 = \frac{3}{2} \left(1 + \pi^2 [n_0(0, 0)]^{2/3} \right). \quad (6.18)$$

The difference is in the fact that the total energy is determined by $\Gamma(0, 0)$ instead of $n(0, 0)$.

An interesting analogy with the generalization of Kato's theorem for highly excited states of Coulomb systems [16, 18, 35] can be noticed here. Using Eq.(5.48) and taking the $2p$ orbital of the hydrogen atom, then the spherical average of the derivative of the density is zero and the value of the density

$$\varrho_{2p}(r) = cr^2 e^{-Zr} \quad (6.19)$$

is also zero at the nucleus. So instead of the density, another quantity

$$\eta_{2p}(r) = \frac{\varrho_{2p}}{r^2} = ce^{-Zr} \quad (6.20)$$

should be defined and the corresponding cusp relation for the density is

$$-2Z\eta_{2p}(0) = 2\eta'_{2p}(0) . \quad (6.21)$$

So, the atomic number Z is determined by η and its derivative taken at $r = 0$. According to the analogue relation (6.17) here E_1 is determined by Γ_1 .

Now I turn to the electron density ϱ :

$$\varrho(\mathbf{r}) = 2 \int |\Psi(\mathbf{r}, \mathbf{r}')|^2 d\mathbf{r}' \quad (6.22)$$

The subspace electron density of the first excited state can be given by

$$\varrho_1(\mathbf{r}) = \frac{2}{3} \int \left(|\Psi^{(1)}|^2 + |\Psi^{(2)}|^2 + |\Psi^{(3)}|^2 \right) d\mathbf{r}' \quad (6.23)$$

After some algebra I am led to

$$\varrho_1(\mathbf{r}) = \frac{\varrho_0(\mathbf{r})}{2\alpha} \left[1 + \frac{2}{3} \frac{(2\alpha - 1)^2}{\alpha} r^2 \right], \quad (6.24)$$

where

$$\varrho_0(\mathbf{r}) = 2 \left(\frac{(2\alpha - 1)}{\pi\alpha} \right)^{3/2} \exp \left(-\frac{(2\alpha - 1)}{\alpha} r^2 \right) \quad (6.25)$$

is the ground-state density. At $r = 0$ I obtain

$$\varrho_1(0) = \frac{\varrho_0(0)}{2\alpha}, \quad (6.26)$$

where

$$\varrho_0(0) = 2 \left(\frac{2\alpha - 1}{\pi\alpha} \right)^{3/2}. \quad (6.27)$$

From Eqs.(6.8) and (6.26) I arrive at the remarkable expression for the energy

$$E_1 = 1 + \frac{3}{2 - \pi \left(\frac{\varrho_0(0)}{2} \right)^{2/3}}. \quad (6.28)$$

That is the first excited state energy is determined uniquely by the value of the ground-state density at $r = 0$. The relationship between E_1 and the subspace density of the first excited state $\varrho_1(0)$ at $r = 0$ is somewhat more complicated:

$$\varrho_1(0) = b \frac{(2E_1 - 5)^{3/2}}{(E_1 - 1)^{5/2}}, \quad (6.29)$$

where $b = 3\pi^{-3/2}$. Again, E_1 is completely determined by $\varrho_1(0)$, though in this case it is easier to express $\varrho_1(0)$ by E_1 .

Finally, relationship between the subspace density of the first excited state ϱ_1 and the pair function of coincidence $n(\mathbf{r}, \mathbf{r})$ is established. Using Eqs. (6.14) and (6.24) I can readily arrive at

$$\varrho_1(\mathbf{r}) = c \left[\frac{3}{4} \pi^3 \frac{\Gamma_1(\mathbf{r}, \mathbf{r})}{(2\alpha - 1)^{3/2}} \right]^{\frac{(2\alpha - 1)}{2\alpha}} \left[1 - \frac{1}{3} \frac{(2\alpha - 1)^2}{\alpha} \ln \left(\frac{3}{4} \pi^3 \frac{\Gamma_1(\mathbf{r}, \mathbf{r})}{(2\alpha - 1)^{3/2}} \right) \right], \quad (6.30)$$

where $c = \frac{1}{\alpha} \left[\frac{(2\alpha - 1)}{\pi\alpha} \right]^{3/2}$.

