

**Electron Correlation in Density
Functional
Theory: Concept and Application**

thesis submitted for the Ph.D degree

BY

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Contents

1	Review of Density Functional Theory	12
2	Hohenberg-Kohn theorem	12
3	Kohn-Sham theory and single particle equations	16
4	Conventional quantum chemical correlation energy versus density functional correlation energy	18
5	The molecular correlation problem	19
6	Dynamical and nondynamical correlation	20
7	The exchange-correlation energy functional $E_{xc}[\rho]$	23
8	$E_{xc}[\rho]$ in homogeneous and inhomogeneous electron systems	26
9	Exchange-correlation in homogeneous electron gas	29
10	Levy's constrained-search formulation	33
11	Abstract	35
12	Introduction	35
13	Definition and construction of ϵ_{xc} and ϵ_c	37
14	Model functionals $\epsilon_c([\rho]; \vec{r})$	41

15 Results for atoms	43
16 Results for molecules	48
17 Conclusions	57
18 Abstract	59
19 Introduction	59
20 Construction of $t_c([\rho]; \vec{r})$	61
21 $T_c^{mod}[n]$ functionals	62
22 Results for atoms	63
23 Results for molecules	65
24 Abstract	74
25 Introduction	74
26 Theoretical formulation	75
27 Computational method	77
28 Discussion of the relationship between the Liu-Parr and Wigner formulas	81
29 Comparison of local and nonlocal Wigner-type functionals	82

30 Abstract	91
31 Introduction	91
32 Methods of Calculations	93
33 Structure and dipole moment of formic acid	98
34 Formate anion	100
35 Structure of formate-formic acid complex	102
36 BSSE	110
37 Bonding energy analysis	111
38 Timings	114
39 Conclusions	115
40 The main conclusions of this thesis	120
41 A disszertáció rövid összefoglalója	122
42 The documentation of publications	124

"The man is reasonable being; and as such, receives from science his proper food and nourishment: But so narrow are the bounds of human understanding, that little satisfaction can be hoped for in this particular, either from the extent or security of this acquisitions."

David Hume

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Introduction

"We are perhaps not far removed from the time when we shall be able to submit the bulk of chemical phenomena to calculation"

J. L Gay-Lussac 1808

The complexity of many-body problem is due to the necessity of describing both the internal properties of the system and its interaction with external potential. This thesis is focused on the electron correlation problem in the density functional theory (DFT). If one aims to get quantitative results for energy differences that govern the processes in chemistry, such as molecular binding energies, excitation energies or ionization potentials, which are very small compared to the bulk of energy which is provided by free atoms. Even the qualitative picture may change due to the effects of electron correlation. An often cited example is the F_2 molecule which is found to be unbound at the Hartree-Fock level of theory, and inclusion of electron correlation is essential for correct description of molecular binding.

Different roads have been pursued in computational molecular physics towards predictive quantum science. Although many aspects of electron correlations are very similar in molecules and in solids, the theoretical developments in different fields have diverged so much to completely different formalisms that they often do not even share a common language. Traditional treatments of electron correlation like configuration interaction (CI) and perturbation expansions suffer from several deficiencies. The former method is almost impossible to carry out for systems with practical significance. An important drawback of the truncated CI is that results become increasingly worse for larger systems: CI does not satisfy the requirement of size-consistency. The Møller-Plesset perturbation series [1] for instance often exhibit divergent behaviour and are found to reflect the dominance of the reference

state in the exact solution. Extension of the basis sets leads frequently to slower convergence [2]. Many other techniques, like Green's functions or diagrammatic approaches lead to complicated representations of the many-body problem as well [1]. The computational demand increases rapidly with the number of electrons. Large systems such as molecular complexes or solids are not amenable yet for routine investigations by *ab initio* methods.

The main advantage of DFT is that one has to work with the three-dimensional electron density $\rho(\vec{r})$ as the basic variable, instead of the more complicated wavefunction $\Psi(\vec{r}_1, s_1, \vec{r}_2, s_2, \dots, \vec{r}_n, s_n)$. The density ρ itself can be obtained from diffraction experiments as well and therefore it can be compared with theoretical results. For practical calculations a couple of program packages are available which are already widely used in quantum chemistry, solid state physics as well as in drug design and for other numerous applications. The enormous growth in the amount of published papers in the leading scientific journals concerning DFT indicates the encouraging future of this field.

The difference between conventional and DFT correlation energy is not trivial, however, the physics behind them should be the same. Within the scope of single particle theory, Gáspar-Kohn-Sham theory (GKS) [4, 5] provides a cost-effective way of treating electron correlation in principle exactly. The missing link between the exact and approximate GKS DFT theory [5, 6], is the exact exchange-correlation energy functional which is unknown. The basic theorem of DFT, the Hohenberg-Kohn theorem [7] offers, unfortunately, no practical guide to the explicit construction of the functionals in question. On top of it there is no hope, at least up to our present knowledge in DFT, to find such an explicit density functional in the next future. An alternative way to improve the situation, however, to "transform" the KS-equations into an exact exchange-only formalism [8, 9], whereas the missing link mentioned above is reduced to the appropriate treatment of the electron correlation. It turned out, that this exchange-only DFT can be put into the somewhat complex optimized effective potential formalism [10]. This formalism requires correlation density functionals in the explicit orbital dependent level [11]. The greatest deficiency

of correlation energy functionals are developed in the last decades is that they account for only dynamical correlation while completely neglect nondynamical or near-degeneracy correlation. This type of correlation, which is originally introduced by Sinanoğlu [12], is extremely important not only in "dissociation catastrophe" but also in molecules at equilibrium geometry in order to achieve the rigorous requirements towards predictive computational quantum physics and chemistry. One of the greatest challenge in DFT is the proper modelling of such a functional. The most popular correlation density functionals of nowadays are based on the homogeneous electron gas model as a starting point and contain suitably chosen gradient corrections in order to account for weak electron density fluctuations. The most obvious derivation of functionals is based on various pair-correlation models, whereas appropriately chosen pair-correlation functions can be used in order to demonstrate parallel and anti-parallel spin correlation correctly. Parallel spin correlation can be divided into Fermi-correlation and like-spin Coulomb correlation: the latter is in spite of the general belief, not a negligible quantity, especially in molecular systems and frequently accounts for not less than 20 % of the total correlation energy [13, 14]. However, in reality the Coulomb correlation of electrons with parallel spins is essentially suppressed by the Fermi correlation [13].

In order to get further insight into the correlation problem in DFT an attempt is made to present local characteristics of the correlation energy density $e_c([\rho], \vec{r})$, which is exact in the sense that it has been obtained during a constrained search procedure [6] whereas the reference density was a full-CI density in an appropriately chosen basis set. Although the electron correlation as well as the exchange have nonlocal feature, the correlation hole around an electron is a fairly local object, and as such can be treated by density functionals.

Particular attention is paid to the virial relation in DFT, which differs from its quantum chemical counterpart. One incarnation of the DFT-virial relation is applied (Levy-Perdew relation) [6] to evaluate new kinetic energy functionals $T_c[\rho]$ which are responsible for the correlation contribution to the fully correlated kinetic energy. Its performance is compared with the best available CI-results. One of the main reason

of modelling $T_c[\rho]$ is that $E_c[\rho]$ can be decomposed into potential $W_c[\rho]$ and $T_c[\rho]$ parts in DFT. The separate modelling of potential and kinetic contributions to correlation provides an alternative way of handling many-body problem in DFT, since there are quite accurate density functionals available for the potential part, however, the remaining part is unknown. Fortunately exact relations, like adiabatic connection scheme, or the virial relation makes the derivation of $T_c[\rho]$ possible. In chapter 2 and 3 results will be shown concerning the above-mentioned philosophy.

In chapter 4 we give an analysis of electron correlation using local functionals. An interesting question is: Which is the simplest form of local correlation energy functionals and how gradient correction effects their performance. The scaling properties of Wigner-type functionals is examined and the coupling-constant integration scheme is applied in order to get a new functional. The relationship between the suitability for coupling-strength integration and the various scaling properties is unknown, however, present study as a simple trial shows that the integrand of the coupling-strength integration or adiabatic connection scheme should satisfy more scaling relations.

Finally in chapter 5 we give an example for the application of DFT. Theory and applications are frequently treated separately, however we believe, that the regular use of the theory in various application fields and the constant search for benchmark results provides the best feedback for the recognition of deficiencies. Results are presented concerning calculations are carried out on a strong hydrogen-bonded system by means of the most accurate density functionals are available up to date. The computed results are in very good agreement with the available experimental results almost within chemical accuracy. Strong hydrogen bonds called low-barrier hydrogen bonds (LBHB) have been proposed to provide a large fraction of the catalytic power of enzymes.

1 Review of Density Functional Theory

2 Hohenberg-Kohn theorem

Let's take into account a system of N spinless, identical fermions. Nonrelativistic quantum mechanics is assumed to apply. A potential energy function of all particle coordinates is assumed as well, which describes the interaction. Nondegeneracy is required since it guarantees that there is a unique density associated with the ground state. The usual particle density function can be given for a general fermionic system:

$$\rho(\vec{r}) = N \int |\Psi_G(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)|^2 d\vec{r}_2 \dots d\vec{r}_N \quad (0.1)$$

where Ψ_G is the ground-state wave function normalized to unity. It is beyond argument that this function is positive semidefinite everywhere:

$$\rho(\vec{r}) \geq 0 \quad (0.2)$$

Obvious restrictions still are $\int \rho(\vec{r}) d\vec{r} = \text{integer}$, and $\rho(\vec{r})$ continuous. The electronic system is described by the following Hamilton operator:

$$\hat{H} = \sum_{i=1}^N \left(-\frac{1}{2} \nabla_i^2\right) + \sum_{i=1}^N v(\vec{r}_i) + \sum_{i < j}^N \frac{1}{|\vec{r}_{ij}|} \quad (0.3)$$

In which

$$v(\vec{r}_i) = - \sum_{\alpha} \frac{Z_{\alpha}}{|\vec{r}_{i\alpha}|} \quad (0.4)$$

is the "external" potential acting on electron i , the potential due to nuclei of charges Z_{α} and $\vec{r}_{i\alpha}$ is nuclear-electron distance. The coordinates \vec{r}_i of electron i denotes its spatial displacement. Atomic units are employed here and throughout this thesis (unless otherwise specified). Both the ground-state energy and the ground-state wave function Ψ are determined by the minimization of the energy functional $E[\Psi]$. For N -electron system the external potential completely fixes the Hamiltonian; thus N and $v(\vec{r})$ determine unambiguously all properties of the ground state (degeneracy presents no difficulty [6]). This of course is not surprising since $v(\vec{r})$ defines the whole nuclear frame for a molecule e.g., which together with the number of electrons determines all the electronic properties.

The first Hohenberg-Kohn theorem establishes the use of electron density as basic variable [7]. In the most compact form as follows: *The external potential $v(\vec{r})$ is a unique functional of $\rho(\vec{r})$ which can be expressed by the functional $v([\rho]; \vec{r})$.* This means that a definite ρ implies that there is a specific v such that ρ is derived via eq. (1.1) by solving the full many-body Schrödinger equation containing the external potential

$$V = \sum_{i=1}^N v(\vec{r}_i). \quad (0.5)$$

The abovementioned "uniqueness" means uniqueness up to an additive constant and represents one ambiguity in the sense that the wave function of a system, and hence the charge density, is unaltered if a constant is added to the potential. The standard proof of this theorem of Hohenberg and Kohn proceeds by *reductio ad absurdum*. Suppose then that there exists a different v' (except for an additive factor), which leads via the Schrödinger equation to a different many-body wave function $\Psi_{G'}$ from which, however, the same ground-state densities $\rho = \rho'$ are derived. The task to be accomplished is that this is inconsistent.

Let E be the energy of $|\Psi_G\rangle$ and E' that of $|\Psi_{G'}\rangle$. Then $E = \langle \Psi_G | H | \Psi_G \rangle$ and $E' = \langle \Psi_{G'} | H' | \Psi_{G'} \rangle$, where H contains v and H' contains v' , but by the general minimum theorem for the true ground state,

$$E' < \langle \Psi_G | H' | \Psi_G \rangle = \langle \Psi_G | H + V' - V | \Psi_G \rangle = E + \langle \Psi_G | V' - V | \Psi_G \rangle. \quad (0.6)$$

Thus,

$$E' < E + \int \rho(\vec{r}) [v'(\vec{r}) - v(\vec{r})] d\vec{r}. \quad (0.7)$$

However, one can apply primed and unprimed quantities interchanged, since the densities associated with $|\Psi_G\rangle$ and $|\Psi_{G'}\rangle$ are assumed to be the same.

$$E < \langle \Psi_{G'} | H | \Psi_{G'} \rangle = E' + \int \rho(\vec{r}) [v(\vec{r}) - v'(\vec{r})] d\vec{r}. \quad (0.8)$$

One can add then Eqs. (1.7)-(1.8) to find an inconsistency: $E + E' < E' + E$. Hence, ρ and ρ' must be different and we may say that $v(\vec{r})$ is a unique functional of ρ .

The complete Hamiltonian is specified in principle if the ground-state density is known and contains the sum of kinetic T , interaction U energies and the external

potential V :

$$H = T + U + V \tag{0.9}$$

In the following section it should be pointed out that the ground-state energy $E_G[\rho]$ has its minimum when $\rho(\vec{r})$ is the correct actual ground-state density. The desired result is a consequence of the general quantum mechanical variational principle which states that the ground-state energy is a functional of the wave function Ψ which has its minimum at the correct value subject to the condition that all variations retain the correct number of particles N ,

$$N = \int \rho(\vec{r}) d\vec{r}. \tag{0.10}$$

Suppose then that Ψ is the ground-state wave function and Ψ' is a trial wave function obtained from the solution of the Schrödinger equation with different external potential v' and let ρ' be the density associated with Ψ' . Then,

$$\begin{aligned} E[\Psi'] &= \langle \Psi' | T + U | \Psi' \rangle + \langle \Psi' | V | \Psi' \rangle = \\ &F[\rho'] + \int v(\vec{r})\rho(\vec{r})d\vec{r} > E_G[\Psi] = F[\rho] + \int v(\vec{r})\rho(\vec{r})d\vec{r}. \end{aligned} \tag{0.11}$$

So, $E_G[\rho]$ is a minimum relative to all density functions associated with some other external potential v' . This establishes the asserted minimum principle for $E_v[\rho']$,

$$E_v[\rho] < E_v[\rho'] \tag{0.12}$$

where v is responsible for the "fixed" external potential. However, the functional $E[\rho]$ is defined only for densities which are ground-state densities for some external potential: for the interacting *v-representable* densities. We then can restate the first Hohenberg-Kohn theorem as there is one-to-one mapping between ground-state wave function and the *v-representable* electron densities. Though it has been shown that the ground-state density uniquely determines the various properties of a ground state it is necessary to discuss some subtle aspects of this relationship as well. Levy and Lieb have been pointed out that many reasonable densities can be non-*v-representable* [17, 18]. The *v-representability* is proved for nearly uniform [7] and near to nondegenerate densities [19], however, there are densities that do not

come from a ground-state wave function of any $v(\vec{r})$ [21]. Fortunately it turned out that density functional theory can be formulated in such a way that only requires a weaker condition, the *N-representability* condition. The density is N-representable if it can be obtained for some antisymmetric wave function and consequently is much weaker condition than the v-representability, since the former is necessary for the latter. The N-representability condition is satisfied for any reasonable density which mathematically can be formulated together with (1.2-1.10) [22]:

$$\int |\nabla\rho(\vec{r})^{1/2}|^2 d\vec{r} < \infty. \quad (0.13)$$

Having in hand the first two statements of density functional theory (DFT), namely the invertibility and variational access [23], it is possible to introduce the universality statement. First decompose the energy functional into two terms which account for electronic repulsions between electrons and interaction with the external potential.

$$E[\rho] = F_{HK}[\rho] + \int \rho(\vec{r})v(\vec{r})d\vec{r} \quad (0.14)$$

with

$$F_{HK}[\rho] = \langle \Psi[\rho] | \hat{T} + \hat{U} | \Psi[\rho] \rangle \quad (0.15)$$

we can state that the functional F_{HK} is *universal* in the sense that it does not depend on the external potential. Consequently F_{HK} is the same functional for all kind of fermionic system whereas \hat{U} is the operator acting on Coulomb repulsion between the fermions while the external potential $v(\vec{r})$ appears only in the second term of (1.14). However, the Hohenberg-Kohn theorem described above does not tell us, unfortunately, how to construct the functional $F_{HK}[\rho]$ being "only" existential theorem. There is no explicit receipt for the evaluation of the exact $F_{HK}[\rho]$ energy functional, however once satisfactory approximation is available we can apply it efficiently for electronic systems like atoms, molecules and solids. It is worth to decompose the universal energy functional $F_{HK}[\rho]$ into "classical" Coulomb repulsion and the so-called exchange-correlation terms as follows,

$$F_{HK}[\rho] = T[n] + \int \frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}d\vec{r}' + E_{xc}[\rho] \quad (0.16)$$

where $E_{xc}[\rho]$ is the exact in principle exchange-correlation energy functional, which is, however, unknown. Various approximations for $E_{xc}[\rho]$ have been developed in the last decade and the future applications are encouraging [6, 23].

3 Kohn-Sham theory and single particle equations

To apply the DFT formalism one needs obviously the energy minimum of eq. (1.14) which requires good approximation for the $T[n]$ and $E_{xc}[n]$ energy functionals. Up to date there is no satisfactory model for the $T[n]$ functional while the $E_{xc}[n]$ functional represents smaller quantities with one or two magnitudes, and consequently the errors in the various approximations can be closer to the desired chemical accuracy which is one of the main goals to be achieved in quantum chemistry. Without any satisfactory approximations for $T[\rho]$ the "classical" Thomas-Fermi equations [6] cannot be used for molecules or solids [25]. With this in mind Kohn and Sham developed an alternative scheme for the solution of the many-body problem of fermionic systems [5]. They introduced single particle equations with local effective potential $v_s(\vec{r})$ and Slater determinant of orbitals u_i . The main advantage of this scheme is that it allows a more straightforward determination of largest part of the kinetic energy functional in a simple way and an exact one-particle picture of interacting electronic systems is introduced. First we make use of a non-interacting particle system with Hamiltonian \hat{H}_s , ground state density ρ and external potential v_s . The ground state is a Slater determinant of orbitals u_i which satisfy the equation for spin unpolarized case,

$$[-1/2\nabla^2 + v_s(\vec{r})]u_i(\vec{r}) = \epsilon_i u_i(\vec{r}) \quad (0.17)$$

with the simple quadrature

$$\sum_i^N |u_i(\vec{r})|^2 = \rho(\vec{r}). \quad (0.18)$$

In this exact single-particle description of many-particle system the kinetic energy $T_s[\rho]$ is introduced with density ρ as if there were no electron-electron interaction.

$$E[\rho] = T_s[\rho] + \int \rho(\vec{r})[v_{ext}(\vec{r}) +$$

$v_J(\text{vecr})$ is the classical Coulomb potential for electrons. It should be emphasized that $E'_{xc}[\rho]$ differs from $E_{xc}[\rho]$ given in eq. (1.19), since the former contains kinetic contribution, which is the difference between $T[\rho]$ and $T_s[\rho]$ [90]. Although $T_s[\rho]$ is different from the true kinetic energy $T[\rho]$, it is of comparable magnitude and is treated exactly in this approach.

$$T_s[\rho] = -1/2 \sum_i^N \int u_i(\vec{r}) \nabla_i u_i(\vec{r}) d\vec{r}. \quad (0.20)$$

The exact treatment of T_s removes many of the deficiencies of the Thomas-Fermi approximation [6], such as the lack of shell structure of atoms or the absence of chemical bonding in molecules and solids [25]. In eq. (1.19) all the terms but the exchange-correlation energy E_{xc} can be evaluated exactly, so that the unavoidable approximations for E_{xc} play a central role in DFT. The central assertion of the Kohn-Sham scheme is that for any ground state density ρ of an interacting system there exists a non-interacting auxiliary system with the same ground state density.

The variational principle applied to (1.19) yields

$$\frac{\delta E[\rho]}{\delta \rho(\vec{r})} = \frac{\delta T_s}{\delta \rho(\vec{r})} + V_{ext}(\vec{r}) + \Phi(\vec{r}) + \frac{\delta E_{xc}[\rho]}{\delta \rho(\vec{r})} = \mu \quad (0.21)$$

where μ is the Lagrange multiplier associated with the constant particle number constraint. The functional derivative of $E_{xc}[\rho]$ with respect to the density is the exchange-correlation potential $v_{xc}([\rho]; \vec{r})$. The mathematical problem is identical with the solution of (1.17) using an auxiliary system of N non-interacting particles with an effective $v_s(\vec{r})$ potential. This can be achieved in a self-consistent procedure. For the interacting and the non-interacting system with the same density the potentials

$$v_s(\vec{r}) = v_{ext}(\vec{r}) + \int \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' + v_{xc}([\rho]; \vec{r}) \quad (0.22)$$

are must be the same within a constant.

The density functional method reduces the many-electron problem exactly to the solution of a single-particle equation of Hartree form. In contrast to the Hartree-Fock potential the effective potential $v_s(\vec{r})$ is *local* and with a local approximation to E_{xc} , the equations present no more numerical complications than the solution of Hartree's equations.