In summary, I derived similar relations for the subspace density and pair density at coincidence of the first excited state of two harmonically interacting electrons with antiparallel spins and isotropic harmonic confinement that were previously found for the ground state. It was shown that the total energy is uniquely determined by the value of the pair density at coincidence at $r = 0$ and the subspace electron density can be expressed by the subspace pair density at coincidence.

Chapter 7

Summary

Electron density is used in density functional theory [1]-[5] instead of N -electron wave function. Electron density has only 3 variables for any many-particle system, which gives a great simplification in the treatment of many particle problem. Although the electron density is the basic variable of the density functional theory, its rigorous information on its structural properties is not available in sufficient quantity. Kato's theorem [13] provides probably the most useful relations [13, 14]. It describes the behaviour of density functionals at the place of the nucleus. The progress I made in this area of DFT is listed below.

1. Cusp relations for the kinetic energy density are derived for highly excited states of atoms, ions or molecules, for which the spherical average of the derivative of the wave function is zero at a nucleus. The two most frequently used kinetic energy density expressions imply different behaviour at the nuclei.
2. Using a non-local exchange kernel $X(\mathbf{r}, \mathbf{r}')$ defined earlier by March and Santamaria, Hartree-Fock theory is shown to yield an exact relation for the kinetic energy density $t(\mathbf{r})$. This involves $X(\mathbf{r}, \mathbf{r}')$ and its low-order gradients with respect to $\mathbf{r}$. A two-level example applicable to either the *Be* atom or the heteronuclear molecule *LiH* confirms the general relation between $t(\mathbf{r})$ and $X(\mathbf{r}, \mathbf{r}')$ presented here.
3. Exact energy expression is presented in the strong-interaction limit of the density functional theory. The derivation utilizes the adiabatic connection. The coupling constant dependent approximations for the exchange-correlation energy are reviewed. Higher-order cusp relations for the wave function and electron density for arbitrary coupling constant is derived. A total energy expression in the strong-interaction limit is presented.
4. The subspace density and pair density at coincidence of the first excited state for two harmonically interacting electrons with antiparallel spins and

isotropic harmonic confinement are calculated. It is shown that the total energy is uniquely determined by the value of the pair density at coincidence at $r = 0$. A relationship between the energy and the subspace density at $r = 0$ is derived.

Chapter 8

Magyar nyelvű összefoglaló

Az 1920-as években, Thomas és Fermi [1]-[3] alapozták meg a sűrűségfunkcionál elméletet. Teljessé azonban az 1960-as években vált, amikor Kohn, Hohenberg és Sham [4, 5] publikálták eredményeiket. Az, hogy a Schrödinger egyenletben mindent, az N -elektronos hullámfüggvény helyett a mindössze 3 változós elektron-sűrűséggel fejezünk ki, lehetővé tette a nagyobb elektronszámú rendszerek tárgyalását.

Thomas és Fermi zseniális észrevétele az volt, hogy az elektronok eloszlását egy atomban lehet statisztikusan is tárgyalni. Thomas feltevései [1] a következők voltak. Egyrészt az elektronok eloszlása egy atomban, a 6-dimenziós fázistérre nézve egyenletes, másrészt létezik egy olyan effektív potenciál, amely önmagában meghatározza az atommag töltését és az elektronok eloszlását. Ezen két feltevés alapján le lehet vezetni a Thomas-Fermi egyenletet.

Egy N -elektronszámot tartalmazó alapállapotú rendszerben a $v(\mathbf{r})$ külső potenciált ismerve, tudom a rendszer $\hat{H}$ Hamilton operátorát is. Vagyis az N elektronszám és a $v(\mathbf{r})$ külső potenciál ismeretében a rendszer minden tulajdonságát meg lehet adni, alapállapotban. Az első Hohenberg-Kohn tétel [4] alapján azonban az N és $v(\mathbf{r})$ helyett be lehet vezetni a $\rho(\mathbf{r})$ elektronsűrűséget, mint központi mennyiséget. A tétel szerint ugyanis a $v(\mathbf{r})$ külső potenciált egyértelműen megadja a $\rho(\mathbf{r})$ elektronsűrűség egy additív állandótól eltekintve. Ugyanakkor a $\rho(\mathbf{r})$ elektronsűrűséget a teljes térre kiintegrálva megkapjuk az elektronok N számát. Vagyis a $\rho(\mathbf{r})$ elektronsűrűség ismeretében meg lehet adni a $v(\mathbf{r})$ külső potenciált és az N elektronszámot is, s ezzel a rendszer $\hat{H}$ Hamilton operátorát is, alapállapotban. A tárgyalásmód ezen szintjén a $v(\mathbf{r})$ nem csak Coulomb-potenciál lehet!

A második Hohenberg-Kohn tétel [4] a variációs elvet mondja ki a rendszer teljes energiájára. A tétel állítása szerint a teljes energia alapállapotban pontosan az egzakt alapállapotú sűrűségnél veszi fel a minimumát, miközben a külső potenciál rögzített.

A tételek a megfelelő funkcionáloknak csak a létezését garantálják. Arra viszont nem adnak útmutatót *hogyan* alkossuk meg a funkcionálokat. A Coulomb-potenciállal rendelkező rendszerek napjainkban elérhető energiafunkcionáljait ál-

talában két különböző, de egymástól nem teljesen független elgondolás alapján alkotják meg. Az egyik a homogén elektrongáz modellen alapszik, míg a másik a félklasszikus sorfejtések technikáját használja fel.

Ha közvetlenül a variációs elv alapján szeretnénk megadni az alapállapot energiakülönbségeit, akkor nehézségekbe ütközünk. A probléma legfőbb oka az egzakt kinetikus energia funkcionál ismeretének hiánya. Ezért közelítéseket alkalmazunk, ami pontatlan eredményekhez vezet. Például a Thomas-Fermi modellben a kinetikus energia funkcionál csak az elektronsűrűség funkcionálja. Nehéz a közelítés ezen szintjéről továbblépni, ha meg szeretnénk őrizni a viszonylagos egyszerűséget.

Pontos, egyben bonyolultabb is a Kohn-Sham [5] modell. A Kohn-Sham módszernek köszönhetően a sűrűségfunkcionál elmélet alkalmassá vált arra, hogy nagy pontossággal végezzenek el számításokat, akár nagyobb rendszerekre is, alapállapotban. A Kohn-Sham egyenletek megoldásai a Kohn-Sham pályák, a kölcsönható rendszer részecske sűrűségét helyesen adják vissza. A Kohn-Sham tételnek köszönhetően Kohn-Sham tárgyalásmódban a $\hat{H}$ Hamilton operátor felírható egy nemkölcsönható kinetikus energia és egy egyrészecskés, effektív, úgynevezett Kohn-Sham potenciál összegeként. Ez a Kohn-Sham potenciál tartalmazza a klasszikus Coulomb kölcsönhatásokat elektron-mag és elektron-elektron között, továbbá az összes nemlokális kölcsönhatást is. A kölcsönható rendszer nemlokális kölcsönhatásait tartalmazó egyrészecske potenciált kicserélődési-korrelációs potenciálnak v_{xc} nevezzük. A sűrűségfunkcionál elméletben a v_{xc} kicserélődési-korrelációs potenciált a kicserélődési-korrelációs energia funkcionál sűrűség szerinti funkcionálderiváltjaként definiáljuk. Az elmélet alapján a kicserélődési-korrelációs energia univerzális, azaz minden rendszerre ugyanaz, ahol a külső kölcsönhatást Coulomb-potenciállal jellemezzük.

Ugyanúgy, mint a Hohenberg-Kohn tételeknél, a probléma itt is az, hogy csak a létezését biztosítják a funkcionáloknak, megalkotásukhoz nem adnak segítséget. A Kohn-Sham tárgyalásmódban a kicserélődési-korrelációs potenciált nem ismerjük. Amit jelenlegi ismereteink alapján tudunk a leendő funkcionálokról, olyan feltételek, amiket mindenképpen teljesíteniük kell.