4 Conventional quantum chemical correlation energy versus density functional correlation energy

In quantum chemistry (QC), the exact correlation energy is defined traditionally as the difference between the exact total nonrelativistic energy and the total self-consistent Hartree-Fock (HF) energy [26]:

$$E_c^{conv} = E_{tot} - E^{HF} \quad (0.23)$$

E_{tot} is the nonrelativistic total energy of the system considered [30]. In DFT the correlation energy is a functional of the density $E_c^{DFT}[\rho]$.

$$E_c^{DFT}[\rho] = \langle \Psi[\rho] | \hat{T} + \hat{U} | \Psi[\rho] \rangle - T_s[\rho] - 1/2 \int \frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}d\vec{r}' - E_x^{HF}[u_i^{KS}[\rho]] \quad (0.24)$$

where $u_i^{KS}[\rho]$ are the self-consistent Kohn-Sham orbitals. In practice, of course, neither the quantum chemical nor the DFT correlation energy are known exactly. The two exact correlation energies are generally not identical and they satisfy the inequality

$$E_c^{conv} \geq E_c^{DFT}. \quad (0.25)$$

At a given $v_0(\vec{r})$ external potential characterizing a particular physical system, if the Hohenberg-Kohn total energy functional is defined as

$$E_{v_0}[\rho] = \langle \Psi[\rho] | \hat{T} + \hat{U} + \hat{V}_0 | \Psi[\rho] \rangle, \quad (0.26)$$

the $E_{v_0}[\rho_{exact}]$ is the exact ground-state energy. On the basis of this quantity the following definitions can be given for the conventional

$$E_c^{conv} = E_{v_0}[\rho_{exact}] - E_{v_0}^{HF}[u_i^{HF}[\rho_{HF}]] \quad (0.27)$$

and the DFT correlation energies

$$E_c^{DFT} = E_{v_0}[\rho_{exact}] - E_{v_0}^{HF}[u_i^{KS}[\rho_{exact}]]. \quad (0.28)$$

Comparing these equations we get the central expression for the difference between the definitions given above.

$$E_c^{DFT} = E_c^{conv} + (E_{v_0}^{HF}[u_i^{HF}[\rho_{HF}]] - E_{v_0}^{HF}[u_i^{KS}[\rho_{exact}]]) \quad (0.29)$$

Table 1: Comparison of exact DFT correlation energies with conventional quantum chemical correlation energies (QC) [28]. Δ denotes the difference between the QC and the DFT correlation energy (in Hartree units). Δ denotes the value of $|E_{c,exact}^{QC} - E_{c,exact}^{DFT}|/E_{c,exact}^{DFT}$ in percent.

	DFT	QC	Δ	$\Delta\%$
H⁻	-0.041 995	-0.039 821	+0.002 174	5.2
He	-0.042 107	-0.042 044	+0.000 063	0.2
Be⁺²	-0.044 274	-0.044 267	+0.000 007	0.02
Ne⁺⁸	-0.045 694	-0.045 693	+0.000 001	0.002
Be	-0.096 2	-0.094 3	+0.001 9	2.0
Ne	-0.394	-0.390	+0.004	1.0

This is the central equation relating the DFT correlation energy to the QC correlation energy [27].

5 The molecular correlation problem

The Heitler-London ansatz excludes ionic configurations in the ground-state wavefunction of H_2 and treats the two electrons *strongly correlated*, consequently the two electrons stay completely out of each other's way [1, 36]. The ground-state is a singlet and can be put into the following form:

$$\Phi_{HL}^S(\vec{r}_1, \vec{r}_2) = 1/2[\phi_1(\vec{r}_1)\phi_2(\vec{r}_2) + \phi_2(\vec{r}_1)\phi_1(\vec{r}_2)](\alpha_1\beta_2 - \beta_1\alpha_2). \quad (0.30)$$

The orbital functions $\phi_{1,2}(\vec{r})$ are centered on atoms 1 and 2, and the spinors α and β refer to spin up and spin down, respectively.

The approach of Hartree, Fock and Slater to the many-electron problem was distinctly different. who treated the electrons as being independent of each other and introduced the concept of the self-consistent field [1, 37]. Within the independent-electron approximation [38, 37], the ground-state wavefunction of H_2 is of the form

$$\begin{aligned} \Phi_{HF}^S(\vec{r}_1, \vec{r}_2) = 1/2[\phi_1(\vec{r}_1)\phi_1(\vec{r}_2) + \phi_1(\vec{r}_1)\phi_2(\vec{r}_2) + \phi_2(\vec{r}_1)\phi_1(\vec{r}_2) \\ + \phi_2(\vec{r}_1)\phi_2(\vec{r}_2)](\alpha_1\beta_2 - \beta_1\alpha_2). \end{aligned} \quad (0.31)$$

One notices that the ionic configuration $\phi_1\phi_1$ and $\phi_2\phi_2$ in eq. (1.31) enter with equal weight when compared with the nonionic configurations. Thus, when the two hydrogen atoms are pulled apart, the wavefunction does not reduce properly to the atomic limit (dissociation catastrophe). On the other hand (1.30) does not reduce properly to the correct wavefunction in the limit of small atomic distances. Then it is not useless to expect that the true ground-state lies between the two extremes (1.30) and (1.31). *Electron correlations reduce the ionic configuration relative to the nonionic ones, but they do not reduce them to zero as 0.30 suggests.* The ground-state of the hydrogen molecule provides a simple system for which some qualitative aspects of the correlation problem, which are applicable to systems containing many more electrons, can be examined. The success of the generalized valence-bond model (eq. 0.30) in describing molecular dissociation is attributable to the incorporation of *longitudinal* or *left-right* correlation effects. The left-right correlation of electrons is the tendency of electron **1** to be located in the atomic region **A** when electron **2** is in the region of nucleus **B**. At large nuclear separations close to the dissociation limit, electron **1,(2)** is totally associated with nucleus **A (B)** and longitudinal correlation effects are extremely important [30, 31].

6 Dynamical and nondynamical correlation

It is useful to split correlation energy into *dynamical* and *nondynamical* correlation [12]. Dynamical correlation occurs with a tight pair of electrons and in neutral equilibrium systems accounts for the greatest part of the overall correlation. As a consequence the pair correlation of the doubly occupied orbitals can be taken as the major source of dynamical correlation [30]. Correlation energy functionals developed in the last decade account for the dynamical correlation, however, completely neglect the *nondynamical* correlation [32, 98]. Nondynamical or near-degeneracy correlation is ubiquitous in several fields: in bond-breaking processes at large internuclear distances, in bond rearrangement processes at transition points, in the case of low-lying excited states of the same symmetry also at normal geometries. For heavy-atom systems it is also significant because of the high density of orbital

levels in the valence shell, in particular for open d and f shells as well as in light molecules such as C_2 or O_3 [33]. The main source of nondynamical correlation is degeneracy or near-degeneracy and is associated with the lowering of the energy through interaction of the Hartree-Fock configuration with low-lying excited states. The near-degeneracy correlation is essential for the correct dissociation of a molecule into its constituent atoms. This correlation is therefore a long-range effect, sending electrons to individual atoms as the molecule dissociates, but it then follows that dynamical correlation is a short range effect and it is the reduction in the repulsion energy which arises from the reduction in the value of the wave function when two electrons approach one another.

Many scientists have discussed "in-out", "angular" and "left-right" correlation (longitudinal) (see e.g. [30]). In-out correlation refers to that correlation obtained from double excitation from occupied to excited orbitals of the same angular type, but with more nodes such as $s \rightarrow s'$, $p \rightarrow p'$ or $\sigma_g \rightarrow \sigma_g'$. In atoms this increases the radial separation of electrons. Double excitations from occupied to excited orbitals of different angular type result in angular correlation effect and it increases the angular separation of electrons. It may be shown that such correlation can also be considered dynamical because it introduces the interelectronic distance r_{12} [32]. When left-right correlation contributes significantly to the molecular correlation, it contains nondynamical correlation which accounts for the correct dissociation of molecules as well as for the correct description of chemical bond. The dissociation catastrophe, when the traditional Hartree-Fock single particle model breaks down, represents spurious nondynamical correlation effect [34]. The experimental binding energy of the nitrogen molecule is 0.33 % of the energy of two isolated nitrogen atoms. The correlation energy changes by 44.6 % when the two nitrogen atoms are bound indicating the significance of the left-right correlation in bonding while dynamical correlation is remained almost unchanged [30]. In H_2 at equilibrium distance $E_{corr} \approx 0.041$ a.u., and at infinite separation $E_{corr} \approx 0.25$ a.u. In the latter case a huge non-dynamical correlation energy is "formed" during the dissociation process [32]. While atomic correlation energy do not contain any nondynamical correlation [32], highly positive cations, like Ne^{6+} "suffers" from significant s-p near-

Table 2: **Correlation energies (a.u.) for molecules at r_e .**
 $E_c^{CAS-SCF}$ and E_c^{exp} have been taken from ref [28] and ref. [32].

	E_c^{exp}	CAS-SCF
H_2	0.042	0.019
LiH	0.088	0.017
FH	0.396	0.024
Li_2	0.125	0.009
Be_2	0.207	0.000
N_2	0.560	0.137
F_2	0.771	0.077
CO	0.546	0.123

degeneracy correlation (strong $2s^2 - 2p^2$ mixing [12]). Due to its tightly bound electronic structure the $2s^2$ and $2p^2$ orbitals are represented by nearly degenerate energy levels [35]. Consequently near-degeneracy correlation provides an example for contrary effects to the splitting of energy levels.

In Table 2 the results of complete active space (CAS-SCF) [1, 32] calculations are presented in order to demonstrate the relative importance of the nondynamical correlation in small diatomics. CAS-SCF excludes angular correlation, which is mainly atomic contribution to correlation in molecules (dynamical correlation) and represents multiconfigurational calculations leaving interactions only between configuration space functions (CSFs) constructed from valence orbitals (active space). Single excitation from these orbitals, whose orbital energies are close to the HOMO or Fermi level, have only significant contribution to the nondynamical correlation. Under these conditions presented above $E_c^{ND} = E_{CASSCF} - E_{HF}$.

One of the biggest challenge remained still in DFT is the proper modelling of nondynamical correlation. Unfortunately this problem is often overlooked and little attention is devoted to this type of correlation in the last decades. However, satisfactory prediction of molecular correlation within chemical accuracy requires accurate models for near-degeneracy correlation. *We believe that it is better to model E_c^{ND} at the orbital dependent level rather than as a simple density functional, since*

ND correlation represents subtle effects of nearly degenerated orbitals close to the Fermi level. The overall electronic density is quite insensible to near-degeneracy effect. Orbital dependent ND correlation functional can be then inserted into the exchange-only OEP or KLI equations [11] together with dynamical correlation functionals.

7 The exchange-correlation energy functional $E_{xc}[\rho]$

The most difficult challenge in DFT is the modelling of exchange-correlation part of energy functional (1.19). In the following section exact relations are described concerning $E_{xc}[\rho]$ [29, 39, 104]. First we will show that *coupling-constant integration* accounts for the kinetic contribution to the correlation energy in DFT [29] and provides a way of expressing the $E_{xc}[\rho]$ in terms of a coupling strength integrated pair-correlation function $g(\vec{r}, \vec{r}')$.

Consider the Hamiltonian for a system of N electrons, $H_\lambda = T + V + \lambda W$, where T is the kinetic energy and V contains the interaction with an external potential and W is responsible for the electron-electron interaction multiplied by the coupling constant parameter λ , which can vary between 0 and 1. In addition, we assume that the external potential v_{ext}^λ can be chosen in such a way that the density ρ is independent of λ (unfortunately we are not aware of a specific proof that such a v_{ext}^λ always exists). Because the ground state for any λ is stationary, the change in the wave function affects the energy only in second order. Therefore the expectation value of the derivative of E_λ with respect to λ can be calculated as the expectation value of the derivative of the Hamiltonian with respect to λ . A ground state is minimized for a given λ is denoted by $\langle \rangle_\lambda$. Applying the Hellmann-Feynman theorem for the variation of the ground state energy with λ we have

$$\begin{aligned} \frac{dE_\lambda}{d\lambda} &= \left\langle \Psi_\lambda \left| \frac{\partial \hat{H}_\lambda}{\partial \lambda} \right| \Psi_\lambda \right\rangle = \left\langle \frac{dV_\lambda}{d\lambda} \right\rangle_\lambda = \\ &\quad \langle \Psi_\lambda | \hat{W} | \Psi_\lambda \rangle + \int d\vec{r} \frac{dv_{ext}^\lambda}{d\lambda}(\vec{r}) \hat{\rho}(\vec{r}). \end{aligned} \quad (0.32)$$

Integration can be carried out with eq. (1.32) over λ from 0 to 1. When $\lambda = 1$, we

have the ground-state energy of system of interest. At $\lambda = 0$, the energy is just the noninteracting kinetic energy $T_s[\rho]$ has been given in eq. (1.20). Hence,

$$E = T_s[\rho] + 1/2 \int_0^1 \frac{dE_\lambda}{d\lambda} d\lambda = T_s[\rho] + \int v_{ext}(\vec{r})\rho(\vec{r})d\vec{r} + \int d\vec{r}d\vec{r}' \frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} + E_{xc}[\rho]. \quad (0.33)$$

It is possible to introduce the pair correlation function $g_\lambda(\vec{r}, \vec{r}')$ which incorporates all the correlation effects manifest between the interacting electrons in an inhomogeneous electronic system [41]. One can find that $E_{xc}[\rho]$ is given by the difference of the last term in eq. (1.33) and the ordinary electrostatic interaction.

$$E_{xc}[\rho] = 1/2 \int d\vec{r}d\vec{r}' \frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} \int_0^1 d\lambda [g_\lambda(\vec{r}, \vec{r}') - 1]. \quad (0.34)$$

The integration with respect to λ is the coupling-strength integration [29]. The definition of the exchange-correlation hole can be given by a symmetric function $h(\vec{r}, \vec{r}')$,

$$\rho_{xc}(\vec{r}, \vec{r}') = \rho(\vec{r}')h(\vec{r}, \vec{r}'), \quad (0.35)$$

where

$$h(\vec{r}, \vec{r}') = \int_0^1 d\lambda [g_\lambda(\vec{r}, \vec{r}') - 1]. \quad (0.36)$$

The sum rule also follows that

$$\int \rho_{xc}(\vec{r}, \vec{r}')d\vec{r}' = -1. \quad (0.37)$$

The formula states that the exchange-correlation hole corresponds to the removal of one electron. The exchange-correlation functional can now be interpreted pictorially as the change in the electrostatic energy of the charge distribution produced by the presence of this "hole" around each electron, or equivalently, as the interaction energy between the normal density distribution and the hole.

$E_{xc}[\rho]$ can be put purely into first-order density matrix formalism. The first-order density matrix is given by the following integration over space:

$$\gamma(\vec{r}, \vec{r}') = N \int \Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)\Psi^*(\vec{r}_1', \vec{r}_2', \dots, \vec{r}_N')d\vec{r}_2 \dots d\vec{r}_N, \quad (0.38)$$

where $\Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$ is the wave-function of the system considered. In order to accomplish this task decompose E_{xc} into its exchange and correlation part. Then $E_x[\rho]$ can be expressed easily in terms of first-order density matrix $\gamma(\vec{r}, \vec{r}')$.

$$E_x[\rho] = 1/4 \int \frac{|\gamma(\vec{r}, \vec{r}')|^2}{|\vec{r} - \vec{r}'|} d\vec{r} d\vec{r}'. \quad (0.39)$$

The Fermi "correlation" included here is among electrons of the same spin only since the spin integration gives zero for contributions from different spin states. The exchange-hole in exchange-only approximation (like Hartree-Fock method) can be given on the basis of (1.35).

$$\rho_x(\vec{r}, \vec{r}') = -1/2 \frac{|\gamma(\vec{r}, \vec{r}')|^2}{\rho(\vec{r})}. \quad (0.40)$$

The sum rule (1.37) is satisfied in Hartree-Fock theory:

$$\int \rho_x^{HF}(\vec{r}, \vec{r}') d\vec{r}' = -1 \quad (0.41)$$

Using the decomposition $\rho_{xc} = \rho_x + \rho_c$, Eqns. (1.37) and (1.41) then lead to

$$\int \rho_c(\vec{r}, \vec{r}') d\vec{r}' = 0 \quad (0.42)$$

concerning the correlation hole $\rho_c(\vec{r}, \vec{r}')$. On the basis of the eqns. (1.37) and (1.41) the exchange energy equals the Coulomb interaction energy of the electrons with a charge distribution containing one unit charge, while the correlation energy results from the interaction of the electrons with a neutral charge distribution [104].

The electron correlation can be expressed in terms of first-order density matrices as well [42]. First we introduce the most common definition of the electron-correlation energy functional $E_c[\rho]$ in DFT.

$$E_c[\rho] = \langle \Psi^{\lambda=1} | \hat{T} + \hat{W} | \Psi^{\lambda=1} \rangle - \langle \Psi^{\lambda=0} | \hat{T} + \hat{W} | \Psi^{\lambda=0} \rangle, \quad (0.43)$$

where Ψ^λ is the antisymmetric wave function yielding the electron density ρ and minimizing $\langle \hat{T} + \lambda \hat{V}_{ee} \rangle$, \hat{T} and \hat{V}_{ee} being the operators for the kinetic energy and electron-electron interaction, respectively.

$$E_c[n] = \frac{1}{2} \int_0^1 d\lambda \int dr \nabla_{r'}^2 [\gamma_{\rho_{1/\lambda}}^{\lambda=1}(r, r') - \gamma_{\rho_{1/\lambda}}^{\lambda=0}(r, r')] \Big|_{r=r'}. \quad (0.44)$$

In this equation the first-order density matrices $\gamma_{\rho_{1/\lambda}}^{\lambda=1}(r, r')$ is obtained e.g. in a constrained search procedure [43], when the exact density ρ is the reference density. $\gamma_{\rho_{1/\lambda}}^{\lambda=0}(r, r')$ corresponds to the noninteracting case, when $\Psi^{\lambda=0}$ is the antisymmetric wave function yielding the density ρ and minimizing $\langle \hat{T} \rangle$. Having in hand $E_x[\rho]$ and $E_c[\rho]$ in terms of first-order density matrices the total energy functional $E_{exact}[\rho]$ (1.14) can be written

$$E_{exact}[\rho] = tr(\hat{H}\hat{\gamma}) = \int [(\nabla_r^2 + v_{ext}(\vec{r}))\gamma(\vec{r}, \vec{r}')]_{\vec{r}=\vec{r}'} d\vec{r} \quad (0.45)$$

$$+ 1/2 \int \frac{\gamma(\vec{r}, \vec{r})\gamma(\vec{r}', \vec{r}') - |\gamma(\vec{r}, \vec{r}')|^2}{|\vec{r} - \vec{r}'|} d\vec{r} d\vec{r}'$$

$$- \frac{1}{2} \int_0^1 d\lambda \int dr \nabla_{r'}^2 [\gamma_{\rho_{1/\lambda}}^{\lambda=1}(r, r') - \gamma_{\rho_{1/\lambda}}^{\lambda=0}(r, r')] \Big|_{r=r'}.$$

The pair correlation function introduced in (1.34) can be expressed in terms of first-order density matrices as well using (1.34)-(1.42).

$$g_c([\rho]; \vec{r}, \vec{r}') = 2 \int_0^1 d\lambda \frac{\nabla_r \nabla_{r'} [\gamma_{\rho_{1/\lambda}}^{\lambda=1}(r, r') - \gamma_{\rho_{1/\lambda}}^{\lambda=0}(r, r')] \Big|_{r=r'}}{\gamma_{\rho_{1/\lambda}}^{\lambda=1}(r, r)\gamma_{\rho_{1/\lambda}}^{\lambda=1}(r', r')} |\vec{r} - \vec{r}'| \quad (0.46)$$

$g_c([\rho]; \vec{r}, \vec{r}')$ accounts for spin parallel and anti-parallel Coulomb-correlation as well.

8 $E_{xc}[\rho]$ in homogeneous and inhomogeneous electron systems

The essence of the Kohn-Sham scheme is that the many-body problem is formulated within a single-particle framework, where the many-body nature of the problem enters via an exchange-correlation potential $v_{xc}(\vec{r})$ (1.21-1.22). This potential is defined as a functional derivative of an $E_{xc}[\rho]$ functional. In this perspective it is a virtue of the Kohn-Sham scheme to provide a basis for a single-particle potential $v_{xc}(\vec{r})$ and for the functional

$$E_{xc}[\rho] = \int \rho(\vec{r}) \epsilon_{xc}(\vec{r}) d\vec{r} \quad (0.47)$$

where $\epsilon_{xc}(\vec{r})$ is the exchange-correlation energy density per particle. One of the most popular approximations in DFT to (1.50) is the so-called local density approximation

(LDA) [6]. Though LDA is a fairly crude approximation for $E_{xc}[\rho]$, however, it provides a good description of a large class of properties. In LDA one uses the exchange-correlation energy density of the homogeneous electron liquid $\epsilon_{xc}^{hom}([\rho_0], \vec{r})$ dependent on the homogeneous density ρ_0 and replaces this for the inhomogeneous system with density $\rho(\vec{r})$ by

$$E_{xc}^{LDA}[\rho] = \int d\vec{r} \rho(\vec{r}) \epsilon_{xc}^{hom}([\rho_0], \vec{r}) |_{\rho_0=\rho(\vec{r})}. \quad (0.48)$$

To be specific, LDA, where $\epsilon_{xc}^{hom}([\rho], \vec{r})$ is the exchange-correlation energy density per electron of a homogeneous electron liquid with density $\rho(\vec{r})$, has been employed in most applications of the scheme, in spite of the fact that the true exchange-correlation interaction is manifestly *nonlocal*. The nonlocal behaviour is clear in the case of exchange, which can be obtained when the nonlocal exchange integral operator \hat{K} acts on a spin orbital $u_i(\vec{r})$ as follows.

$$\hat{K}_j(\vec{r})u_i(\vec{r}) = \left[\int d\vec{r}' u_j(\vec{r}') r_{12}^{-1} u_i(\vec{r}') \right] u_j(\vec{r}). \quad (0.49)$$

Unlike to the *local* Coulomb operator, the exchange operator is a nonlocal operator since there does not exist a simple potential $K(\vec{r})$ uniquely defined at a local point in space \vec{r} [1, 36, 37, 38]. The results of operating with the exchange integral operator on a spin orbital depends on the value of the orbital throughout all space. It should be noted here that gradient corrected local density exchange-correlation functionals are sometimes referred to as *nonlocal* functionals. This is an unfortunate choice of terminology as it gives the impression that $E_{xc}[\rho]$ is somehow delocalized in the space. However, gradient correction is accounting only for the local fluctuations in an inhomogeneous electron gas [45] and it does so *locally* by introducing the gradient of the electron density at each point in real space into the $E_{xc}[\rho]$. Nevertheless, throughout the thesis we use the widely accepted name *local* for those density functionals which excludes the gradient of the density.