Napjainkban tehát a sűrűségfunkcionál elmélet három generációját különböztetjük meg. A sűrűségfunkcionál elmélet *első generációjában* explicite sűrűségtől függő funkcionálokat használnak a nemkölcsönható kinetikus energia és a kicserélődési-korrelációs energia közelítésére. A legegyszerűbb közelítés a Thomas-Fermi modell, amely a kicserélődési-korrelációs energiát teljes mértékben elhagyja, s csak a nemkölcsönható kinetikus energiára ad közelítést. Ezekre a funkcionálokra a Hohenberg-Kohn variációs elv közvetlenül használható, amely Thomas-Fermi típusú egyenletekhez vezet. Mivel egyedül az elektronsűrűség funkcionáljai, ezért numerikusan könnyen megoldhatók. A rendszer alapállapot energiájára azonban elfogadhatatlanul nagy hibával ad csak értéket.

A sűrűségfunkcionál elmélet *második generációjában* a nemkölcsönható kinetikus energiát az egyelektron pályák funkcionáljaként egzaktul kezelik, s a kicserélődési-korrelációs energiát a sűrűség funkcionáljaként írjuk fel. Lényegében a sűrűségfunkcionál elmélet Kohn-Sham tárgyalását adja vissza. Ekkor a Hohenberg-Kohn egyenleteket kell ön-konzisztens módon megoldani, ahol az $E_{xc}(\rho)$ kicserélődési-

korrelációs energiafunkcionál explicite függ az elektronsűrűségtől. Numerikusan könnyen kezelhető, s igen jó eredményeket ad a legtöbb atomra, molekulára és szilárdtestre.

Végül, a sűrűségfunkcionál elmélet *harmadik generációjában* egzaktul kezeljük a nemkölcsonható kinetikus energiát és a kicserélődési energiát. Csak a korrelációs energia az elektronsűrűség funkcionálja, a $\hat{H}$ operátor többi tagja mind pályafüggő funkcionál. Az így kapott Kohn-Sham egyenleteket kell megoldani. A sűrűség-funkcionál elmélet második és harmadik generációja között az a különbség, hogy a kicserélődési-korrelációs energiát másképp kezelik.

Lényegében a disszertáció célja is az, hogy az energiafunkcionálok viselkedésére újabb feltételeket adjunk meg, további segítséget nyújtva az egzakt energiafunkcionálok megtalálásához. Valószínűleg a leghasznosabb feltételek egyike a Coulomb szingularitással kapcsolatos feltételek, amelyeket Kato [13] tétele alapján lehet lev-ezetni. Kato tétele azt mondja meg, hogyan kell viselkedniük a funkcionáloknak az atommag helyén. Ez alapján meg lehet mondani azt is, hol van az atommag és mennyi az atommag rendszáma. Azonban Kato tétele csak Coulomb kölcsönhatással jellemezhető rendszerekre igaz. Kato tételét egyszerűen gerjesztett állapotokra is lehet általánosítani [15]. A nemkölcsonható és kölcsönható rendszereket adiabatikusan össze lehet kapcsolni, és a kölcsönható és nemkölcsonható rendszerek adiabatikus összekapcsolásával egyszerűen gerjesztett állapotra vonatkozó elméletet lehet felállítani.

Az ezt követő fejezetben Coulomb szingularitással kapcsolatos feltételeket vez-ettem le a kinetikus energiasűrűségekre (3. fejezet). A 4. fejezetben összefüggést adtam meg a kinetikus és kicserélődési energiasűrűség között a Hartree-Fock elmélet alapján. Majd az adiabatikus kapcsolás segítségével egy egzakt kifejezést származ-tattam az erősen korrelált rendszererek teljes energiájára (5. fejezet). Az adia-batikus csatolás [19]-[23] biztosítja a kapcsolatot a kölcsönható és a neki megfe-lelő nemkölcsonható rendszerek között. Mostanában publikálták [24]-[27], hogy az adiabatikus csatolás fontos az erősen korrelált rendszerek tanulmányozásához. Továbbá két, harmónikusan kölcsönható elektron egy gerjesztett állapotához tar-tozó sűrűséget is megadtam az 6. fejezetben, amikor a kölcsönhatás izotrópikus és harmónikus.