The exchange-correlation hole in LDA can be given by the coupling constant integrated $g_{xc}^{hom}([\rho]; \vec{r}, \vec{r}')$ pair correlation function of the homogeneous electron gas. Accurate expressions for $g_{xc}^{hom}([\rho]; \vec{r}, \vec{r}')$ are known, however, only the exchange part

is known exactly, which is unaffected by the coupling constant integration.

$$g_x^{hom}([\rho]; \vec{r}, \vec{r}') = 1 - 9/2 \left[\frac{\sin(k_F(\vec{r}) |\vec{r} - \vec{r}'|) - k_F(\vec{r}) |\vec{r} - \vec{r}'| \cos(k_F(\vec{r}) |\vec{r} - \vec{r}'|)}{(k_F(\vec{r}) |\vec{r} - \vec{r}'|)^3} \right]^2 \quad (0.50)$$

where k_F is the local Fermi wavevector [46].

$$k_F(\vec{r}) = [3\pi^2\rho(\vec{r})]^{1/3}. \quad (0.51)$$

The local approximation, generalized in order to describe spin polarization, has provided a remarkably successful description of quite a number of atomic, molecular and solid-state systems and properties [6, 23]. For many of these systems there is no *a priori* justification for using LDA. In some application, LDA is known to give insufficient accuracy and to fail to account for certain features; for instance, it "overbinds" molecules and gives exponentially decaying $v_{xc}(\vec{r})$ for neutral atoms, rather than proper-law behaviour, $1/r$ [44]. Therefore, a considerable amount of activity has been devoted to nonlocal approximations to the exchange-correlation functional [45]-[47]. The $E_{xc}[\rho]$ is given by

$$E_{xc}[\rho] = \int \rho(\vec{r})\epsilon([\rho(\vec{r})])d\vec{r} + \int C([\rho(\vec{r})])\frac{|\nabla\rho(\vec{r})|^2}{\rho^{4/3}(\vec{r})}d\vec{r}, \quad (0.52)$$

where $C([\rho(\vec{r})])$ is a function of the density. In the simple case of weak density variations, however, the gradient correction do not seem to improve upon the LDA [48]. LDA is formally justified for homogeneous systems with slowly-varying densities [6], however, most of the real systems, like atoms, molecules or solids contain rapidly varying density, and it is somewhat understandable, why LDA works quite efficiently for such a systems. In uniform electron gas the electron density is in the presence of small (external) charge while in the presence of atomic nuclei one has nonuniform electron gas especially close to the nuclei (inner region). The expected main reason is the fact that LDA satisfies the criterion of charge conservation, starting that the exchange-correlation hole should contain exactly one electron as it follows from the sum rule (1.37). The sum rule can be taken as one of the strongest known constraints upon approximation to exchange-correlation.

Let us now consider systems in which the density is slowly varying on the scale

of the local value of $k_F(\vec{r})$, i.e.

$$|\nabla\rho(\vec{r})|/\rho(\vec{r}) \ll k_F(\vec{r}), \quad (0.53)$$

We emphasize that the condition 0.53 does not exclude large variations of ρ , provided they occur over sufficiently large distances. Under these conditions we have almost constant density, i.e. $\rho(\vec{r}) = \rho_0 + \delta\rho(\vec{r})$ together with $\int \delta\rho(\vec{r})d\vec{r} = 0$ the summation of subseries of gradient terms in this limit gives to the lowest order in the inhomogeneity $\delta\rho$ [45],

$$E_{xc}[\rho] \simeq \int \rho(\vec{r})\epsilon_{xc}([\rho(\vec{r})])d\vec{r} - 1/4 \int K_{xc}(\vec{r} - \vec{r}', \rho)[\rho(\vec{r}) - \rho(\vec{r}')]^2 d\vec{r}d\vec{r}', \quad (0.54)$$

where K_{xc} is directly related to the dielectric function of the homogeneous electron liquid of density ρ [23] and can be obtained from the static density-density response function of the homogeneous electron gas of density ρ [44].

9 Exchange-correlation in homogeneous electron gas

The homogeneous electron gas or liquid is a hypothetical system which has no true counterpart in the real world. Nevertheless, a great deal of work has been devoted to it. The interacting homogeneous electron gas, also known as the free electron gas or the jellium model, is an example of a translationally invariant system. This particular system can be taken as a model for many metals, if we deal with the drastic assumption that the charge density of the positive "background" of the metal is uniformly smeared out over the volume of the system so that the electrons can move practically freely through the material. The positive "background" of the model system must be taken as ions with hard core electrons form closed shell. The valence electrons are then weakly bound and are therefore only weakly localized in the crystal lattice. One can expect then that the electron gas gives some reasonable results for several properties of alkali metals [23, 24]. The uniform electron gas model (or simply uniform limit) is frequently used as common test case for different density functionals [15, 14, 46] as well as for the understanding of the homogeneous

system which is necessary as a starting point for theories of inhomogeneous systems. In order to get further insight into the problems of electron gas we give the brief derivation of some local correlation functionals.

The complete Hamiltonian for the electron gas is

$$\hat{H} = \hat{H}_i + \hat{H}_e + \hat{V}_{e-i}. \quad (0.55)$$

Here \hat{H}_i is the electrostatic energy of the background ions:

$$\hat{H}_i = e^2/2 \int d\vec{R}d\vec{R}' \frac{(N/\Omega)^2}{|\vec{R} - \vec{R}'|} \quad (0.56)$$

which is a simple constant (fixed crystal lattice is considered). \hat{H}_e contains the kinetic energy of the electrons as well as their mutual Coulomb repulsion

$$\hat{H}_e = \sum_{i=1}^N \frac{\hat{p}_i^2}{2m} + 1/2 \sum_{\substack{i,j=1 \\ i \neq j}}^N \frac{e^2}{|\vec{r}_i - \vec{r}_j|} \quad (0.57)$$

and \hat{V}_{e-i} is the interaction of the electrons with the background ions (external potential). With the imposition of periodic boundary conditions in a cube of volume Ω the Coulomb potential can be expanded in a Fourier series [24]. Let us focus on the kinetic and electronic part of the Hamiltonian only here. The Hartree-Fock energy per particle can be given for the spinpolarized electron gas as follows:

$$\begin{aligned} E_{HF}^{el.gas}/N &= \frac{\hbar^2}{10m2\pi^2} \frac{1}{(N/\Omega)} (\vec{k}_+^5 + \vec{k}_-^5) \\ &\quad - \frac{1}{2(N/\Omega)} \int_0^{\vec{k}_+} \int_0^{\vec{k}_+} \frac{d^3\vec{k}}{(2\pi)^3} \frac{d^3\vec{k}'}{(2\pi)^3} \frac{4\pi e^2}{|\vec{k} - \vec{k}'|^2} \\ &\quad - \frac{1}{2(N/\Omega)} \int_0^{\vec{k}_-} \int_0^{\vec{k}_-} \frac{d^3\vec{k}}{(2\pi)^3} \frac{d^3\vec{k}'}{(2\pi)^3} \frac{4\pi e^2}{|\vec{k} - \vec{k}'|^2}. \end{aligned} \quad (0.58)$$

The density itself equals with

$$\rho = \frac{2}{(2\pi)^3} \frac{4\pi}{3} k_F^3 \quad (0.59)$$

where $(2\pi)^{-3}$ factor is coming from the phase space, where the volume is h^3 , factor of 2 is responsible for the two spin directions. k_F is the radius of the Fermi-sphere.

We give the brief derivation of the exchange integrals. If we take z -axis in the integration over \vec{k}' to be parallel to \vec{k} . Thus

$$|\vec{k} - \vec{k}'|^2 = k^2 + k'^2 - 2kk'\cos\Theta \quad (0.60)$$

where Θ is the angle between \vec{k}' and \vec{k} . With this inserted in the exchange

$$\begin{aligned} \frac{4\pi e^2}{(2\pi)^3} \int_0^{k_{\pm}} \frac{d^3\vec{k}'}{|\vec{k} - \vec{k}'|^2} = \\ \frac{4\pi e^2}{(2\pi)^3} \int_0^{k_{\pm}} k' dk' \int_0^{\pi} \int_0^{2\pi} \frac{\sin\Theta d\Theta d\phi}{k^2 + k'^2 - 2kk'\cos\Theta}. \end{aligned} \quad (0.61)$$

For the exchange integral we obtained the following expression by elementary methods:

$$\epsilon_k^{\pm} = \frac{\hbar^2 k^2}{2m} - \frac{e^2}{\pi} \left[k_{\pm} + \frac{1}{2k}(k_{\pm}^2 - k^2) \ln \left| \frac{k_{\pm} + k'}{k_{\pm} - k} \right| \right]. \quad (0.62)$$

The exchange-contribution to the total energy per particle can be evaluated by one additional one-dimensional integration over k which can be done by elementary integration as well.

$$\begin{aligned} E_{HF}^{el.gas}/N = \frac{\hbar^2}{10m2\pi^2} \frac{1}{(N/\Omega)} (\vec{k}_+^5 + \vec{k}_-^5) \\ - \frac{e^2}{(2\pi)^3} \frac{1}{(N/\Omega)} (\vec{k}_+^4 + \vec{k}_-^4). \end{aligned} \quad (0.63)$$

One can gain another representation of this result in terms of the Wigner-Seitz radius r_s [73]. This quantity is defined as the radius of the sphere that contains the volume per particle of the system.

$$\Omega/N = \frac{4\pi}{3} r_s^3. \quad (0.64)$$

If we use this definition in equation (1.61) and furthermore express all lengths in units of the Bohr radius $a_0 = \hbar^2/(me^2)$, we obtain for the Hartree-Fock energy of the spin-unpolarized electron gas

$$E_{HF}^{el.gas}/N = \frac{e^2}{2a_0} \left[\frac{2.21}{r_s^2} - \frac{0.916}{r_s} \right]. \quad (0.65)$$

It can be proved that the exchange term is the first order term in perturbation theory, if the entire interaction is regarded as a perturbation. The zeroth order terms

immediately give us the kinetic energy of the electron gas [24]. At this point the question arises as to whether we can obtain parts of the correlation energy in the same way by including higher order terms in the perturbation expansion. It turned out that every order in perturbation theory beyond the first order diverges. Only in special cases managed to get sensible results by diagrammatical methods for the limiting case of $r_s \rightarrow 0$ e.g. The difficulty can be overcome in another way if we realize that the main reason of the divergence of the higher order perturbation terms originates in the long-range tail of the Coulomb potential. Hence, one thing that seems natural to do is to divide the total Coulomb interaction into a short-range and a long-range parts. The short-range part then can be calculated by perturbation theory, since this part should not give rise to divergent expressions. However, nonperturbative approach is required to calculate the long-range correlation energy. The division into long- and short-range parts can be done in the following way:

$$\hat{H} = \sum_i \frac{\hat{p}_i^2}{2m} + 1/2 \sum_{i \neq j} \sum_{k \neq 0} \frac{4\pi e^2}{\Omega k^2} e^{i\vec{k}(\vec{r}_i - \vec{r}_j)} = \sum_i \frac{\hat{p}_i^2}{2m} + \hat{V}_{sr} + \hat{V}_{lr} \quad (0.66)$$

where

$$\hat{V}_{sr} = 1/2 \sum_{i \neq j} \sum_{k > k_c} \frac{4\pi e^2}{\Omega k^2} e^{i\vec{k}(\vec{r}_i - \vec{r}_j)} \quad (0.67)$$

and

$$\hat{V}_{lr} = 1/2 \sum_{i \neq j} \sum_{\substack{k < k_c \\ k \neq 0}} \frac{4\pi e^2}{\Omega k^2} e^{i\vec{k}(\vec{r}_i - \vec{r}_j)}. \quad (0.68)$$

Here the limiting momentum k_c is a suitably chosen constant. The short-range correlation energy from second-order perturbation theory,

$$E_{corr}^{sr} = - \sum_n \frac{\left| \langle \Phi_n | \hat{V}_{sr} | \Phi_0 \rangle \right|^2}{E_n - E_0}. \quad (0.69)$$

Here Φ_0 is the Slater determinant of plane waves in the ground state occupation and E_0 is the corresponding kinetic energy (the expectation value of \hat{H}_0). The summation runs in principle over the complete system of all configurations Φ_n , which can be constructed from plane waves. However, the matrix element vanishes whenever Φ_n differs from Φ_0 in more than the configuration of two orbitals. The remaining terms

can be integrated approximately. The dominant contributions in (k_c/k_F) are

$$E_{corr}^{sr}/N = \left[\frac{2}{\pi}(1 - \ln 2) \ln(k_c/k_F)^2 \right] \frac{e^2}{2a_0} + C. \quad (0.70)$$

Incorporating the Coulomb energy of the lattice, the harmonic lattice vibration energy and first-order anharmonic corrections, one get for k_c [23, 24],

$$k_c = 0.667r_s^{-1/2} = 0.353r_s^{1/2}k_F, \quad (0.71)$$

and for the low-density limit (long-range part)

$$E_{corr}^{lr}/N = -\frac{0.876}{r_s} + \frac{2.76}{r_s^{3/2}} - \frac{2.94}{r_s^2}. \quad (0.72)$$

For the intermediate density range Wigner suggested the following analytical parametrization [73, 103]:

$$E_c^W = -\int d\vec{r} \frac{0.88}{7.8 + r_s}. \quad (0.73)$$

Furthermore we should mention here the correlation functional of Gell-Mann and Brueckner [49] which was obtained analytically in the high density limit,

$$E_c^{GB} = \int d\vec{r} \frac{2(1 - \ln 2)}{\pi^2} \ln r_s - 0.142 \quad (0.74)$$

10 Levy's constrained-search formulation

It is possible to apply a variational procedure which is "constrained" because the space of trial wave functions comprises only those that give the reference density $\rho_0(\vec{r})$, in contrast to the search for the minimum of $\langle \Psi | \hat{T} + \hat{W} + \sum_i^N v_{ext}(\vec{r}_i) | \Psi \rangle$ which is unconstrained (except for normalization) because the space of trial wave functions is the whole N-particle Hilbert space. The constrained-search formula eliminates the v-representability constraint on the domain of variation in the Hohenberg-Kohn variational principle (1.11). One can divide the ground-state energy minimization procedure of Levy [6, 43] into two steps:

$$E_0 = \underset{\Psi}{Min} \langle \Psi | \hat{T} + \hat{W} + \sum_i^N v_{ext}(\vec{r}_i) | \Psi \rangle \quad (0.75)$$

$$\begin{aligned}
&= \text{Min}_{\rho} \left\{ \text{Min}_{\Psi} \rightarrow \rho \langle \Psi | \hat{T} + \hat{W} + \sum_i^N v_{ext}(\vec{r}_i) | \Psi \rangle \right\} \\
&= \text{Min}_{\rho} \left\{ \text{Min}_{\Psi \rightarrow \rho} \langle \Psi | \hat{T} + \hat{W} | \Psi \rangle + \int v_{ext}(\vec{r}) \rho(\vec{r}) d\vec{r} \right\}
\end{aligned}$$

In the second line here, the inner minimization is constrained to all wave functions that give $\rho(\vec{r})$, while the outer minimization releases this constraint by searching all $\rho(\vec{r})$. The variation in (1.75) is easier to carry out than in eq. (1.11) since it requires no more than nonnegativity, proper normalization, and continuity of the trial densities. The v-representability problem in the original approach has been eliminated.

Correlation energy density from *ab initio* first- and second-order density matrices: a benchmark for approximate functionals

11 Abstract

In this chapter a procedure is introduced to construct numerically the exchange-correlation $\epsilon_{xc}(\vec{r})$ and correlation $\epsilon_c(\vec{r})$ energy densities of density functional theory using the correlated first- and second-order density matrices from *ab initio* calculations. $\epsilon_c(\vec{r})$ as well as its kinetic and potential components are obtained for the two-electron *He* atom and *H*₂ molecule. The way various correlation effects manifest themselves in the form of $\epsilon_c(\vec{r})$ is studied. The $\epsilon_c(\vec{r})$ is compared with some density functional local and gradient-corrected models $\epsilon_c^{mod}(\vec{r})$. The investigation of the shape of the model energy densities $\epsilon_c^{mod}(\vec{r})$ is extended to the *Be*₂ and *F*₂ molecules and the corresponding correlation energies E_c have been calculated and discussed for a number of atomic and molecular systems. The results show the importance of a proper modelling of $\epsilon_c(\vec{r})$ in the molecular bond midpoint region.

12 Introduction

In the past few years there has been considerable progress within DFT [6] in the calculation of various properties of electronic systems. This progress is mainly due to the introduction of gradient-corrected exchange-correlation functionals [14, 16] (see also eqs. (1.52-1.54)) that give an overall improvement over LDA. For instance the atomisation energies of a representative set of molecules are improved significantly, thereby correcting the notorious overbinding of LDA [89, 88]. Therefore it follows that one of the important advantages of density functional theory consists in its efficient treatment of the Coulomb correlation in many-electron systems. The correlation energy functional $E_c[\rho]$ as well as the more general exchange-correlation

energy functional $E_{xc}[\rho]$ are represented in DFT with the following integrals

$$E_{xc}[\rho] = E_x[\rho] + E_c[\rho], \quad (0.1)$$

$$E_{xc}[\rho] = \int e_{xc}([\rho]; \vec{r}) d\vec{r}, \quad (0.2)$$

$$E_c[\rho] = \int e_c([\rho]; \vec{r}) d\vec{r}, \quad (0.3)$$

$$e_{xc}([\rho]; \vec{r}) = \rho(\vec{r}) \epsilon_{xc}([\rho]; \vec{r}), \quad (0.4)$$

$$e_c([\rho]; \vec{r}) = \rho(\vec{r}) \epsilon_c([\rho]; \vec{r}). \quad (0.5)$$

Here $E_x[\rho]$ is the exchange energy functional, preferably defined in terms of the Kohn-Sham orbitals, e_{xc} and e_c are the exchange-correlation and correlation energy densities, ϵ_{xc} and ϵ_c are the corresponding energy densities per particle and ρ is the electron density. Modelling of $\epsilon_c([\rho]; \vec{r})$ with approximate functionals became an essential part of the development of DFT [6, 23].

Usually, approximate functional forms of $\epsilon_c([\rho]; \vec{r})$ are derived from the homogeneous or inhomogeneous electron gas models [50] with due account of various scaling and asymptotic properties and with the parameters fitted to reproduce E_c values for selected atomic systems. The parameters can also be obtained non-empirically from sum-rule conditions[51]. However, the form of ϵ_c as a function of the electron coordinate \vec{r} is seldom taken into consideration and little is still known about the local behavior of the standard ϵ_c models.

A possible reason for this is that eq.0.3 does not define e_c uniquely, since the same E_c value can be obtained with different functionals $e_c(\vec{r})$ and $e'_c(\vec{r}) = e_c(\vec{r}) + f(\vec{r})$ whose difference $f(\vec{r})$ integrates to zero

$$\int f(\vec{r}) d\vec{r} = 0. \quad (0.6)$$

Nevertheless, in order to perform a consistent analysis of correlation effects and to provide a physically reasonable modelling of ϵ_c , one can choose some suitable definition of $\epsilon_c(\vec{r})$ using a particular expression for E_c in terms of a spatial integral over an integrand that is expressed in terms of partially integrated many-electron wavefunctions. Examples of accurate $\epsilon_c(\vec{r})$ obtained in this way for a variety of atoms and molecules, although non-unique, can be helpful for the modelling of accurate

$\epsilon_c(\vec{r})$. Uniqueness is examined in a somewhat detailed manner in Chapter 3 and in Appendix A.

In this paper a procedure is proposed to construct ϵ_{xc} and ϵ_c numerically using correlated first- and second-order density matrices from *ab initio* calculations. This scheme is applicable to an arbitrary many-electron system, however, in this paper we restrict its application to two-electron systems. $\epsilon_c(\vec{r})$ as well as its kinetic $t_c(\vec{r})$ and potential $w_c(\vec{r})$ components are obtained for the *He* atom and *H₂* molecule (in the latter case for both equilibrium internuclear distance and near-dissociation limit). The corresponding functions $e_c(\vec{r})$ are compared with the gradient-dependent models $e_c^{mod}(\vec{r})$ of Perdew and Wang (PW) [15, 52], Lee, Yang and Parr (LYP) [20], Wilson and Levy [35], and also with some local models [53, 54]. To further examine the observed trends, the form of $e_c^{mod}(\vec{r})$ is investigated for the *Be₂* and *F₂* molecules and E_c values are calculated and discussed for a number of atomic and molecular systems.

13 Definition and construction of ϵ_{xc} and ϵ_c

The coupling-strength integration given in eq. (1.34) provides an alternative way of defining correlation energy: it can be constructed from its potential and kinetic contributions [55], $E_c[\rho] = W_c[\rho] + T_c[\rho]$. The main reason for this partition of E_c is the equality $E_c = -T_c$ which does not hold in DFT (for detailed explanation see Chapter 3).