A sűrűségfunkcionál elmélettel számos, különféle rendszert, például molekulákat modelleznek. Egy jól ismert példa a biotechnológiai alkalmazása. Ide tartozik a proteinek tanulmányozása is, amely lényeges a fehérjék szabályozási folyamatainak megértéséhez, vagy a DNS szekvenciák meghibásodási és javítási folyamatainak a leírásához. Egy másik alkalmazási területként megemlíthető a farmakológia is, ahol az új gyógyszer, hatóanyag megtervezése előbb számítógépes szimulációval történik, s csak ezután állítják elő a tényleges prototípust.

A sűrűségfunkcionál elmélet ezen területén elért eredményeimet az alábbi pon-tokban foglaltam össze:

1. A kinetikus energiasűrűségekre vezettem le Coulomb szingularitással kapcsola-tos feltételeket, magasan gerjesztett állapotú atomokra, ionokra és molekulákra. Ekkor a hullámfüggvény gömbi átlagának a deriváltja az atom-

mag helyén zérus. A két leggyakrabban használt kinetikus energiasűrűség másképp viselkedik az atommag helyén.

2. March és Santamaria által megadott $X(\mathbf{r}, \mathbf{r}')$ nem-lokális kicserélődési sűrűséget felhasználva, a Hartree-Fock elmélet alapján egzakt relációt vezettem le a kinetikus energiasűrűségre. Az összefüggés tartalmazza az $X(\mathbf{r}, \mathbf{r}')$ nem-lokális kicserélődési sűrűséget s annak alacsonyabb rendű gradienseit.
3. Magasabb rendű Coulomb szingularitással kapcsolatos feltételeket származtattam a hullámfüggvényre és az elektronsűrűségre, tetszőleges értékű csatolási állandóra. A sűrűségfukcionál elmélet erős kölcsönhatású határesetében megadtam egy egzakt energiakifejezést.
4. Meghatároztam két harmónikusan kölcsönható elektron egy gerjesztett állapotában a sűrűséget. Az elektronok közti kölcsönhatás izotróp, az elektronok spinje antiparallel beállású. Megadtam egy kifejezést a rendszer teljes energiájára is. A rendszer teljes energiája és a gerjesztett állapothoz tartozó sűrűség között származtattam egy összefüggést.

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List of publications

- [R1] Zs. Jánosfalvi, K. D. Sen and Á. Nagy; Cusp conditions for non-interacting kinetic energy density of the density functional theory; Phys. Lett. **A 344** (2005) p.1-6
- [R2] Á. Nagy, I.A. Howard, N.H. March and Zs. Jánosfalvi; Subspace density of the first excited state for two harmonically interacting electrons with isotropic harmonic confinement; Phys. Lett. **A 335** (2005) p.347-350
- [R3] Á. Nagy and Zs. Jánosfalvi; Exact energy expression in the strong-interaction limit of the density functional theory; Phil. Mag. **B** (2004) (accepted)
- [R4] N. H. March, Zs. Jánosfalvi, Á. Nagy and S. Suhai; Kinetic and exchange energy related non-locally in Hartree-Fock theory of an inhomogeneous electron liquid; Phys. and Chem. Liq. (2005) (accepted)

Posters

- [R5] "Exact Energy Expression in the Strong-Interaction Limit of the Density Functional Theory"; 3rd Graduate School on Condensed Matter Physics Strongly Correlated Systems International Summer School; (Debrecen, Hungary, 6-11 September, 2004).
- [R6] "Cusp Conditions for Energy Densities of the Density Functional Theory"; 10th International Conference on the Applications of the Density Functional Theory in Chemistry and Physics; (Vrije Universiteit Brussel, Brussels, Belgium, 7-12 September, 2003).
- [R7] "Cusp Conditions for Kinetic Energy Densities of the Density Functional Theory"; Eight European Workshop on Quantum Systems in Chemistry and Physics; (Hellas, Islands of Spetses 30 August - 4 September, 2003).