To define ϵ_{xc} and ϵ_c , we use the following expressions for E_{xc} and E_c [55]

$$E_{xc}[\rho] = \frac{1}{2} \int \rho(\vec{r}) w_{xc}(\vec{r}) d\vec{r} + \int \rho(\vec{r}) [v_{kin}(\vec{r}) - v_{s,kin}(\vec{r})] d\vec{r}, \quad (0.7)$$

$$E_c[\rho] = \frac{1}{2} \int \rho(\vec{r}) w_c(\vec{r}) d\vec{r} + \int \rho(\vec{r}) [v_{kin}(\vec{r}) - v_{s,kin}(\vec{r})] d\vec{r}. \quad (0.8)$$

The first terms of eqs.0.7,0.8 are the potential contributions to E_{xc} and E_c , with w_{xc} and w_c being potentials of the exchange-correlation and correlation holes, respec-

tively

$$w_{xc}(\vec{r}_1) = \int \frac{\rho_2^{\lambda=1}(\vec{r}_1, \vec{r}_2) - \rho(\vec{r}_1)\rho(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|\rho(\vec{r}_1)} d\vec{r}_2 = \int \frac{\rho(\vec{r}_2)[g^{\lambda=1}(\vec{r}_1, \vec{r}_2) - 1]}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_2, \quad (0.9)$$

$$w_c(\vec{r}_1) = \int \frac{\rho_2^{\lambda=1}(\vec{r}_1, \vec{r}_2) - \rho_{2s}(\vec{r}_1, \vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|\rho(\vec{r}_1)} d\vec{r}_2 = \int \frac{\rho(\vec{r}_2)[g^{\lambda=1}(\vec{r}_1, \vec{r}_2) - g_s(\vec{r}_1, \vec{r}_2)]}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_2. \quad (0.10)$$

In eqns. (0.9,0.10) $\rho_2^{\lambda=1}(\vec{r}_1, \vec{r}_2)$ and $g^{\lambda=1}(\vec{r}_1, \vec{r}_2)$ are the diagonal part of the second-order density matrix and the pair-correlation function with the electron interaction λ/r_{12} at full strength, $\lambda = 1$, while $\rho_{2s}(\vec{r}_1, \vec{r}_2)$ and $g_s(\vec{r}_1, \vec{r}_2)$ correspond to $\lambda = 0$, i.e. the one-determinantal wavefunction Ψ_s built from the Kohn-Sham orbitals $\phi_i(\vec{r})$

$$\rho_{2s}(\vec{r}_1, \vec{r}_2) = \rho(\vec{r}_1)\rho(\vec{r}_2) - \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N \phi_i(\vec{r}_1)\phi_i^*(\vec{r}_2)\phi_j^*(\vec{r}_1)\phi_j(\vec{r}_2). \quad (0.11)$$

$w_c(\vec{r})$ represents the potential of the full exchange-correlation hole density minus the exchange-only hole density of the Kohn-Sham determinant, i.e. the potential of the Coulomb hole.

Eqns. (0.7,0.8) have the same second term, which is the kinetic contribution to E_c with the local potential $v_{kin}(\vec{r})$ being defined as follows [56]

$$\begin{aligned} v_{kin}(\vec{r}_1) &= \frac{1}{2} \int |\nabla_1 \Phi(s_1, \vec{x}_2, \dots, \vec{x}_N | \vec{r}_1)|^2 ds_1 d\vec{x}_2 \dots d\vec{x}_N = \\ &= \frac{\nabla_{1'} \nabla_1 \rho^{\lambda=1}(\vec{r}_1', \vec{r}_1)|_{\vec{r}_1'=\vec{r}_1}}{2\rho(\vec{r}_1)} - \frac{[\nabla \rho(\vec{r}_1)]^2}{8\rho^2(\vec{r}_1)}. \end{aligned} \quad (0.12)$$

In eq. (0.12) $\Phi(s_1, \vec{x}_2, \dots, \vec{x}_N | \vec{r}_1)$ is the conditional probability amplitude [57] of the total wavefunction $\Psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N)$ ($\{\vec{x}_i\} = \{\vec{r}_i, s_i\}$, $\{\vec{r}_i\}$ are the space and $\{s_i\}$ are the spin variables)

$$\Phi(s_1, \vec{x}_2, \dots, \vec{x}_N | \vec{r}_1) = \frac{\Psi(\vec{x}_1, \dots, \vec{x}_N)}{\sqrt{\rho(\vec{r}_1)/N}} \quad (0.13)$$

and $\rho^{\lambda=1}(\vec{r}_1', \vec{r}_1)$ is the first-order density matrix for $\lambda = 1$. $\Phi(s_1, \vec{x}_2, \dots, \vec{x}_N | \vec{r}_1)$ embodies all effects of electron correlation (exchange as well as Coulomb) in that its square is the probability distribution of the remaining $N-1$ electrons associated with positions $\vec{x}_2, \dots, \vec{x}_N$ when one electron is known to be at \vec{r}_1 . v_{kin} can be interpreted as a measure of how strongly the motion of the reference electron at \vec{r}_1 is correlated

with other electrons in the system, in the sense that it reflects the magnitude of change in Φ with changing \vec{r}_1 (so it is a measure of the *change* in correlation hole with reference position \vec{r}_1). $v_{s,kin}$ is defined analogously to v_{kin} in terms of the Kohn-Sham functions

$$\begin{aligned} v_{s,kin}(\vec{r}_1) &= \frac{1}{2} \int |\nabla_1 \Phi_s(s_1, \vec{x}_2, \dots, \vec{x}_N | \vec{r}_1)|^2 ds_1 d\vec{x}_2 \dots d\vec{x}_N = \\ &= \frac{1}{2} \sum_{i=1}^N \left| \nabla_1 \frac{\phi_i(\vec{r}_1)}{\rho^{\frac{1}{2}}(\vec{r}_1)} \right|^2, \end{aligned} \quad (0.14)$$

$$\Phi_s(s_1, \vec{x}_2, \dots, \vec{x}_N | \vec{r}_1) = \frac{\Psi_s(\vec{x}_1, \dots, \vec{x}_N)}{\sqrt{\rho(\vec{r}_1)/N}}. \quad (0.15)$$

From eqns. (0.7,0.8) one can define ϵ_{xc} and ϵ_c as follows

$$\epsilon_{xc}(\vec{r}) = \frac{1}{2} w_{xc}(\vec{r}) + v_{kin}(\vec{r}) - v_{s,kin}(\vec{r}), \quad (0.16)$$

$$\epsilon_c(\vec{r}) = \frac{1}{2} w_c(\vec{r}) + v_{kin}(\vec{r}) - v_{s,kin}(\vec{r}). \quad (0.17)$$

Note, that in DFT alternative definitions of ϵ_{xc} and ϵ_c are often used, in which they are expressed via integrals over the coupling parameter λ [114, 113], see also eq. (1.36),

$$\epsilon_{xc}(\vec{r}_1) = \int \int_0^1 \frac{\rho(\vec{r}_2) [g^\lambda(\vec{r}_1, \vec{r}_2) - 1]}{|\vec{r}_1 - \vec{r}_2|} d\lambda d\vec{r}_2, \quad (0.18)$$

$$\epsilon_c(\vec{r}_1) = \int \int_0^1 \frac{\rho(\vec{r}_2) [g^\lambda(\vec{r}_1, \vec{r}_2) - g_s(\vec{r}_1, \vec{r}_2)]}{|\vec{r}_1 - \vec{r}_2|} d\lambda d\vec{r}_2. \quad (0.19)$$

In this paper, however, we choose definitions (0.16,0.17) as more convenient ones for our purpose. Having available functions $\rho(\vec{r}_1)$, $\rho(\vec{r}_1', \vec{r}_1)$, $\rho_2(\vec{r}_1, \vec{r}_2)$, $\{\phi_i(\vec{r}_1)\}$ for a real system with $\lambda = 1$, one can calculate ϵ_{xc} and ϵ_c via eqs. (0.16,0.17), so knowledge concerning the dependence on λ is not needed.

Bearing this in mind, we propose to construct $\epsilon_{xc}(\vec{r})$ and $\epsilon_c(\vec{r})$ as well as the exchange-correlation Kohn-Sham potential $v_{xc}(\vec{r})$ numerically by a combined procedure from the correlated first- and second-order density matrices obtained with *ab initio* calculations. This procedure is based on recently proposed methods [60, 61, 118] to construct $v_{xc}(\vec{r})$ and $\{\phi_i(\vec{r})\}$ from $\rho(\vec{r})$ for general atomic and molecular systems (cf. also refs. [62, 63, 64, 65, 66] for earlier v_{xc} determinations/proposals).

The procedure consists of the following steps:

- 1) A set $\{\phi_i(\vec{r})\}$ and $v_{xc}(\vec{r})$ are obtained from the correlated $\rho(\vec{r})$ using one of the abovementioned methods. We use the simple and efficient method of ref. [61] (a similar method has been developed in [60]), which has recently been successfully applied to molecules [67].
- 2) $v_{kin}(\vec{r})$ is calculated from correlated $\rho(\vec{r}', \vec{r})$ via eq. (0.12) and $w_{xc}(\vec{r})$ is calculated from $\rho(\vec{r})$ and $\rho_2(\vec{r}_1, \vec{r}_2)$ via eq. (0.9).
- 3) $v_{s,kin}(\vec{r})$ is calculated from $\{\phi_i(\vec{r})\}$ and $\rho(\vec{r})$ via eq. (0.14) and $w_c(\vec{r})$ is calculated from $w_{xc}(\vec{r})$ and $\{\phi_i(\vec{r})\}$ via eqs. (0.9-0.11).
- 4) The energy densities $\epsilon_{xc}(\vec{r})$, $\epsilon_c(\vec{r})$, $e_{xc}(\vec{r})$, $e_c(\vec{r})$ are obtained according to 0.4, 0.5, 0.16, 0.17.

This scheme can be taken as a constrained search procedure (see eq. 1.75) [43], whereas the reference density is the fully correlated CI density. For two-electron systems this procedure is essentially simplified, since in this case there is only one occupied Kohn-Sham orbital $\phi_1(\vec{r})$, equal (up to a phase factor) to $\rho^{\frac{1}{2}}(\vec{r})/\sqrt{2}$. Therefore, the first step of the procedure is effectively eliminated and $\epsilon_{xc}(\vec{r})$, $\epsilon_c(\vec{r})$ can be calculated directly from $\rho(\vec{r}', \vec{r})$ and $\rho_2(\vec{r}_1, \vec{r}_2)$. In particular, by the definition 0.14, $v_{s,kin}$ vanishes for a two-electron system, so that $\epsilon_c(\vec{r})$ turns into

$$\epsilon_c(\vec{r}) = \frac{1}{2}w_c(\vec{r}) + v_{kin}(\vec{r}). \quad (0.20)$$

Exchange in this case reduces to a pure electron self-interaction and $w_c(\vec{r})$ transforms into

$$w_c(\vec{r}_1) = \int \frac{\rho(\vec{r}_2)[g^{\lambda=1}(\vec{r}_1, \vec{r}_2) - \frac{1}{2}]}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_2. \quad (0.21)$$

The function (0.20) contains interesting information about the local effect of the Coulomb correlation of two electrons with opposite spins.

In this paper $\epsilon_c(\vec{r})$ (with its kinetic $v_{kin}(\vec{r})$ and potential $\frac{1}{2}w_c(\vec{r})$ components) and $e_c(\vec{r})$ are obtained for the two-electron *He* atom and *H₂* molecule in order to study the local effect of correlation in these simple cases and to provide the first example of accurate correlation energy densities calculated from correlated wavefunctions. These functions has been obtained from full configuration interaction (CI) calculations of the ground states of *He* and *H₂* in a basis of contracted Gaussian functions.

For He the basis has been used, which was obtained in [56, 68] by expansion of the Slater-type functions of a $5s, 4p, 3d$ basis [69] in six Gaussians (STF-6GF). CI calculation in this basis yields $E_c = -0.041$ a.u., i.e. more than 97 % of the correlation energy is recovered for He .

For the H_2 molecule calculations have been performed at the equilibrium distance $R(H - H) = 1.401$ a.u. and also in the near-dissociation limit at $R(H - H) = 5.0$ a.u. A basis with five s- and two p-type functions [70, 71] and an extra d-type Gaussian with the exponent $\alpha = 1.0$ has been used for the H atoms. In this basis $E_c = -0.039$ a.u. has been obtained for the equilibrium distance, which corresponds to more than 95 % of the correlation energy. Calculation of $\rho(\vec{r}', \vec{r})$ and $\rho_2(\vec{r}_1, \vec{r}_2)$ from the full CI wavefunctions with the subsequent construction of $v_{kin}(\vec{r})$ and $w_c(\vec{r})$ has been performed with a specialized density functional extension [56, 68] of the *ab initio* ATMOL package [72]. The functions $\epsilon_c(\vec{r})$ and $e_c(\vec{r})$ thus obtained will be presented and compared with the corresponding local and gradient-dependent models in the next sections.

14 Model functionals $\epsilon_c([\rho]; \vec{r})$

The model functionals $\epsilon_c([\rho]; \vec{r})$ to be compared here with each other and with those obtained from *ab initio* calculations are the local density approximation (LDA) in the parameterization of Perdew and Wang [106], the local Wigner (LW) function [73] and the gradient-dependent PW [60, 16], LYP [20] and WL [35] models. The LDA function $\epsilon_c^{LDA}(r_s)$ [106] represents the dependence of the correlation energy density per electron of the homogeneous electron gas model [50] on the Wigner radius r_s

$$r_s = \left[\frac{3}{4\pi\rho} \right]^{\frac{1}{3}} \quad (0.22)$$

in a wide range of densities (here we consider closed-shell systems with the spin-polarization parameter ζ being equal to zero). $\epsilon_c^{LDA}(r_s)$ interpolates between the logarithmic dependence on r_s in the high-density limit [74] and the inverse-power dependence on r_s in the low-density limit (the Wigner crystal) [73].

The PW model $\epsilon_c^{PW}(r_s, \nabla\rho(\vec{r}))$ [15, 16] is the gradient extension of the LDA

$$\epsilon_c^{PW}(r_s, \nabla\rho(\vec{r})) = \epsilon_c^{LDA}(r_s) + H(r_s, \nabla\rho(\vec{r})) \quad (0.23)$$

with the correction term $H(r_s, \nabla\rho(\vec{r}))$ being, essentially, a logarithmic function of the Padé approximant of the argument t

$$t = c \frac{|\nabla\rho(\vec{r})|\sqrt{r_s}}{\rho(\vec{r})}. \quad (0.24)$$

The parameters of $H(r_s, \nabla\rho(\vec{r}))$ were fitted to reproduce the integral 0.19 of the model correlation hole, the latter being obtained with the real space cut-off of the correlation hole function of the second-order gradient expansion approximation (GEA) [51].

The rest of the model functionals to be considered can be defined as Wigner-like functionals, which are represented with the following formula

$$\epsilon_c^{mod}([\rho]; \vec{r}) = \frac{a}{c + f_1(\rho(\vec{r}), \nabla\rho(\vec{r})) + r_s} + f_2(\rho(\vec{r}), \nabla\rho(\vec{r})). \quad (0.25)$$

In the simplest case $f_1 = f_2 = 0$ and (0.25) reduces to the LW function [73], which interpolates between the inverse dependence on r_s in the low-density limit and the typical correlation energy per electron for a certain type of systems for higher densities. Various modifications of the LW function were proposed in the literature with the parameters determined to reproduce correlation of the valence electrons in metals [53] or E_c values of certain atoms [75]. In this paper we use the LW function with the parameters $a = -0.02728$ and $c = 0.21882$, which have been fitted in [76] to reproduce the conventional E_c values [77] of eight closed-shell atomic systems $He, Li^+, Be^{2+}, Be, B^+, Ne, Mg, Ar$.

With f_1 and f_2 of the following form

$$f_1(\rho(\vec{r}), \nabla\rho(\vec{r})) = d \frac{|\nabla\rho(\vec{r})|}{\left(\frac{\rho(\vec{r})}{2}\right)^{\frac{4}{3}}}, \quad (0.26)$$

$$f_2(\rho(\vec{r}), \nabla\rho(\vec{r})) = b \frac{|\nabla\rho(\vec{r})|}{\rho^{\frac{4}{3}}(\vec{r})[c + f_1(\rho(\vec{r}), \nabla\rho(\vec{r})) + r_s]} \quad (0.27)$$

formula 0.25 defines the Wilson-Levy (WL) functional [35]. Its parameters were fitted to reproduce the E_c value for He and the scaling relations for the E_c functional [78] for the eight abovementioned atomic systems.

With $f_1 = 0$ and f_2 being a rather lengthy function of $\rho(\vec{r})$ and $\nabla\rho(\vec{r})$ (so we do not present it in the text) formula 0.25 defines the Lee-Yang-Parr (LYP) functional [20]. It was derived as the second-order gradient expansion of the Colle-Salvetti formula [79], in which originally a parameter was fitted to reproduce the E_c value for the *He* atom. We use the gradient-only representation of the LYP functional, which was obtained in [80] by partial integration.

In order to make a consistent comparison and in accordance with the original formulation of the LYP and WL functionals, the Hartree-Fock (HF) densities $\rho^{HF}(\vec{r})$ have been used to calculate the model functionals $e_c^{mod}([\rho]; \vec{r})$ and correlation energies E_c for atoms and molecules, except for H_2 at $R = 5.0$ bohr, where the HF density differs strongly from the exact density and the Kohn-Sham orbital differs strongly from the HF orbital [81]. HF calculations have been performed with the GAMESS program package [82] in a triple zeta Gaussian basis set with additional 3d-polarization functions (Dunning's TZVP basis [83]). $e_c^{mod}([\rho]; \vec{r})$ and E_c have been calculated from the HF wavefunctions with the density functional program DETEDF [76]. A numerical integration by the Monte Carlo method [84] has been used to obtain E_c values. The corresponding results will be presented and discussed in the next sections.

15 Results for atoms

Figure 2.1 displays $\epsilon_c(r)$ (r is the atomic radial coordinate) as well as its potential $\frac{1}{2}w_c(r)$ and kinetic $v_{kin}(r)$ components obtained from the full CI functions $\rho(\vec{r}', \vec{r})$ and $\rho_2(\vec{r}_1, \vec{r}_2)$ for the *He* atom. The form of $\epsilon_c(r)$ is determined primarily by that of its potential component. Both ϵ_c and w_c are everywhere negative functions, while v_{kin} is everywhere positive. Both ϵ_c and w_c are monotonous functions of r with their minima at the nucleus due to strong in-out correlation of the reference electron at $r = 0$. Contrary to this, v_{kin} is a rather shallow non-monotonous function with a maximum that is placed near that of the radial density $r^2\rho(r)$. Near the nucleus v_{kin} goes closer to zero (note the exact asymptotics $v_{s,kin}(r \downarrow 0) = 0$ of the Kohn-Sham

kinetic potential in this case [55, 56]).

Figure 2.1 Correlation energy density $\epsilon_c(r)$ and its components $0.5w_c(r)$ and $v_{kin}(r)$ for He

In Figure 2.2a,b $e_c(r)$ obtained from the CI calculations and the corresponding radial function $4\pi r^2 e_c(r)$ are compared with those of PW, LYP, WL, and LW models. The various functions e_c appear to have quite different local behaviors. In particular, e_c^{LYP} and e_c^{LW} have a rather shallow form in the inner region $r < 0.3$ a.u. (see Figure 2.2a), while e_c , e_c^{PW} and e_c^{WL} are appreciably more sharp functions of r . In this inner region the w_c contribution dominates, which is just the potential of the Coulomb hole (cf. eq. (0.10)). It is known that the Coulomb hole in this region represents mostly in-out correlation, being negative around the nucleus and the position of the reference electron and becoming positive much further outwards [81]. The resulting negative w_c and ϵ_c in this region are clearly underestimated by all model functionals (except for the nuclear peak of ϵ_c^{WL} which has no energetic effect due to the vanishingly small volume). At larger r values, i.e. r in the region 0.5-1.4 a.u.,

where the Coulomb hole has a characteristic polarization shape [81], all the model energy densities ϵ_c^{mod} are larger (i.e. more negative) than ϵ_c , as is clearly visible in Fig. 2.2b, where the radial weight factor $4\pi r^2$ makes this property stand out more clearly. All the radial functions corresponding to model energy densities have their maxima around $r = 0.5$ a.u., while the maximum in e_c occurs at somewhat shorter r (ca. 0.3). The PW, LYP and WL radial functions have rather similar behavior in the region $r < 1.25$ a.u., while the LW function is more diffuse and the exact $4\pi r^2 e_c(r)$ is relatively more contracted (see Figure 2b). It is evident from the shape of the various model $4\pi r^2 e_c^{mod}$ that they may integrate to an E_c value close to the one obtained from the exact e_c since the underestimation for r values below ca. 0.4 a.u. will be compensated by the overestimation for larger r . Indeed, parameters in all of the model e_c^{mod} 's except PW have been adapted to achieve this exactly or approximately.

Table 2.1 represents E_c values for 13 closed-shell atomic systems calculated with the model functionals $\epsilon_c^{mod}(\vec{r})$. In spite of the abovementioned differences in the local behavior, all models yield for *He* E_c values which are close to the conventional $E_c = -0.042$ a.u. (to be more precise, one should mention a slight overestimation $E_c = -0.046$ a.u. of the (nonempirical) PW model). The only exception is the LDA, which is not presented in Figures 1,2 but is included in Table 3.

Figure 2.2 Correlation energy density $e_c(r)$ and model functionals

The same trend holds in the general case of neutral atoms. LDA yields E_c values

Table 3: Correlation energies of atoms obtained by various approximate correlation energy functionals.

WL, LYP, PW, LW, LDA and EXP denotes Wilson-Levy functional [35], Lee-Yang-Parr functional [20], Perdew and Wang *gradient corrected* functional [15, 51] Local Wigner functional [73, 76] Perdew and Wang *local* correlation functional [52]. EXP denotes the experimental correlation energies (A.Savin,H.Stoll,H.Preuss, Theor. Chim. Acta **70**, 407. (1986)) respectively. For Ne and Ne⁶⁺ we used the more accurate values from the following reference: E. R. Davidson, S. A. Hagstrom and S. J. Chakravorty, Phys. Rev. **A44**, 7071. (1991). All the energies are in a.u. The calculations were performed using the large TZV+3D basis.

	WL	LYP	PW	LW	LDA	EXP
He	.042	.043	.046	.042	.112	.042
Be	.094	.094	.094	.094	.223	.094
Ne	.383	.383	.383	.374	.743	.392
Mg	.444	.459	.451	.462	.888	.444
Ar	.788	.750	.771	.771	1.426	.787
Kr	1.909	1.748	1.916	1.948	3.267	
Xe	3.156	2.742	3.150	3.174	5.173	
Li ⁺	.044	.047	.051	.060	.134	.044
Be ²⁺	.045	.049	.053	.075	.150	.044
Ne ⁶⁺	.109	.129	.123	.187	.334	.187
B ⁺	.101	.106	.103	.114	.252	.111
Li ⁻	.0805	.0732	.078	.069	.182	.073
F ⁻	.368	.362	.362	.332	.696	.400

which are about twice as large (in absolute magnitude) as the conventional ones and E_c values of other models. This well-known feature of the LDA originates from the difference in correlation between the extended homogeneous electron gas model (which is represented by the LDA) and finite inhomogeneous atomic systems [85]. For the former system the Coulomb correlation of electrons with like spins brings about the same contribution to E_c as that of the opposite-spin electrons. However, in finite atomic systems correlation of like-spin electrons is substantially suppressed by their exchange, so that it brings a small contribution to E_c .

All other models considered yield rather close E_c values for neutral atomic systems, which agree satisfactorily with the available empirical data. One can only mention some relative underestimation of correlation for heavier atoms in the LYP model (See Table 2.1). As a matter of fact, the least deviation from the conventional E_c values is achieved in the WL model. On the other hand, one should note the success of the PW model, which without empirical parameters manages to describe adequately both the homogeneous electron gas (as its zero-gradient limit) and atoms.

For ionic systems the picture is less consistent. WL, LYP and, to a lesser extent, PW reproduce the conventional E_c values for the two-electron Li^+ and Be^{2+} systems, while they fail to reproduce it for the four-electron Ne^{6+} . However, the opposite trend is observed for the LW model. All functionals fail to reproduce accurately the E_c value for the F^- anion.

To sum up, the results obtained illustrate a somewhat confused situation for the atomic applications of various ϵ_c models. In spite of their different functional form and local behavior, a number of ϵ_c^{mod} functions yield rather close-lying satisfactory E_c values. From the particular case of the He atom discussed above (See Figure 2.2a,b) one can assume that also for the general case their will be considerable local differences amongst the $\epsilon_c^{mod}(r)$, and between the $\epsilon_c^{mod}(r)$ and the exact $\epsilon_c(r)$, in the inner region as well as at large distances. As the differences in these regions have opposite sign, they do not affect the E_c values due to cancellation. As has been demonstrated in this section all the ϵ_c^{mod} , in spite of their differences (more diffuse or more contracted towards the nucleus; all more diffuse than e_c) can produce sat-

isfactory overall E_c values. Unfortunately, as will be shown in the next section, the molecular performance of ϵ_c models is not so satisfactory.

16 Results for molecules

In Figure 2.3 ϵ_c for H_2 is presented as the first example of a molecular correlation energy density obtained from the correlated *ab initio* $\rho(\vec{r}', \vec{r})$ and $\rho_2(\vec{r}_1, \vec{r}_2)$. ϵ_c as well as its potential $\frac{1}{2}w_c$ and kinetic v_{kin} components are plotted for both equilibrium internuclear distance $R(H - H) = 1.401$ a.u. (Figure 2.3a) and for large distance $R(H - H) = 5.0$ a.u. along the bond axis as a function of the distance z from the bond midpoint. v_{kin} and w_c ($= V^{cond} - V^{HF}$) individually have been calculated before, see ref. [56].

The form of w_c , v_{kin} and ϵ_c reflects the left-right electron correlation, the dominating correlation effect in H_2 . The notion of the left-right correlation implies that if the reference electron is in the neighbourhood of the H nucleus, there is a large probability for the other electron to be in the neighbourhood of the other H nucleus. Left-right correlation is greatly amplified in the dissociation limit due to the strong near-degeneracy effects.

Figure 2.3 Correlation energy density $\epsilon(z)$ and its components $0.5w_c(z)$ and $v_{kin}(z)$ for H_2 at equilibrium distance (a) and near dissociation limit (b) along the bonding axis. The bond midpoint is at $z = 0.0$ and hydrogen atomic position is at $z = 0.7$ (a) or $z = 2.5$ a.u. (b).

The most noticeable features in Figure 2.3 are the wells of $w_c(z)$ and $\epsilon_c(z)$ around the nucleus and the peaks of $v_{kin}(z)$ and $\epsilon_c(z)$ at the bond midpoint. The well of $w_c(z)$ with the minimum at the H nucleus reflects the appreciable reduction of the electron-electron repulsion in this region due to the left-right correlation. w_c is the Coulomb hole potential (see eq. (0.10)) and is also a part of v_{xc} (together with the potential from the Fermi hole it constitutes the total hole potential, which is an important part of v_{xc}). The attractive nature of w_c will have the effect of making the density more compact around the H nuclei, which is precisely what is required in view of the much too diffuse density that results in an exchange-only treatment [56]. Closer to the bond midpoint, the left-right correlation becomes less important and $w_c(z)$ is closer to zero. Having the same qualitative features, the functions $w_c(z)$ for

the equilibrium and large $H - H$ distances differ quantitatively. The minimum of $w_c(z)$ for $R(H - H) = 5.0$ a.u. is about twice as deep as that for $R(H - H) = 1.401$, in accordance with the stronger near-degeneracy left-right correlation at large distance. On the other hand, the local maximum of $w_c(z)$ at the bond midpoint is much closer to zero for $R(H - H) = 5.0$. Indeed, when the reference electron is at the bond midpoint, which is in this case a region of very low density, we may expect hardly any Coulomb hole, since the symmetrical exchange hole of depth $-\rho(\vec{r})/2$ will in this case already be a good description of the total exchange-correlation hole.

Left-right correlation finds a spectacular way to manifest itself through the bond midpoint peak of $v_{kin}(z)$ [56]. By the definition (0.12), $v_{kin}(\vec{r})$ is determined by the average rate of change of the conditional amplitude $\Phi(s_1, \vec{x}_2, \dots, \vec{x}_N | \vec{r}_1)$ with changing position \vec{r}_1 of the reference electron. Φ has the maximal gradient at the bond midpoint $z = 0$, since when the reference electron crosses the bond midpoint, the other electron has to switch quickly from one atom to another due to the left-right correlation. As a consequence, $v_{kin}(z)$ possesses a peak at $z = 0$, which reflects the corresponding "jump" of the conditional amplitude. This peak becomes much higher for large $H - H$ distance, because of increase of left-right correlation in the dissociation limit. We can also mention the non-monotonous behavior of $v_{kin}(z)$ in Figure 2.3a, with a local minimum at the H nucleus. The exact v_{kin} is not necessarily zero at the nucleus in this case, but clearly still exhibits this tendency.

The abovementioned individual features of $w_c(z)$ and $v_{kin}(z)$ can be clearly recognized in the plots of the resulting $\epsilon_c(z)$. This is especially true for $R(H - H) = 5.0$ a.u. (See Figure 3b). In this case $\epsilon_c(z)$ inherits the bond midpoint peak of $v_{kin}(z)$ and the well around the nucleus of $\frac{1}{2}w_c(z)$, with the height of the peak and the depth of the well being very close to those for v_{kin} and $\frac{1}{2}w_c$. Because of this, ϵ_c becomes a sign-changing function: it is positive in the bond midpoint region, it changes sign near $z = 1$ a.u. and it is negative at larger z . For the equilibrium geometry, on the other hand, $\epsilon_c(z)$ is everywhere negative (See Figure 3a). In this case both $\frac{1}{2}w_c(z)$ and $v_{kin}(z)$ have appreciable contributions to $\epsilon_c(z)$ at all z considered. Still, ϵ_c has the same qualitative features, namely, a maximum at the bond midpoint and a well around the H nucleus.

In Figure 2.4 $e_c(z)$ obtained for H_2 from *ab initio* $\rho(\vec{r}', \vec{r})$ and $\rho_2(\vec{r}_1, \vec{r}_2)$ is compared with those of the PW, LYP, WL, and LW models. As has been mentioned in subsection *Models*, the gradient models were parametrized from atomic data (LYP, WL) or obtained from the GEA for the inhomogeneous electron gas model with suitable cutoffs (PW). However, as regards the density gradients, there is a basic difference between atoms and molecules. For atoms $|\nabla\rho(\vec{r})|$ is never small, while for molecules it is close to zero in the important bond midpoint region. One can expect also, that correlation effects in this molecular region differ from those in the homogeneous or weakly inhomogeneous electron gas models. Because of this, $e_c^{mod}(\vec{r})$ may have rather accidental behavior in the bond midpoint region. Therefore, it is interesting to investigate the form of the model $e_c^{mod}(z)$ and compare them with that of the exact $e_c(z)$ which, as has been shown for the corresponding function $\epsilon_c(z)$, embodies in a transparent manner the effects of correlation.

Considering first the bond region, figure 2.4a shows a rather different behavior of the various energy density functions in the region between the nuclei for the equilibrium $H - H$ distance. In complete analogy with $\epsilon_c(z)$, the characteristic feature of $e_c(z)$ in this region is the maximum (close to zero) at

Figure 2.4 Correlation energy density $\epsilon_c(z)$ and its components $0.5w_c(z)$ and $e_{kin}(z)$ and $e_{kin}(z)$ for $H - 2$ at equilibrium distance (a) and near dissociation limit (b) along the bonding axis. The bond midpoint is at $z=0.0$ and hydrogen atomic position is at $z=0.7$ (a) or $z= 2.5$ a.u (b)

the bond midpoint. The PW, LYP and LW models also have maxima at the

bond midpoint, however, they are considerably more shallow functions of z than is $e_c(z)$. On the other hand, the Wilson-Levy energy density $e_c^{WL}(z)$ is a much more negative function in the bond region, exhibiting a sharp minimum at $z = 0$. This minimum seems to be an artefact of the WL function and it will appear for an arbitrary molecular system as a consequence of the functional form of the WL model (eqs.0.25 - 0.27) and the relation $d \gg b$ between the parameters of this model.

Near the nuclei the various model energy density functions are similar to those found for the *He* atom (compare Figures 2.2a and 2.4a), as may be expected from their dependence on the density. The wells of the exact e_c around the nuclei are also reminiscent of the shape of e_c in *He*, but it should be noted that the underlying correlation is very different: the Coulomb hole is now due to left-right correlation rather than to in-out correlation. This difference becomes manifest in the outer tail. Whereas in *He* the model energy densities become more negative than e_c at distances from the nucleus larger than ca. 0.4 a.u., in H_2 e_c remains more negative in the complete tail region (see fig. 2.4a for large values of z). This may be understood from the strong left-right correlation that will be present when the reference electron is at these positions. This difference in the physics of the correlation compared to *He* is clearly not recognized by the model correlation functionals. Obviously, there will again be compensation of errors, the model functionals giving more negative contributions around the bond midpoint. The failure of the models to describe properly the left-right correlation becomes very clear in the case where it becomes very strong, due to near-degeneracy, in the near-dissociation limit, $R(H-H) = 5.0$ a.u. (fig. 4b). In this case $e_c^{mod}(z)$ have been calculated with ρ obtained with the CI, since the HF density (which we use to calculate e_c^{mod} in all other cases) differs substantially from the CI one for the dissociating H_2 molecule [56]. Fig. 2.4b shows that the $e_c(z)$ obtained from the correlated $\rho(\vec{r}', \vec{r})$ and $\rho_2(\vec{r}_1, \vec{r}_2)$ possesses deep and wide wells around the nuclei. Contrary to this, all model functions exhibit much smaller wells around the nuclei. The model energy densities are completely determined by the electron density, which is practically the *H* atom density, and cannot recognize from this electron density the strong left-right correlation in the H_2 system with a concomitant deep Coulomb hole around the reference electron.

They will in fact integrate to almost zero since the correlation energy is zero in the H atom, whereas the exact e_c will integrate to -0.1563 a.u. [86]. As a matter of fact, the gradient corrected density functionals for exchange deviate by approximately the same amount from the exact exchange (cf. second term in eq. (0.11)), so that the total E_{xc}^{mod} is fairly accurate. This compensation of "errors" in the correlation functionals by opposite "errors" in the exchange functionals seems to be fairly systematic, resulting in accurate total E_{xc} values from the existing gradient-corrected total functionals.

We note that the large peak in v_{kin} at the bond midpoint (fig.2.3b) is much diminished by the multiplication by the small $\rho(z)$ at the bond midpoint but it is still visible in a small positive value of e_c at $z = 0$. The model e_c^{mod} are everywhere negative functions.

In order to examine if the observations made above apply to larger systems we briefly look at the $e_c^{mod}(z)$ calculated for the Be_2 and F_2 molecules at their equilibrium bond distances. In Figures 5a and 6a the model functions are plotted for the bonding regions only. Like H_2 , F_2 is a molecule with a single covalent bond and for both molecules $e_c^{mod}(z)$ have a similar form (Compare Figures 4a and 5a). In particular, e_c^{WL} displays the same sharp minimum at $z = 0$, while e_c^{PW} , e_c^{LYP} and e_c^{LW} are rather shallow functions with maxima at $z = 0$. A marked difference between $e_c^{mod}(z)$ for H_2 and F_2 is the atomic shell structure of the gradient models e_c^{PW} and e_c^{WL} in the latter case, i.e. the additional non-monotonous dependence of e_c^{mod} on z with extrema between the atomic shells (See Figure 2.5a). Since ρ itself is a monotonous function of z in atomic regions, the LW model does not display the atomic shell structure. It is interesting to note, however, that, in spite of its dependence on $|\nabla\rho(\vec{r})|$, the LYP model also does not show the shell structure in this case.

Unlike H_2 and F_2 , Be_2 is a system with a weak bond with contributions from the interatomic correlation (dispersion forces) of electrons of two closed-shell Be atoms. Because of this, all $e_c^{mod}(z)$ are close to zero in the bonding region of Be_2 (See Figure 2.6a; note the difference in scale with fig. 2.5a). In particular, e_c^{WL} displays its characteristic bond midpoint minimum but with very small depth and shallow

form. e_c^{LYP} exhibits in this case atomic shell structure with a maximum at $z \approx 1$ a.u., while e_c^{PW} is a much more shallow function of z as compared to other gradient models.

Obviously, the differences amongst the model correlation energy densities are as large for these systems as they were found to be for H_2 and more work will be needed, including the calculation of accurate e_c , to clarify the topology of these energy densities. Table 2.2 represents E_c values calculated for 21 closed-shell molecules with the PW, LYP, WL and LW models. For H_2 the error compensation referred to above clearly is quite effective, the E_c values obtained from the model functionals all yielding a reasonable estimate of the experimental number. In fact, for all the molecules all functionals yield similar, reasonable, E_c values in spite of the considerable local differences between the energy densities. Considering the results more closely we note that the models produce appreciable deviations from the conventional empirical total E_c^e energies [77]. In quite a few cases for each functional these deviations

Figure 2.5 Correlation energy densities $e_c^{mod}(z)$ for F_2 in the bonding region (a) and in the atomic region (b). The bond midpoint is at $z = 0$, the F nucleus is at $z = 1.339$ a.u.

exceed 0.05 a.u. The best results are obtained with the WL functional, in particular, for all dimers from B_2 to F_2 it provides the closest correspondence between the calculated and empirical E_c values. This fits with the results of [87], where better

dissociation energies for dimers and monohydrides were obtained with the combination of the HF and WL functionals as compared to those obtained with the HF and PW functionals. Still, both PW and LYP models yield better E_c values than the WL ones for 8 out of 21 molecules. In particular, PW and LYP are better for H_2 , Be_2 , NH_3 and for all hydrocarbons considered (the only exception in the latter case is C_2H_2 , for which WL yields a slightly better value than LYP; note that the triply bonded C_2H_2 is isoelectronic with N_2). A possible explanation for this behaviour of the Wilson-Levy functional can be gleaned from Figures 2.4-2.6, which demonstrate that there is a clear minimum in e_c^{WL} in the bond midpoint region. The WL model produces an extra contribution to E_c from this region. Since the values of the model energy densities e_c^{mod} are much lower in the bond region than in the atomic regions (cf. the different scales in figs. 2.5,2.6a compared to figs. 2.5,2.6b) it is not immediately obvious that the larger correlation energies for Wilson-Levy do indeed originate from the bond region. We have explicitly verified this by partitioning the molecular volume in various regions and considering the partial contributions. Taking for instance for F_2 for the bond region the disc $-1.0 \leq z \leq +1.0$, this region accounts for ca. 20% of the total E_c , but its contribution already is more negative for Wilson-Levy compared to the other models by a larger amount than the total E_c is. So the atomic regions do give the largest contribution to E_c , but do not cause the more negative value of the Wilson-Levy E_c (actually they slightly counteract this effect of the bond region). This more negative bond region contribution of Wilson-Levy brings the E_c values closer to the "experimental" E_c^e and in this sense accounts effectively for the strong near-degeneracy correlation effects in dimers. Usually, $E_c[\rho]$ functionals derived from atomic data or from the electron gas model tend to underestimate correlation in dimers and this is true for the PW, LYP and LW models (See Table 2.2). Still, as has been pointed out above, the bond midpoint minimum of e_c^{WL} is an artificial topological feature of the WL functional, which will appear independently of the presence or absence of the strong near-degeneracy correlation effects. Due to this, the WL model overestimates E_c for hydrocarbons, for which the energetical effect of the near-degeneracy left-right correlation is not as strong as for multiply-bonded dimers. It is also of course unsatisfactory that the bond midpoint

Table 4: **Correlation energies of molecules obtained by various model correlation energy functionals.**

The notations of model functionals are the same as in Table 1. EXP denotes the experimental correlation energies [28]. For CO and C₂H₄ the experimental correlation energies were estimated by using experimental atomization energies on the basis of the ref [127]. All the energies are in a.u. The calculations were performed using the large TZV+3D basis.

molecule	WL	LYP	LW	PW	EXP
H ₂	0.049	0.038	0.029	0.046	0.041
Li ₂	0.136	0.133	0.134	0.137	0.122
Be ₂	0.231	0.200	0.193	0.205	0.205
B ₂	0.336	0.289	0.265	0.296	0.330
C ₂	0.446	0.384	0.344	0.391	0.514
N ₂	0.532	0.483	0.435	0.490	0.546
O ₂	0.621	0.583	0.533	0.588	0.657
F ₂	0.683	0.675	0.633	0.671	0.746
H ₂ O	0.386	0.340	0.314	0.347	0.367
NH ₃	0.376	0.318	0.268	0.338	0.338
CH ₄	0.369	0.294	0.241	0.320	0.293
HF	0.377	0.363	0.335	0.367	0.387
LiH	0.088	0.089	0.083	0.092	0.083
LiF	0.417	0.418	0.343	0.415	0.447
HCN	0.525	0.464	0.410	0.478	0.527
CO	0.516	0.484	0.440	0.488	0.550
H ₂ O ₂	0.690	0.638	0.569	0.652	0.691
C ₂ H ₂	0.504	0.443	0.386	0.466	0.476
C ₂ H ₆	0.678	0.551	0.426	0.577	0.553
C ₂ H ₄	0.593	0.497	0.417	0.529	0.528
CO ₂	0.865	0.791	0.720	0.807	0.829

behaviour of the Wilson-Levy functional is opposite to the effect of strong left-right correlation as represented with the functions $\epsilon_c(\vec{r})$ and $e_c(\vec{r})$ obtained from the correlated $\rho(\vec{r}', \vec{r})$ and $\rho_2(\vec{r}_1, \vec{r}_2)$. One can see from Figures 2.3,2.4 that correlation produces a maximum (and not minimum) in the bond midpoint region.

Figure 2.6 Correlation energy densities $e_c^{mod}(z)$ for Be_2 in the bond region (a) and in the atomic region (b). The bond midpoint is at $z=0$, the Be nucleus is at $z = 1.730$ a.u.

17 Conclusions

In this paper it has been proposed to construct the exchange-correlation and correlation energy densities from the first- and second-order correlated density matrices obtained with *ab initio* calculations. The functions $\epsilon_c(\vec{r})$ as well as their kinetic $v_{kin}(\vec{r})$ and potential $\frac{1}{2}w_c(\vec{r})$ components have been presented for the two-electron He atom and H_2 molecule. A manifestation of various correlation effects through the form of these functions has been discussed. The corresponding functions $e_c(\vec{r})$ have been compared with $e_c^{mod}(\vec{r})$ of some local and gradient approximations. The model energy densities $e_c^{mod}(\vec{r})$ have been compared also for the Be_2 and F_2 molecules and E_c values have been calculated for a number of atoms and molecules.

The present results show that, in spite of some success of the gradient models, further improvement of the DFT approximations to $e_c(\vec{r})$ is desirable, especially, to describe properly the correlation in molecular systems. The "errors" of the GGA correlation functionals in molecules with strong near-degeneracy correlation seem to be compensated systematically by opposite "errors" in the GGA exchange functionals (either Becke [89] or Perdew-Wang [16]), explaining the success of the

molecular applications of the generalized gradient approximation (GGA) reported recently [16, 88]. In those cases a combined treatment of exchange and correlation may be more useful.

As for correlation models, the functions $\epsilon_c(\vec{r})$ obtained from the correlated $\rho(\vec{r}', \vec{r})$ and $\rho_2(\vec{r}_1, \vec{r}_2)$ can serve as a benchmark for successful models $e_c^{mod}(\vec{r})$. The procedure presented in Section 13 allows to construct $\epsilon_c(\vec{r})$ and $e_c(\vec{r})$ for an arbitrary many-electron system, which opens new possibilities for the DFT modelling. When developing a new $\epsilon_c^{mod}(\vec{r})$, one can take into account not only E_c estimates or the scaling and asymptotic properties of the E_c functional, but also the local behavior of the essentially accurate $\epsilon_c(\vec{r})$ obtained from *ab initio* wavefunctions for a representative set of atomic and molecular systems. A promising option is to approximate directly the potential $\frac{1}{2}w_c(\vec{r})$ and kinetic $v_{kin}(\vec{r})$ components which, as has been shown in the present paper, have a characteristic form. The corresponding work as well as the application of the proposed procedure of $\epsilon_c(\vec{r})$ construction to systems with more than two electrons is in progress.

Kinetic contribution to correlation energy density: benchmark to $T_c[\rho]$ energy functionals

18 Abstract

Since in density functional theory (DFT) the classical form of virial theorem does not hold due to localization effect of exchange-correlation, it is important to investigate the kinetic contribution to correlation. Nearly exact $t_c([\rho]; \vec{r})$ kinetic contribution to correlation energy densities are constructed for two electronic He and H_2 and for LiH and compared with various model $t_c^{mod}([\rho]; \vec{r})$ energy densities. For comparative purpose the "global" $T_c^{mod}[\rho]$ energies are also given for several atomic and molecular systems. The model functionals are derived using the Levy-Perdew relation. Stoll's correction is employed for those models, which are based on the electron gas model or capable of reproducing the uniform electron gas limit. This correction makes it possible to treat opposite and parallel spin correlation distinctly. The proper modelling of $t_c([\rho]; \vec{r})$ functionals provides the opportunity of separate treatment of potential part $W_c[\rho]$ and $T_c[\rho]$ part of correlation. The virial ratio $-T_c/E_c$ is compared for several neutral and ionic systems and is found in the range of 0.75-0.85 for neutral atomic systems, while for tightly bound atoms, like Be^{2+} a value of 0.96 is computed.

19 Introduction

In this chapter, first, the discussion of the virial theorem is given in DFT, then, a procedure for determining the exact kinetic contribution to the correlation energy density will be shown. The general quantum mechanical virial theorem is satisfied only in exact exchange-only density functional theory [90, 6]. From the Kohn-Sham equation (1.17-1.22) after some algebra the corresponding form of virial theorem can be obtained which relates the noninteracting kinetic energy functional $T_s[\rho]$ to the

exact Kohn-Sham $v_s([\rho]; \vec{r})$ potential [90]

$$2T_s[\rho] = \int \rho(\vec{r}) \vec{r} \nabla v_s([\rho]; \vec{r}). \quad (0.1)$$

However, the exact exchange-correlation energy functional $E_{xc}[\rho]$ contains kinetic part of Kohn-Sham theory and satisfies the equation [78]

$$T_s[\rho] - T[\rho] = E_{xc}[\rho] + \int \rho(\vec{r}) \vec{r} \nabla v_{xc}([\rho]; \vec{r}) d\vec{r} \quad (0.2)$$

This equation, which reflects the complexity of virial theorem in DFT, and is due to the localization effect of exchange-correlation, introduces the kinetic contribution to correlation energy functional of Kohn-Sham theory $T_c[n]$ to which this paper is addressed.

$$T_c[\rho] = T[\rho] - T_s[\rho] \quad (0.3)$$

$T_s < 0$ while $T_c > 0$ [90]. A constrained search method (eq. 1.75) [43, 6] for solving the exact Kohn-Sham equation has been applied previously where the nearly exact density $\rho(\vec{r})$ was known [43]. However, these studies were confined to only the study of the local characteristics of exchange-correlation potential, and $T_c[n]$ values have been obtained for several atomic cases. The first molecular $v_{xc}(\vec{r})$ and $T_c[\rho]$ have been calculated by *ab initio* methods for H_2 and LiH [100]. Most recently, a procedure has been proposed to construct correlation energy density and its kinetic contribution from *ab initio* first- and second order density matrices. Examples for two-electronic systems He and H_2 [93] and for several small molecules have been presented [7]. In this present work the local characteristics of $T_c[\rho]$ functionals are studied in the sense of the following equation:

$$T_c[\rho] = \int \rho(\vec{r}) t_c([\rho]; \vec{r}) d\vec{r} \quad (0.4)$$

The nearly exact $t_c([\rho]; \vec{r})$ energy densities are constructed for two electronic He, H_2 and for LiH and compared with various model $t_c^{mod}([\rho]; \vec{r})$ energy densities as it is put in ref.[93]. Although eq. 0.4 does not define $t_c(\vec{r})$ uniquely, can be helpful for modelling $t_c(\vec{r})$ as well as the correlation energy density $e_c(\vec{r})$. An argument for the comparativity of different forms of $T_c[n]$ and $t_c([\rho]; \vec{r})$ is given in Appendix A.

For comparative purpose the "global" $T_c^{mod}[\rho]$ energies are also presented for several atomic and molecular cases.

20 Construction of $t_c([\rho]; \vec{r})$

According to Savin and Levy et al. [42], $T_c[n]$ can be given in terms of first order density matrices:

$$T_c[\rho] = \int \nabla_{r'}^2 [\gamma_\rho^{\lambda=1}(\vec{r}, \vec{r}') - \gamma_\rho^{\lambda=0}(\vec{r}, \vec{r}')] |_{r=r'} d\vec{r}' \quad (0.5)$$

The correlation effect clearly manifests through the fully interacting $\gamma_\rho^{\lambda=1}(\vec{r}, \vec{r}')$ density matrix. On the basis of eq. 3.4-3.5 $t_c([\rho]; \vec{r})$ can be given as follows:

$$t_c([\rho]; \vec{r}) = \frac{1}{\rho(\vec{r})} \nabla_{r'}^2 [\gamma_\rho^{\lambda=1}(\vec{r}, \vec{r}') - \gamma_\rho^{\lambda=0}(\vec{r}, \vec{r}')] |_{r=r'} \quad (0.6)$$

The noninteracting kinetic energy contains Weizsäcker and Pauli term [90]-[92]. The Pauli term is the noninteracting kinetic potential $v_{s,kin}(\vec{r})$ used in e.g. ref [100]:

$$t_s([\rho]; \vec{r}) = t_w([\rho]; \vec{r}) + v_{s,kin}([\rho]; \vec{r}) \quad (0.7)$$

$$t_w([\rho]; \vec{r}) = \frac{|\nabla \rho(\vec{r})|^2}{8\rho^2(\vec{r})} \quad (0.8)$$

$v_{s,kin}(\vec{r})$ can be given in terms of conditional amplitude $\Phi_s(\vec{r}_2, \dots, \vec{r}_N | \vec{r}_1)$ [5,6]

$$v_{s,kin}(\vec{r}) = \int |\nabla \Phi_s(\vec{r}_2, \dots, \vec{r}_N | \vec{r}_1)|^2 d\vec{r}_2 \dots d\vec{r}_N = \frac{1}{2} \sum_{i=1}^{MO} \left| \nabla_r \frac{u_i([n]; \vec{r})}{n^{\frac{1}{2}}(\vec{r})} \right|^2, \quad (0.9)$$

$$\Phi_s(\vec{r}_2, \dots, \vec{r}_N | \vec{r}_1) = \frac{\Psi_s(\vec{r}_1, \dots, \vec{r}_N)}{\sqrt{\rho(\vec{r}_1)/N}} \quad (0.10)$$

and $\Psi_s(\vec{r}_1, \dots, \vec{r}_N)$ and $u_i([\rho]; \vec{r})$ are the Kohn-Sham Slater-determinant and orbitals obtained during the constrained search calculation. The fully interacting and the noninteracting kinetic energy densities are as follows:

$$t([\rho]; \vec{r}) = \frac{1}{\rho(\vec{r})} \nabla_{r'}^2 \gamma_\rho^{\lambda=1}(\vec{r}, \vec{r}') |_{r=r'} \quad (0.11)$$

$$t_s([\rho]; \vec{r}) = \frac{1}{\rho(\vec{r})} \nabla_{r'}^2 \gamma^{\lambda=0}(\vec{r}, \vec{r}') \Big|_{r=r'} . \quad (0.12)$$

The difference of them then gives us the required quantity

$$t_c([\rho]; \vec{r}) = \frac{1}{8} \sum_{i=1}^{MO} \frac{|\nabla \rho_i(\vec{r})|^2}{\rho_i(\vec{r})} - \frac{|\nabla \rho|^2}{8\rho^2(\vec{r})} - \frac{1}{2} \sum_{i=1}^{MO} \left| \nabla_r \frac{u_i([\rho]; \vec{r})}{\rho^{\frac{1}{2}}(\vec{r})} \right|^2 . \quad (0.13)$$

21 $T_c^{mod}[n]$ functionals

The model functionals $t_c([\rho]; \vec{r})$ to be compared here with each other and with those obtained from *ab initio* calculations are the Wilson-Levy (WL) functional [35], the gradient dependent Perdew-Wang (PW) [106] and the reparametrized local Wigner-function [11]. The $T_c^{mod}[n]$ functions are expressed using the Levy-Perdew relation [78, 95].

$$T_c^{mod}[\rho] = \frac{\partial E_c^{\lambda, mod}[\rho_\lambda]}{\partial \lambda} \Big|_{\lambda=1} - E_c^{mod}[\rho] . \quad (0.14)$$

The equivalency of eq. 5-6 and eq. 14 does not follow immediately, therefore an explicit proof is given in Appendix A. In local density approximation (LDA), which is valid in the limit of slowly varying density [78], the local form of eq. 14 and t_c in eq. 13 are comparable. Consequently, the comparison can be made in atomic and molecular systems, where $\rho(\vec{r})$ is close to the slowly varying limit. Usually the density is varying rapidly at the nuclei in the inner region. Using Stoll's correction[96]

$$T_c^{mod}[\rho_\alpha, \rho_\beta] = \int \rho(\vec{r}) t_c^{mod}(\rho_\alpha, \rho_\beta) d\vec{r} - \int \rho_\alpha(\vec{r}) t_c^{mod}(\rho_\alpha; 1) d\vec{r} - \int \rho_\beta(\vec{r}) t_c^{mod}(\rho_\beta; 1) d\vec{r}, \quad (0.15)$$

new model functionals are introduced (see Appendix B), namely the LDA in the parametrization of Perdew and Wang [106] (VWN-S). n_α and n_β denote the electronic density of electrons with spin α and β . Becke constructed a new gradient corrected functional, which was chosen to satisfy certain requirements, e.g. it has correct uniform electron gas limit, the opposite and parallel-spin correlation is treated distinctly, perfectly self-interaction free and provides good fit to exact correlation energies of atomic systems (Bc95) [14]

$$T_c^{Bc95} = T_c^{\alpha\beta} + T_c^{\alpha\alpha} + T_c^{\beta\beta}. \quad (0.16)$$

The $T_c^{LW}[\rho]$ functional (local Wigner [73]) was chosen in a three-parameter form

$$T_c^{LW}[\rho] = a \int \frac{n}{b+r_s} \left(\frac{r_s}{b+r_s} - c \right) d\vec{r} \quad (0.17)$$

In this paper we use LW function with the parameter $a = 0.02705$, $b = 0.09431$ and $c = 0.11621$, which have been obtained to reproduce the calculated T_c values [94] of eight closed-shell atomic systems He, Li^+ , Be^{2+} , Be, B^+ , Ne, Mg and Ar. To be consistent with other results when comparison is made, the unrestricted Hartree-Fock (UHF) densities have been used to calculate the model functionals $t_c([\rho]; \vec{r})$ and $T_c^{mod}[\rho]$ energies for atoms and molecules. The UHF-calculations have been performed with the GAMESS [82] and GAUSSIAN-92 [97] program packages in a triple zeta Gaussian basis set with additional 3 set of polarization functions on all the atoms. A further extension of basis set is employed when anions (Li^- , F^-) and molecules are treated by means of diffuse functions. A numerical integration by the Monte Carlo method [76] has been used to obtain $T_c[\rho]$ values. $t_c^{mod}([\rho], \vec{r})$ and T_c have been calculated from the HF wave functions with the density functional program DETEDF [76]. The corresponding results will be presented and discussed in the next section.

The correlated wavefunctions for LiH, BH and FH have been obtained with single and double excited configuration interaction (CISD) calculations of the ground states at equilibrium distances [100]. Calculations have been performed within the direct CI approach by means of the ATMOL package [93, 55]. Core polarization functions have been employed at the CISD calculations. The details of CISD computations have been given in ref. [55, 100]. The constrained search calculations [43, 45] with respect to the reference CI density is done by the modified ATMOL [55] package (see ref. [98]).

22 Results for atoms

In Fig 3.1, $t_c([\rho]; \vec{r})$ is displayed and compared with various $t_c^{mod}([\rho]; \vec{r})$. $v_{kin}(\vec{r})$ and consequently $t_c(\vec{r})$ has significant (positive) contribution to the correlation energy

density at those positions of the reference electron where the conditional amplitude changes rapidly and $\nabla\Phi$ is large [94, 93]. So that the maxima around $r = 0.5$ a.u. behaves like a "potential barrier" when one moves the reference electron from the nucleus outward. This distance coincides with the radius calculated for the Coulomb hole of He [93] and with the maxima of radial charge density. Thus $t_c(\vec{r})$ reflects the shape of the Coulomb hole and the atomic shell-structure [55]. At the border of the shell the conditional amplitude Φ goes through a sudden change and this results in nonmonotous behaviour to $t_c(\vec{r})$, meanwhile the $w_c(\vec{r})$ potential part of $\epsilon_c(\vec{r})$ has considerably different local form [55]. Because of the significant positive contribution of $t_c(\vec{r})$ to correlation, $\epsilon_c(\vec{r})$ vanishes more rapidly than $w_c(\vec{r})$. In the inner region of the He all the model correlation energy functionals provide damping too fast when compared to the exact energy density [98, 55]. This may well be due to the too positive implicit contribution of $T_c^{mod}[\rho]$ part in $E_c^{mod}[\rho]$. This implicit contribution can be approximated by the Levy-Perdew relation [78] (eq. 3.14). Comparing Fig. 3.2 with Fig. 2.2 of ref. [98], indeed a too positive $t_c^{mod}(\vec{r})$ energy density is found around the inner region with spurious model cusps at the nucleus compared with the nearly exact curve. The assumption we made on comparativity between t_c of eq. 3.8 and of eq. 3.18, is based on LDA with slowly varying densities. The comparison can be made with good approximation, except at the nucleus, where the density is rapidly varying [45]. Contrary to this $t_c^{mod}(\vec{r})$ damps too fast in the outer region while $e_c^{mod}(\vec{r})$ shows reverse characteristics (see Fig 2.1). The best local agreement with $t_c(\vec{r})$ is found for Bc95 and LW models. Since the latter one is parametrized directly on nearly exact T_c values, its good performance, at least locally, is not so surprising while Bc95 is fitted on "experimental" correlation energies of atoms He and Ne [14]. Altering from the homogeneous electron-gas model, real atomic and molecular systems can be taken as inhomogenous systems, and as such, they contain much more smaller parallel-spin contribution to correlation [13]. Stoll's correction [96] accounts well for like-spin correlation. However, VWN-S functional [110] still retains its well-known behaviour of LDA and overestimates $t_c([n]; \vec{r})$ and T_c , especially in the outer region. Bc95, which can be seen as a gradient-corrected modification of VWN-S, performs much better.

In Table 3.1, T_c^{mod} values are presented for atomic species and compared with several nearly exact T_c . The main conclusion which can be drawn is that all $T_c^{mod}[n]$ functionals overestimate T_c for atoms, especially WL and VWN-S, even if we take into account that T_c , calculated for atoms with atomic number larger than 10, is far from being exact. The values T_c for He, Li and Be are calculated from very nearly the exact densities [93], thus the most certain comparison can be taken for these species. According to the above-mentioned conclusions based on Fig 3.1, we do believe that the functionals considered here overestimate T_c because of their notorious overestimation of energy densities in inner region of atoms, while the underestimation of $t_c([\rho]; \vec{r})$ in the outer region somewhat cancels this error. Despite of the fact that VWN-S model is based on only the homogeneous electron-gas model and do not contain any empirical parameter, performs quite well. Among the gradient dependent functionals PW91 and Bc91 provide values in quite good agreement with T_c .

23 Results for molecules

In Fig. 3.2 t_c for H_2 is presented and compared with various $t_c^{mod}([\rho]; \vec{r})$ as well as the correlation energy density $\epsilon_c([\rho]; \vec{r})$ is displayed [98] for nearly exact and for several model functionals for comparative purpose. The bond midpoint peak and the local minimum at the H nucleus results in nonmonotonous behaviour to $t_c(\vec{r})$ [98] and can be interpreted as a pure manifestation of non-dynamic correlation effect, while in He dynamic correlation is the only source of electron correlation. Owing to the model functionals derived on the basis of the Levy-Perdew relation [78], they provide incorrectly similar local characteristic behaviour to their correlation energy density counterparts [98]. This underlying deficiency of $t_c^{mod}([\rho]; \vec{r})$ can be understood via the local form of Levy-Perdew relation, which holds in LDA [6] (Appendix A).

$$t_c^{mod}([\rho]; \vec{r}) = \left. \frac{\partial \epsilon_c^{\lambda, mod}([\rho_\lambda]; \vec{r})}{\partial \lambda} \right|_{\lambda=1} - \epsilon_c^{mod}([\rho]; \vec{r}). \quad (0.18)$$

Since the local behaviour of $\epsilon_c^{mod}([\rho]; \vec{r})$ is found to be nearly correct [6], the incorrect feature of $t_c^{mod}([\rho]; \vec{r})$ clearly manifests via the scaling derivative $\left. \frac{\partial \epsilon_c^\lambda}{\partial \lambda} \right|_{\lambda=1}$. This may

Table 5: **Atomic $T_c[\rho]$ values calculated by various approximate functionals**
All the energies are in a.u. The calculations were performed using the large TZV+3D basis. $E_c[n]$ and $T_c[n]$ denote the corresponding empirical energies [28, 77] and T_c calculated from CI wave-function [100]. C is the virial ratio $-T_c/E_c$ given in eq. 21.

atom	WL	PW91	VWN-S	LW-3	Bc95	$-E_c[n]$	$T_c[n]$	C
He	.040	.045	.054	.037	.039	.042	.037	.88
Li	.054	.051	.076	.057	.048	.045	.038	.84
Be	.085	.073	.106	.081	.080	.094	.074	.79
B	.116	.101	.141	.108	.110	.125	.095	.76
C	.155	.134	.179	.140	.142	.156	.12	.77
N	.210	.176	.222	.176	.180	.189	.15	.79
O	.252	.216	.265	.217	.224	.258	.19	.74
F	.304	.262	.310	.261	.271	.323	.24	.74
Ne	.366	.313		.309		.390		
Na	.389	.339	.388	.342	.345	.401	.31	.77
Mg	.424	.371	.425	.376	.387	.444	.34	.77
Al	.462	.406	.464	.410	.423	.491	.35	.71
Ar	.747	.630		.603		.787	.71	.90
Kr	1.844	1.613		1.417		1.891		
Xe	3.057	2.667				3.088		
Li^+	.043	.043	.064	.052	.047	.044	.0404	.92
Be^{2+}	.044	.046	.072	.065	.052	.042	.0404	.96
Ne^{6+}	.105	.104		.146		.187		
B^+	.093	.082	.120	.097	.091	.111		
H^-	.031	.026	.035	.017	.025	.041	.028	.68
Li^-	.069	.059	.086	.060	.063	.073		
F^-	.345	.289	.332	.275	.295	.400		

well be due to the well-known behaviour of model correlation energy functionals, that they do not satisfy certain scaling relations [132]. Comparing $t_c(\vec{r})$ and $\epsilon_c(\vec{r})$ in Fig. 3.2, it is clear, that $\frac{\partial \epsilon_c^\lambda}{\partial \lambda}|_{\lambda=1}$ is a function of \vec{r} , which changes sign when the reference electron moves from the the nucleus to the bond midpoint reflecting the shape of the Coulomb hole [99]. $t_c^{WL}(\vec{r})$ is excluded in Fig. 3.2, since it provides the same unacceptable local characteristics as it was found in ref [98] (see Fig. 2.4a,b). It is interesting to note that functional PW, which is the gradient extension of LDA, considerably differs locally from VWN-S and Bc95 which are rather similar to each other, especially in the bonding region. Possible reason can be gleaned from the underlying physics, which has been applied when model functionals have been developed. The PW model is obtained from the generalized approximation (GEA) for the inhomogeneous electron gas model with suitable cutoffs and contains no other empirical data [51]. Bc95 model provides another way of extension of the VWN model via Stoll's correction and via suitable choose of gradient correction [14]. However, this functional contains two fitting parameters, which have been set to reproduce the empirical correlation energy of He and Ne [14].

In order to extend the observations made above to larger systems the $t_c(\vec{r})$ and $t_c^{mod}(\vec{r})$ are plotted for LiH at equilibrium distance along the bonding axis for the atomic region of Li (Fig. 3.3a) and for the bonding region (fig. 3b) separately. The $t_c(\vec{r})$ obtained from CI wave-function [99, 100] displays not only a nonmonotonous but also a heavily oscillating curve, especially at the nucleus of Li. While "globally" the T_c calculated for LiH is positive, locally it can be negative. $t([\rho]; \vec{r})$ and $t_s([\rho]; \vec{r})$ are always positive quantities, however, they show step structure along the radial distance due to the shell structure of Li [55, 99] in different phases. The difference of them, which gives $t_c(\vec{r})$, can be then negative at certain places. This local anomaly makes proper modelling difficult even impossible. And indeed, $t_c^{mod}(\vec{r})$ functionals build up spurious cusps on the atoms in the molecule as well, nevertheless, in the bonding region a satisfactory local characteristics is obtained. The interatomic peak of $t_c(\vec{r})$ is somewhat reproduced only by the model WL because of artificial topological reason [98].

Table 6: **Molecular $T_c[\rho]$ values calculated by various approximate functionals**

All the energies are in a.u. The calculations were performed using the large TZV+3D basis. $E_c[n]$ and $T_c[n]$ values are taken from ref [77] and ref [100], respectively.

atom	WL	PW91	VWN-S	LW-3	Bc95	$-E_c[n]$	eq. 21	$T_c[n]$
H_2	.044	.035	.045	.026	.033	.041	.033	.035
Li_2	.122	.108	.157	.116	.115	.122	.097	
Be_2	.200	.160	.219	.167	.169	.205	.163	
B_2	.303	.226	.293	.229	.241	.330	.262	
C_2	.406	.301	.371	.296	.318	.514	.408	
N_2	.494	.383	.451	.369	.396	.546	.433	
O_2	.582	.466	.537	.449	.480	.657	.521	
F_2	.647	.543	.619	.525	.554	.746	.592	
LiH	.083	.075	.103	.073	.077	.083	.066	.057
BH	.151	.125	.167	.124	.130	.153	.121	.099
FH	.356	.295	.337	.281	.301	.387	.307	.237
CO	.480	.386	.453	.370	.395	.550	.436	
H_2O	.351	.280	.319	.255	.281	.367	.341	
NH_3	.346	.260				.338	.268	
CH_4	.332	.242				.293	.232	
HCN	.485	.371				.527	.418	
C_2H_2	.544	.396				.528	.419	

For further analysis, Table 3.2 represents T_c values calculated for certain molecules, which provide a good picture of "first row" chemistry. Unfortunately, nearly exact $T_c[\rho]$ values are available only for H_2 and for several hydrides [100]. These values are calculated from eq. 3.3 directly using CI wave-functions. However, alternative way of calculating nearly exact T_c for molecules is possible as well, when experimental atomization energy (AE) is available [28, 126]. In this case $T[n]$ can be expressed directly from AE, and T_c equals with

$$T_c^{exp}[\rho] = E_{AE}^{molecule} + \sum_i E_{ai} - T_s[\rho] \quad (0.19)$$

where E_{ai} is the corresponding total atomic energy [28]. The values of 0.035, 0.069, 0.132 and 0.377 a.u. are obtained for H_2 , LiH, BH and FH, respectively. This procedure deals with experimental-like $T^{exp}[n]$, while $T_s[n]$ is only nearly exact and its accuracy depends on the quality of the employed CI wave-function. The more accurate reference CI density is applied at constrained search method the larger $T_s[n^{ref}]$ can be obtained. Consequently, $T_c^{exp}[n^{ref}]$ is somewhat larger, while $T_c[n^{ref}]$ evaluated from CI calculation is smaller, than T_c which can be obtained when the reference density is the exact one. Gritsenko et al. obtained T_c values for certain hydrides from CISD calculations [100] (see Table 3.2). They also made the following extrapolation,

$$T_c^e = T_c \frac{E_c^{exp}}{E_c^{CI}} \quad (0.20)$$

where E_c^{exp} is the empirical [77] or conventional correlation energy [28, 27]. The extrapolated T_c^e values of 0.061, 0.110 and 0.304 are obtained for LiH, BH and FH, respectively which are significantly lower than the values obtained by eq. 19.

The same trend holds for Table 3.2, as it was found for Table 3.1 PW91 and Bc95 provide values with acceptable accuracy for molecules where comparison is possible. For the other cases, where T_c is unknown yet, it can be approximated if we take into account, that T_c is roughly proportional to E_c [101] with the equation

$$T_c[\rho] \approx -CE_c[\rho]. \quad (0.21)$$

In eq. 21 C can be evaluated on the basis of available atomic T_c values. C is found to be 0.793 on the basis of average rate of T_c of 11 (Table 5.) atomic species.

Using eq 21, in Table II., T_c values are presented with which a careful comparison can be made. C can be seen as the ratio $-T_c[\rho]/E_c[\rho]$, which is less than 1 in DFT due to the localization effect of correlation. The Kohn-Sham kinetic energy functional $T_s[n]$ minimizes the kinetic energy for the reference density and is still higher than the Hartree-Fock kinetic energy [101]. As a result, the ratio $-T_c[\rho]/E_c[\rho]$ is consistently lower than 1 [100], ranging from 0.75 to 0.85 for neutral atomic species. It is interesting to note that for H^- and Be^{2+} the values of 0.68 and 0.96 are found. These values reflect the diffuse character of H^- and the tightly bound feature of Be^{2+} . The ratio C can be given in term of the scaling derivative $\frac{\partial E_c^\lambda}{\partial \lambda}|_{\lambda=1}$,

$$C = -\frac{T_c[\rho]}{E_c[\rho]} = -\frac{(\partial E_c^\lambda / \partial \lambda)_{\lambda=1} - E_c[\rho]}{E_c[\rho]}. \quad (0.22)$$

For tightly bound atoms $\frac{\partial E_c^\lambda}{\partial \lambda}|_{\lambda=1}$ is small [78], while for diffuse systems like anions or certain molecules, it can be relatively large.

Keeping this in mind one can conclude that $T_c^{mod}[\rho]$ functionals derived from atomic data or from the electron gas model tend to underestimate T_c for those molecules which have been taken into account in Table 3.2. This is true for the PW and Bc95 models and especially for LW function. Functional WL, due to its artificial topological feature in the bond midpoint, overestimates T_c significantly (for details see ref [98]). Bc95 and VWN-S have a shallow minimum and they are rather similar to each other. The difference between the T_c values of VWN-S and Bc95 is due to the local difference in the outer region.

Figure 3.1 Correlation contribution to interacting kinetic energy density $t_c(\vec{r})$ and model functionals $t_c^{mod}(\vec{r})$ for He

Conclusion

Correlation functionals are designed to model the dynamic correlation that keeps electrons apart at short interelectronic distances. Near degeneracy or non-dynamical correlation is not described at all by most DFT correlation functionals, and both the kinetic energy and the interaction of the electron density with the external potential is included implicitly through the parameter fitting. Due to this, $T_c^{mod}[\rho]$ functionals which are originated from Levy-Perdew relation (eq. 14) still retain the deficiency of $E_c^{mod}[\rho]$ counterparts. Left-right correlation, which is topologically clearly represented in the bond midpoint peak of $t_c([\rho]; \vec{r})$, is incorrectly reproduced by model functionals. T_c values based on CISD calculations provide ratios for C 0.69, 0.65 and 0.61 for LiH, BH and FH, respectively. It is beyond argument that these values need further improvement, however, the possibility of extension of CI calculations is limited. Therefore it is not useless to employ proportionability of T_c to E_c like eq. 21. A possible way of going beyond the accuracy of present day $E_c[\rho]$ functionals can be the modelling of the potential part $W_c[n]$ [6] and the kinetic contribution $T_c[n]$ separately. Although $t_c([\rho]; \vec{r})$ is nonuniquely defined under the integration sign in eq. 4, the comparison is possible between different definitions of

t_c , like the one is given in eq. 3 or in eq. 14 in LDA with slowly varying densities.

Figure 3.2 Correlation contribution to interacting kinetic energy density $t_c(\vec{r})$ and model functionals $t_c^{mod}(\vec{r})$ for H_2 at equilibrium distance. The bond midpoint and atomic position of H can be seen at $Z=0.0$ and $Z=0.7$, respectively. The corresponding correlation energy density $e_c([\rho];\vec{r})$ is displayed for the nearly exact case and for several models as well (b). The enlarged figure of $t_c([\rho];\vec{r})$ and $t_c^{mod}([\rho];\vec{r})$ are plotted separately (a).

Figure 3.3 Correlation contribution to interacting kinetic energy density $t_c(\vec{r})$ and model functionals $t_c^{mod}(\vec{r})$ for LiH in the atomic region (a) and in the bonding region of LiH. Atomic positions H and Li can be seen at $Z=-1.5$ and $Z=1.5$, respectively.

Application to atoms, ions, and molecules of the Liu-Parr local correlation energy functional

24 Abstract

The Liu-Parr new local form of the correlation energy functional has been applied to first- and second-row neutral atoms and both diatomic and polyatomic molecules. This local form originates from the adiabatic connection and functional expansion formulation in DFT. It consists of a sum of three of four integrals of density to the $1, 2/3, 1/3,$ and 0 powers. Numerical results show that among five commonly used local forms of the correlation energy, this one best reproduces the experimental values, and in some cases it is even comparable with the LYP non-local form. Its connection with the Wigner formula are discussed. The scaling properties of Wigner-type functionals are investigated, as well as the coupling constant integration is applied on the scaled form of the nonlocal Wigner-type Wilson-Levy correlation functional.

25 Introduction

Although the electron correlation energy is just a few percent of the total energy of a chemical system, it is still about the same, sometimes even larger than the magnitude of energy changes in important physical and chemical processes. Among the several theoretical ways to take care of it is DFT [6]-[23]. The first attempt along this line was by Wigner [73], who proposed a formula in the local density approximation (LDA) framework. In the last two decades, there have been many achievements on this topic in DFT [105]. Perhaps the best-known developments are the so-called gradient expansion approximation (GEA) and the generalized gradient approximation (GGA), e.g., LYP [20], PW91 [106], etc. Quite accurate correlation energies can be computed in these formulations, and nowadays they are being widely

used in various software packages, even though there are reports indicating that they failed under [107, 109].

Developments of an improved local form of the correlation energy is of special interest for large systems. Experience shows that with density gradients and Laplacians incorporated in them, GGA formulas are computationally time-consuming for large systems, and also produce convergence difficulties in self-consistent-field (SCF) calculations. Wigner gave the first local form of the correlation energy density functional [73], Vosko, Wilk and Nusair (VWN) proposed another [110], followed by Perdew (the Perdew local form (PL)) [111] Based on the adiabatic connection formulation, Zhao, Levy and Parr (ZLP) [112] advised a so-called "Wigner-scaled" local correlation energy density functional. Recently, based on the functional expansion and adiabatic connection formulations in DFT, we have obtained a new form [113], which is a sum of integrals of the density to 1, 2/3, 1/3 and 0 powers, for both the correlation energy E_c and its kinetic component T_c . Numerical tests for neutral atoms demonstrated the effectiveness of such series of local functionals. In this section, we extend the application to ions and molecules. It will be found that the new form is superior to other local forms and comparable to the LYP form, which is non-local in nature.

26 Theoretical formulation

In Refs. [113]-[114], it has been established that the correlation energy density functional $E_c[\rho]$ can be expanded effectively in terms of homogeneous functionals $A_n[\rho]$, $n = 1, 2, 3, \dots$, i.e.

$$E_c[\rho] = \sum_{n=1}^{\infty} \frac{A_n[\rho]}{n!}. \quad (0.1)$$

It was shown [113] that $A_n[\rho]$ is homogeneous of degree $(1-n)$ in coordinate scaling, that is,

$$A_n[\rho_\gamma] = \gamma^{1-n} A_n[\rho] \quad (0.2)$$

with

$$\rho_\gamma(\vec{r}) = \gamma^3 \rho(\gamma\vec{r}). \quad (0.3)$$

This scaling of the density keeps it normalized for all γ . Cosequently, one has [113]

$$- \int \rho(\vec{r}) \vec{r} \nabla \frac{\delta A_n[\rho]}{\delta \rho(\vec{r})} d\vec{r} = (1 - n) A_n[\rho]. \quad (0.4)$$

Liu [117] has proved that the exact form of $A_n[\rho]$ should have the form

$$A_n[\rho] = 1/2 \int \frac{\rho(\vec{r}) \rho(\vec{r}')}{|\vec{r} - \vec{r}'|} [a_n([\rho]; \vec{r}, \vec{r}')] d\vec{r} d\vec{r}'. \quad (0.5)$$

where $a_n([\rho]; \vec{r}, \vec{r}')$ is another unknown functional (that is the pai-correlation function introduced in eq. (1.36)) homogeneous of degree $(-n)$ in coordinate scaling, i.e.

$$a_n([\rho_\gamma]; \vec{r}, \vec{r}') = \gamma^{-n} a_n([\rho]; \vec{r}, \vec{r}') \quad (0.6)$$

for $n = 1, 2, 3, \dots$. As an approximation, at first, we suppose that all $A_n[\rho]$ are local, that is,

$$A_n[\rho] = \int f(\rho(\vec{r})) d\vec{r}. \quad (0.7)$$

With this assumption, one finds [118]-[119]

$$A_n[\rho] = -1/3 \int \vec{r} \nabla \rho(\vec{r}) \frac{\delta A_n[\rho]}{\delta \rho r} d\vec{r}. \quad (0.8)$$

Combinations of Eqs. (2.4) and (2.8) gives

$$\int \rho(\vec{r}) \frac{\delta A_n[\rho]}{\delta \rho r} d\vec{r} = \left(\frac{4 - n}{3} \right) A_n[\rho], \quad (0.9)$$

for $n = 1, 2, 3, \dots$, which means that $A_n[\rho]$ is homogeneous of degree $(4 - n)/3$ in density scaling. With the uniqueness theorem in Appendix of ref [113], one finally obtains the analytical expression for all $A_n[\rho]$

$$A_n[\rho] = C_n \int \rho^{(4-n)/3}(\vec{r}) d\vec{r} \quad (0.10)$$

with $n = 1, 2, 3, \dots$ and constants to be determined. The consequence is that, under the local assumption, the correlation energy density functional $E_c[\rho]$ (and similiary its kinetic component $T_c[\rho]$) can be expressed as

$$E_c = C_1 N + C_2 \int \rho^{2/3} d\vec{r} + C_3 \int \rho^{1/3} d\vec{r} + C_4, \quad (0.11)$$

where N is the total number of electrons of the system, and the constants C_1 to C_4 are to be determined.

Table 4.1 showed us that the difference between the DFT-version of correlation (1.24 and 1.41) and conventional correlation (1.23) at least for small systems is quite small. We thus suspect that the conventional correlation energy can also be approximately expressed as in (4.11). Numerical data below will support this hypothesis.

27 Computational method

The densities used in (2.11) for first 18 neutral atoms are both the Hartree-Fock (HF) and CI densities. The HF densities are calculated explicitly using the wavefunctions of Clementi and Roetti [120], and the CI densities are obtained using the ATOMCI program [121]. A full CI calculation was performed on He. Multireference CI [1, 30] calculations with single and double excitations were performed on the other atoms. The densities for positive ions, e.g., Be isoelectronic series and Ne ion series, are explicitly computed from HF wavefunctions of Clementi and Roetti [120]. The HF densities for 21 diatomic and polyatomic molecules are from the GAMES [122] program package. We first perform HF calculations in triple-zeta Gaussian basis set with additional 3d polarization functions (Dunning's TZP basis) [123]-[124] to obtain the SCF and HF wave functions. A numerical integration is then carried out to obtain the densities and integrals of density to the 2/3 and 1/3 powers.

The coefficients that appear in (4.11) are obtained by the least-squares fit using the best theoretical values of the correlation energy for the first 18 atoms and their HF and CI densities. The best CI correlation values of neutral atoms, ions and molecules are from refs. [28, 124], respectively. Five schemes are employed in the fits, denoted by CI3, CI4, HF3, HF4 and EcTc, respectively. CI3 means using the CI densities of first 18 neutral atoms and their "best" correlation energies to fit the first three coefficients in (2.11), while CI4 means using the CI densities to fit all four parameters in their equation, and similarly with HF3 and HF4. Scheme EcTc,

however, is from ref. [113], in which E_c and T_c are fitted together to obtain the four coefficients by using CI densities. The coefficients for EcTc are $C_1=-0.0532$, $C_2=0.0121$, $C_3 = -0.0003$ and $C_4 = -0.00070$.

For comparison, we also present correlation energy values of other approximate functionals, for example Wigner [73], PL [106], VWN [110] and ZLP [112] local forms and the Lee-Yang-Parr (LYP) [20] gradient-dependent formula which is based on the Colle-Salvetti [125] orbital-dependent correlation functional. Results calculated by the GAUSSIAN92-DFT code [97], and those of the Wigner form are computed using densities described above and Süle and Nagy's reparametrized Wigner form [76]. To obtain the results of ZLP local form, we reparametrized the two parameters α_0 and κ appearing in their formula by using the HF densities and the exact values of conventional correlation energies of first 18 neutral atoms. We obtain $\alpha = 0.050587$ and $\kappa = 0.227154$. ZLP values are then calculated using the HF densities for above ions and molecules.

First, in Table 4.1, we present our fitted results. One sees that CI3, CI4, HF3 and HF4 give almost the same results. This justifies the use of HF densities in calculating correlation energies of atoms. Besides, since there is no essential difference between three- and four-parameter fits, we prefer to use the simpler three-parameter formula. In what follows, we will only present HF3 results for ions and molecules. A feature of these fits is that the successive coefficients become smaller very rapidly in the series except for the constant term. In column 7 we show that using the CI densities and the coefficients for the DFT-version correlation energy [113], we can fairly well predict the conventional correlation energy, especially for heavy atoms. In column 8 best theoretical DFT E_c values are shown. Compared with the conventional values, one finds that they follow the same trends semiquantitatively.

In Table 4.2 results of application of schemes HF3 and EcTc, together with those of Wigner, VWN, PL, ZLP and LYP, for 21 diatomic and polyatomic molecules are shown. Curves of the exact values versus approximate ones are plotted in Fig. 4.1 For clarity, only one of our results, scheme EcTc, is shown in this and later figures. It is seen that among VWN, PL, Wigner, ZLP and (4.11), the new formula gives the

Table 7: **Exact, fitted and predicted correlation energies^a for the first- and second-row neutral atoms (a.u.).**

^a The fitted parameters are: CI3: $C_1 = -0.05855, C_2 = 0.01676, C_3 = -0.00048$; CI4: $C_1 = -0.05690, C_2 = 0.01480, C_3 = -0.00043, C_4 = 0.01143$; HF3: $C_1 = -0.05931, C_2 = 0.01762, C_3 = -0.00057$; HF4: $C_1 = -0.05742, C_2 = 0.01535, C_3 = -0.00050, C_4 = 0.01299$, **b** From ref. [126]

Atom	Exact	CI3	CI4	HF3	HF4	EcTc	E_c^{DFTB}
H	0.0	-0.004	0.003	-0.005	0.003	-0.018	0.0
He	-0.043	-0.049	-0.042	-0.049	-0.041	-0.063	-0.042
Li	-0.045	-0.058	-0.056	-0.060	-0.057	-0.070	-0.051
Be	-0.094	-0.070	-0.071	-0.072	-0.073	-0.094	-0.093
B	-0.125	-0.113	-0.115	-0.112	-0.114	-0.137	-0.129
C	-0.156	-0.163	-0.164	-0.162	-0.163	-0.185	-0.161
N	-0.188	-0.218	-0.218	-0.218	-0.217	-0.237	-0.188
O	-0.258	-0.274	-0.272	-0.275	-0.273	-0.289	-0.261
F	-0.325	-0.332	-0.328	-0.334	-0.330	-0.342	-0.322
Ne	-0.390	-0.392	-0.387	-0.394	-0.388	-0.397	-0.376
Na	-0.396	-0.410	-0.408	-0.413	-0.411	-0.410	-0.401
Mg	-0.438	-0.421	-0.423	-0.424	-0.426	-0.432	-0.452
Al	-0.470	-0.454	-0.457	-0.456	-0.460	-0.466	-0.491
Si	-0.505	-0.511	-0.513	-0.499	-0.502	-0.521	-0.527
P	-0.540	-0.550	-0.552	-0.549	-0.552	-0.560	-0.559
S	-0.605	-0.599	-0.601	-0.599	-0.601	-0.607	-0.629
Cl	-0.666	-0.658	-0.658	-0.658	-0.658	-0.662	-0.689
Ar	-0.722	-0.716	-0.714	-0.717	-0.715	-0.715	-0.744

Table 8: Prediction of the conventional correlation energies for 21 diatomic and polyatomic molecules (a.u.)

Molecule	VWN	PL	LYP	Wigner	ZLP	HF3	EcTc	Exact
H_2	-0.131	-0.096	-0.038	-0.029	-0.030	-0.024	-0.043	-0.041
LiH	-0.291	-0.217	-0.089	-0.083	-0.082	-0.076	-0.099	-0.083
Li_2	-0.441	-0.329	-0.133	-0.134	-0.129	-0.080	-0.114	-0.122
Be_2	-0.613	-0.462	-0.200	-0.193	-0.185	-0.152	-0.191	-0.205
CH_4			-0.294	-0.241	-0.233	-0.253	-0.295	-0.293
B_2	-0.807	-0.614	-0.289	-0.265	-0.254	-0.246	-0.286	-0.330
NH_3			-0.318	-0.268	-0.258	-0.286	-0.320	-0.338
H_2O			-0.340	-0.314	-0.286	-0.321	-0.345	-0.367
HF	-0.906	-0.701	-0.363	-0.335	-0.318	-0.357	-0.372	-0.387
LiF			-0.418	-0.343	-0.375	-0.431	-0.445	-0.447
C_2H_2			-0.443	-0.386	-0.365	-0.397	-0.442	-0.476
C_2	-1.010	-0.773	-0.384	-0.344	-0.332	-0.355	-0.390	-0.514
HCN			-0.464	-0.410	-0.394	-0.430	-0.466	-0.527
C_2H_4			-0.497	-0.417	-0.403	-0.438	-0.493	-0.528
N_2	-1.224	-0.942	-0.483	-0.435	-0.414	-0.461	-0.489	-0.546
CO	-1.228	-0.946	-0.484	-0.440	-0.419	-0.463	-0.490	-0.550
C_2H_6			-0.551	-0.426	-0.423	-0.479	-0.547	-0.553
O_2	-1.429	-1.103	-0.583	-0.533	-0.505	-0.572	-0.592	-0.657
H_2O_2			-0.638	-0.569	-0.542	-0.611	-0.642	-0.691
F_2	-1.667	-1.295	-0.675	-0.633	-0.597	-0.676	-0.689	-0.746
CO_2			-0.791	-0.720	-0.680	-0.766	-0.797	-0.829

best prediction for these molecules. The results are comparable to those of the LYP formula for these species, as shown in the figure. VWN produces its well-known overestimation behaviour which is due the lack of self-interaction correction [42]. ZLP was originally obtained from the Wigner function by the adiabatic connection formulation [112]. However, its performance varies quite substantially from case to case.

28 Discussion of the relationship between the Liu-Parr and Wigner formulas

It is interesting to discuss the relationship of our formula with the Wigner form. Recall that the Wigner form resulted from analytical parametrization of high- and low-density limits of the homogeneous electron gas [73] for the intermediate density range, while (4.11) was obtained analytically, under the locality assumption, from adiabatic connection and functional expansion formulations of coupled Hamiltonian based on the constrained-search procedure [6]-[43]. Consider the Wigner form,

$$E_c^{Wigner}[\rho] = \int \frac{a\rho(\vec{r})}{1 + \kappa\rho^{1/3}(\vec{r})} d\vec{r}, \quad (0.12)$$

where a and κ are constants to be determined. Recently, Süle and Nagy [76] reparametrized it to reproduce the conventional E_c values of eight closed-shell atomic species, giving $a = -0.1247$ and $\kappa = 2.82234$. In the high-density limit, (2.12) can be expanded up to the third order has

$$E_c^W[\rho]_{high-density} = aN - a\kappa \int \rho^{2/3}(\vec{r}) d\vec{r} + a\kappa^2 \int \rho^{1/3}(\vec{r}) d\vec{r} - a\kappa^3, \quad (0.13)$$

which is exactly the same series as we obtained in (4.11), except for different coefficients. This shows that in the high-density regime, Eqs. (4.11) and (4.12) may be parametrized to produce almost the same results. For the low-density limit, however, one gas

$$E_c^W[\rho]_{low-density} = \frac{a}{\kappa} \int \rho^{4/3}(\vec{r}) d\vec{r} - \frac{a}{\kappa^2} \int \rho^{5/3}(\vec{r}) d\vec{r} + \frac{a}{\kappa^3} \int \rho^2(\vec{r}) d\vec{r} - \dots \quad (0.14)$$

All terms on the right-hand side of (4.14) are not allowed in the local density approximation of the correlation energy, as proved in ref [113]. It is therefore clear that the Wigner form takes good account of the high-density regime, but it does poorly in the low-density one. It is believed that the electron dynamic correlation is a short-range behavior, and for atoms and molecules it becomes important only when the electron density is high, i.e. not far from nuclei. This fact somehow compensates the weakness of the Wigner form, and thus it turns out to be one of the commonly used approximate forms for the correlation energy density functional we

have so far. Owing to the simple, general and relatively accurate performance of the correlation energy functional of (4.11), we expect it would be readily applicable to other systems.

29 Comparison of local and nonlocal Wigner-type functionals

The difficulties in obtaining correlated wavefunction for polyatomic molecules are well known [6]. There are somewhat established, by now, techniques to obtain the correlation correction in small molecules. For large molecules this is not the case in practise. In this work we use a proposal originally put forward by Wigner [73], where one assumes that there is a functional of the Hartree-Fock (HF) density capable of yielding reasonable estimates of the correlation correction. This is the so-called "Hartree-Fock + Density Functional" (HF-DFT) idea, which is very easy to implement, and the obtained results are in comparable accuracy with other correlation methods (MP2 e.g.) for much lower cost. The recently published HF-DFT results for molecules are comparable with results obtained using the highly accurate CCSD(T) method [127].

In the last few years, the success of density functional models as a good way to improve HF results has been widely recognised [81]. The results of the systematic work done by many groups in the study of exchange and/or correlation energy (CE) density functionals have shown that the calculation of the correlation energy by means of DF models is much simpler to implement than traditionally used configuration interaction or perturbation theory techniques or the recently developed coupled-cluster method, while the results are of comparable quality [129]. The lately developed CE functionals give surprisingly good results in spite of the fact that the exact functionals are unknown. In the last few years one of the most popular functionals is the BLYP, which is a combination of the Becke exchange (B88) [89] and the Lee-Yang-Parr [20] correlation functionals. The success of the BLYP functional is probably due to the cancellation of errors, because B88 overestimates the exchange

by 10 percent, while LYP underestimate correlation by a factor of 2, a compensation of errors can occur which could give the impression of high accuracy and theoretically it is not clear to use arbitrary mixture of HF and DF exchange energy. Therefore we prefer here the HF+DFT model, whereas we add only correlation correction via appropriate density functional. rather than the arbitrary combination of exchange and correlation functionals like the BLYP model. However, it should be mentioned, that BLYP reproduces correctly the shape of the exchange-correlation hole, consequently, the $E_{xc}[\rho]$ functional behaves correctly, while its constituents, the exchange and correlation parts suffer from severe deficiencies [14] (and references therein).

We shall report here the comparative test of Wigner-like local and nonlocal functionals [73]. One of these functionals is the most recently developed Wilson-Levy [35] (WL) functional, which was constructed to satisfy certain uniform and nonuniform coordinate scaling relations.

$$E_c^{WL}[\rho] = \int \frac{a\rho + b |\nabla\rho| / \rho^{1/3}}{c + d |\nabla\rho| / (\rho/2)^{4/3} + r_s} dr \quad (0.15)$$

where ρ is the electronic density, a, b, c, and d are parameters determined by Wilson and Levy [35], and r_s is the Wigner-Seitz radius,

$$r_s = (3/4\pi\rho)^{1/3}. \quad (0.16)$$

The Gombás-Lie-Clementi (GLC) [130] functional has the form

$$E_c^{GLC}[\rho] = \int \frac{a\rho^{4/3}}{1 + b\rho^{1/3}} dr \quad (0.17)$$

where a=0.0357 and b=0.0311 as given by Gombás [53]. This expression has also been proposed for the exchange-correlation energy with different parameters by Lee and Parr [113].

We also propose here the original form of the local Wigner (LW) CE functional with new parameters which was obtained by the program DETEDF [76] using the same set of closed shell species for parametrization as Wilson and Levy [35].

$$E_c^{LW}[\rho] = \int \frac{a\rho}{b + r_s} dr \quad (0.18)$$

where $a=-0.02728$, $b=0.21882$. The Lee-Yang-Parr (LYP) [20] correlation energy formula is the following:

$$E_c^{LYP}[\rho] = \int \frac{a}{1 + d\rho^{-1/3}}(\rho + b\rho^{-2/3}(C_F\rho^{5/3} - 2t_W + (\frac{1}{9}t_W + \frac{1}{18}\nabla^2\rho)))e^{-c\rho^{-1/3}} dr \quad (0.19)$$

where t_W is the Weizsacker kinetic energy term, a , b , d , c , and C_F are constants. In the parametrization procedure only one experimental value, the CE of the He , was used for the WL and LYP functionals.

The Wilson-Levy functional as well as the Wigner's original functional [73] satisfy certain coordinate scaling relations [132] like

$$\lim_{\lambda \rightarrow \infty} \lambda^{-1} E_c[\rho_\lambda] = 0, \quad (0.20)$$

and

$$\lim_{\lambda \rightarrow \infty} E_c[\rho_\lambda] \geq a[\rho]. \quad (0.21)$$

where $a[\rho]$ is bounded bellow. The functional WL satisfies both the uniform and nonuniform coordinate scaling requirements for $\lambda \rightarrow 0$ and $\lambda \rightarrow \infty$ which can be demonstrated on the following scaled Wilson-Levy functional. Uniform scaling represents coordinate "shift" along all the spatial directions (x,y,z).

$$\rho_\lambda(x, y, z) = \lambda^3 \rho(\lambda x, \lambda y, \lambda z). \quad (0.22)$$

Nonuniform scaling is performed only at certain coordinates which result in e.g. the following nonuniformly scaled density.

$$\rho_\lambda^x(x, y, z) = \lambda \rho(\lambda x, y, z). \quad (0.23)$$

The scaled form of (3.15) functional is as follows [35]:

$$E_c^{WL}[\rho_\lambda] = \int \frac{a\rho + b |\nabla\rho| / \rho^{1/3}}{c + d |\nabla\rho| / (\rho/2)^{4/3} + \lambda^{-1} r_s} dr \quad (0.24)$$

The scaling procedure is nothing else than the insertion of scaled density $\rho_\lambda = \lambda^3 \rho$ into the functional considered [132]. After scaling one has to return from the scaled $d\lambda^3 \vec{r}$ coordinate to the original $d\vec{r}$ which results in simplification with λ^3 in the scaled energy density $\epsilon_c^\lambda([\rho_\lambda])$. During the scaling procedure it has been taken account that

$|\nabla\rho_\lambda|/\rho_\lambda^{1/3} = \lambda^3 |\nabla\rho|/\rho^{1/3}$. The factor λ^3 is disappeared when simplification is performed. We obtained the following correlation functional using coordinate scaling within the coupling-constant integration scheme [128],

$$E_c[\rho] = \int_0^1 d\lambda E_c^\lambda[\rho_\lambda] \quad (0.25)$$

where λ is the coupling constant parameter. The fulfilment of certain scaling relations raises the following questions: *Which form of correlation functionals represents the best candidate for coupling-constant integration? Is there any connection between the scaling properties and the suitability for coupling-strength integration?* Unfortunately we do not know the exact answers for these questions which is a consequence of the fact that the exact exchange-correlation energy functional is unknown yet [90]. The only possibility in our hand is the simple trial of functionals developed by using the exact relations concerning pair-correlation functions, exchange-correlation holes and itself the exact $E_{xc}[\rho]$ functional (see subsection 1.5-1.6).

The following new Wigner-type gradient corrected functional is obtained using eq. (4.25). It is to be emphasized that $E_c^{WL,\lambda}$ does not include any correlation contribution to the kinetic energy T_c , which is necessary for satisfying the Levy-Perdew virial relation [78] in DFT.

$$E_c[\rho] = \int d\vec{r} \frac{a\rho + b|\nabla\rho|/\rho^{1/3}}{r_s} \left(1 - \frac{c + d|\nabla\rho|/(\rho/2)^{4/3}}{r_s} \ln \left[\frac{r_s + c + d|\nabla\rho|/(\rho/2)^{4/3}}{c + d|\nabla\rho|/(\rho/2)^{4/3}} \right] \right). \quad (0.26)$$

The parameters a, b, c and d are optimized in such a way to minimize the following expression

$$G = \sum_{i=1}^8 \left[\frac{\partial E_c[\rho_\lambda^i]/\partial\lambda|_{\lambda=1}}{E_c[\rho^i]} \right]^2, \quad (0.27)$$

where $i = He, Li^+, Be^{2+}, Be, B^+, Ne, Mg$ and Ar . These species represent atomic correlation quite well and consequently provide good basis for the parametrization procedure. This expression is obtained using the Levy-Perdew relation [78] and is assumed that the scaling derivative $\partial E_c[\rho_\lambda]/\partial\lambda|_{\lambda=1}$ is small in magnitude even Hartre-Fock density is inserted into (4.27) [35]. Only one experimental value, the correlation energy of He [28] is employed, since (4.27) contains only theoretical

expressions [35]. The parametrization procedure is carried out by the program DETEDF [76] using the SIMPLEX algorithm [133] and the coefficients that resulted from minimizing (4.27) are $a = -3.711598$, $b = 0.34421$, $c = 14.56911$ and $d = 1.35224$.

We show here the test of Wigner-like functionals on a limited set of molecules to get more information about the performance of these functionals. In this study we also examine larger systems in order to obtain more complete understanding of the performance and the future applicability of DFT for the study of organic reaction mechanism. We performed first HF-calculation [82] and then with the use of the AIMPAC [131] suit "wavefunction-file" we obtained the electronic density and the gradient of the density then we calculated the CE using high quadrature for integration. All of the HF-calculations employed the HF/6-311G(3df,2p) basis set. CE calculations were carried out using the local Wigner-like Gombás-Lie-Clementi (GLC) functional, and the nonlocal Wilson-Levy functional, and for comparison we also give the CE obtained by the Lee-Yang-Parr (LYP) [20] functional which are incorporated into the program DETEDF [76]. This program is capable of reading wavefunction file of program GAMESS [82] in order to construct the electronic density and the gradient of the density. The numerical integration is also done by this program using Monte Carlo high quadrature [133]. Experimental geometries were used for molecular calculations [129].

The comparative test of Wigner-like functionals in Table 9 shows that the very simple local GLC-functional gives surprisingly good results, which are very close to the CE obtained by the nonlocal LYP-functional for molecules. Unfortunately GLC underestimates the CE of atoms with atomic number less than 10 significantly, and overestimates it with atomic number more than 10 which is probably due to the fact, that this functional was fitted for small molecules in order to reproduce well the molecular CE rather than the atomic ones.

In Figure 4.1 we have plotted the calculated and experimental CE for atoms vs. atomic number. LW shows nearly linear dependence along the atomic number while the experimental CE curve has a "cusp" at charge 10. The nonlocal CE functionals

describe well the characteristics of the CE curve, while the neon with charge 10 gives a breaking point in trends this is well reproduced by all the functionals. For Ar all of them give smaller value than the experimental observation except the WL, which is very close to the experimental CE.

The Wilson-Levy functional seems to slightly overestimate the CE for molecules while the values obtained for atoms are in very good agreement with the experimental observation (Table 9). According to Fuentealba and Savin [87] the WL is superior for small and medium sized molecules. It's worth mentioning that the WL the only nonlocal CE functional, which binds the Be_2 molecule, but unfortunately F_2 remains big challenge for every functional as they don't give positive binding energy for it, however the WL gives the less negative value [87]. This fact is also suggest that the WL functional represents a positive step in the way to improve CE functionals. On the other hand it seems that WL-functional overestimates more significantly the CE for large molecules, while in the case of smaller molecules the agreement is very good with the experimental observation. In chapter 2 it has been discussed already, that this notorious overestimation behaviour of WL is due to its artificial bond midpoint peak [98].

We have also studied the relationship between the asymptotic behaviour of the CE density and the performance of the CE functionals (Figure 4.2) in order of deeper understanding of correlation problem. In Figure 4.2 we have plotted CE densities for neon using triple-zeta valence Gaussian basis set with 3 polarization set. The WL functional has the highest cusp while the local Wigner functionals have lower and lower. Worth mentioning that the parametrization for molecules resulted in the lowest cusp in the case of GLC for atoms. The WL functional near the cusp at the rapidly varying region has fast damping, while LW much more slowly tends to zero. The LYP functional has negative cusp with respect to the others which is due to the Weizsäcker term which includes square gradient of the density. In Figure 4.2 the plot of $4r^2\pi$ product of CE density vs. radial distance shows that the highest maximum occurs in the slowly varying region for the WL functional. This region is responsible for correct accounting for the CE since the local Wigner and LYP

functional give much lower maximum in this region and the calculated CE of these functionals are worse than the one of WL functional. In the region with rapidly varying density there is also a maximum which is the highest for the LW functional, but this is thinner than the maximum in the region with slowly varying density and has smaller contribution to the total CE. For neon the local Wigner CE functionals give slightly lower value while the nonlocal WL gives one closer to the experimental observation which is due to the correct description of asymptotics of long range CE density, and not to the higher correlation cusp at radial distance zero as if we cutoff the cusp region of the WL CE density and make equal with the LW values, it doesn't result in any change in the final calculated total CE.

Table 9 confirm the already well-established result that CE functionals give a marked improvement over the HF values. Functional WL provides values in quite good agreement with the empirical results, however, for larger molecules overestimates CE significantly, which is due to the artificial bond-midpoint peak mentioned in chapter 2. The coupling constant integrated form of WL (WLA) behaves unexpectedly rather the similar way to WL, except perhaps for F_2 , whereas the obtained value of 0.695 represents significant improvement over all the other functionals. The local functional of Gombás (GLC) poorly underestimates the experimental molecular correlation energies and accounts only for the 80 % of total the CE, especially in the case of those molecules, which are "suffering" from significant amount of non-dynamical correlation. These molecules are typically the multiple bonded diatomics e.g. like C_2 , N_2 , or CO etc. F_2 with its single-bonded structure should be taken as one of the greatest challenge for correlation functionals. Functional LYP [20], which is simple modification of the Colle-Salvetti orbital-dependent functional (CS) [125], excludes kinetic contribution to correlation, consequently underestimates CE as well, at least for diatomics. However, it should be emphasized, that the model CS is based on a well defined pair-correlation model, which is coupling-constant (λ) independent and due to this does not account for T_c .

Figure 4.1 Atomic correlation energies vs. atomic number

Figure 4.2 Correlation energy density along the radial distance for Ne

Table 9: Correlation energies of molecules obtained with local and non-local Wigner-like functionals.

molecule	WL	WLA	GLC	LYP	EXP
H₂	0.049	0.048	0.038	0.065	0.041
Li₂	0.136		0.193	0.133	0.122
Be₂	0.221	0.227		0.200	0.205
B₂	0.336		0.332	0.289	0.330
C₂	0.449	0.448	0.403	0.380	0.514
N₂	0.532	0.538	0.475	0.483	0.546
O₂	0.621		0.547	0.583	0.657
F₂	0.683	0.695	0.617	0.675	0.746
H₂O	0.386	0.383	0.341	0.340	0.367
NH₃	0.365	0.381	0.338	0.318	0.338
CH₄	0.369	0.373	0.339	0.294	0.293
HF	0.377	0.382	0.342	0.363	0.387
CO	0.516	0.525	0.484	0.550	0.553
C₂H₂	0.504		0.462	0.443	0.476
C₂H₆	0.678	0.691	0.601	0.551	0.553
C₂H₄	0.593	0.614	0.534	0.497	
CH₃OH	0.705		0.612	0.595	
B₂H₆	0.618		0.537	0.462	
NH₄⁺	0.386		0.337	0.318	

WL, WLA, GLC and LYP denote Wilson-Levy functional [35], Gombás-Lie-Clementi functional [130], Lee-Yang-Parr functional [20] respectively. EXP denotes the experimental correlation energies [77]. All the energies are in a.u.. The calculations were carried out at experimental geometries.

Density functional study of strong hydrogen-bonded systems The hydrogen diformiate complex

30 Abstract

Gas phase calculations have been carried out on hydrogen-diformiate in order to model the low-barrier hydrogen bond. The structure and various properties of $HCOO^- \cdot HOOCH$ (hydrogen diformate) anionic hydrogen-bonded system are studied. Single, double as well as triple hydrogen-bonded structures are obtained by geometry optimization up to the level of MP2/6-311++G(d,p) and by various density functional approaches. Optimized structures and calculated complexation energies are compared with experimental observation. At least 78 percent covalent character is found in the strong O-H-O-type hydrogen-bond. Multiple H-bonded structures provide calculated binding energies which are in the closest agreement with experiment. The experimental complexation energy is reproduced within almost chemical accuracy in the range of 35-37 kcal/mol, while the experimental observation is 36.8 kcal/mol. The secondary interaction-like C-H...O contacts represent at least 3-4 kcal/mol energy lowering. The O-O bond distance is found in the range of 2.41-2.45 Å by various density functional methods, while the experimental value is 2.45 Å. The estimated counterpoise correction to basis set superposition error is also presented in the binding energies. The performance of density functional methods based on gaussian and Slater-type basis is compared using the G92-DFT and ADF codes, respectively. For comparison the energetics of hydrogen diacetate is given as well.

31 Introduction

Enzymes can achieve rate enhancements, which often require > 20 kcal/mol of transition state stabilization. Recent proposals to account for these large energies have invoked low-barrier hydrogen bonds (LBHB) [134, 135]. Strong hydrogen bonds

play central role in biological systems . Their significance is already well-known in biocatalysis and in determining the structure of biopolymers [135]. Most recently Warshel et al. argued the role of strong hydrogen-bonding in enzyme catalysis [141] reflecting on the paper of Cleland et al. [135]. Anionic hydrogen-bonded systems called "low barrier hydrogen bonds" can have association enthalpies as high as 36.8 kcal/mol (e.g. $HC\bar{O}O^- \cdot HO\bar{O}CH$ complex) , while ordinary hydrogen-bonds of the type between water molecules are relatively weak (5 kcal/mol) [136, 139]. Hydrogen bonds represent great challenge for quantum chemistry, when one would like to bring the calculated properties close to the chemical accuracy [142], especially when one deals with extended systems. Density functional theory (DFT) may provide a reasonable solution. Kohn-Sham DFT [5, 6] provides exact in principle solution of Schrödinger eigenvalue problem, however, in particular one has to face the problem that the exact exchange-correlation energy density functional is not yet known. The recently developed gradient corrected functionals account well for the variety of properties of molecules [142, 98]. Some recent studies have been devoted to the description of hydrogen-bonded systems by density functional methods [149]-[157], and, as a consequence DFT describes weakly-bonded systems well for relatively small cost with near chemical accuracy when calculating thermodynamic dimerization characteristics [156].

We have chosen the hydrogen-diformate ($HC\bar{O}O^- \cdot HO\bar{O}CH$), which represents a simple model system for carboxyl-carboxylate dyad. This dyad plays a significant role in the active center of aspartate proteases [143]. These enzymes have been recently identified in HIV-1 (Human Immunodeficiency Virus) and it is found that the viral protease is essential in the replication of HIV-1. Thus, the HIV protease is a potential target for AIDS therapy and drug design [137, 144]. Most of our knowledge about the catalysis of aspartate proteases is based only on X-ray and crystallographic studies and chemical intuition [143]. However, a more precise formulation of the mechanism requires a more sophisticated approach. Recently, there have been attempts to go beyond the abovementioned level, using only theoretical mechanistic studies based on semiempirical [144] or simple Hartree-Fock approximations [145].

As a first step for understanding the bond cleavage of polypeptides during catalysis, we investigate here the hydrogen-bonding of the model system of aspartate proteases by sophisticated *ab initio* as well as density functional methods. To the best of our knowledge, there is only a very limited number of publications [146]. From theoretical point of view the formate-formic acid complex represents an interesting system, since this is one of the strongest known H-bonded molecular complexes. However, the characteristics of strong H-bond are not well-known yet. An increased degree of covalency, which causes a remarkable shortening of the O-O distance of the bridge oxygens, is recently attached to the hydrogen-bonded system like $\text{HCOO}^- \cdot \text{HOOCH}$ [138]. A recently published low temperature neutron diffraction study proposed covalent character for O-H-O strong hydrogen bonds [140]. To account for the covalent vs. electrostatic character convincingly we performed bonding energy analysis. A still unanswered question is whether the hydrogen-bond (HB) as well as the complex are truly symmetric or rather unsymmetric, and whether single or double bonded structures account the best for the experimental observation. To answer these questions we have undertaken DF and correlated *ab initio* calculations on hydrogen diformiate. Several single, double and also one triple hydrogen-bonded structures have been obtained by geometry optimization and the most stable conformer is identified. Various calculated properties of these structures are compared with and stressed against the available experimental data. The applicability of DFT has been investigated and compared with correlated *ab initio* methods. We have also tested density functionals which incorporate gradient correction and some Hartree-Fock exchange [158, 170]. This hybrid approach has proved to be remarkable for hydrogen-bonded systems [142]. Our aim is also to compare the efficiency of the almost completely numerical ADF program [165] with the G92-DFT program, which is numerical only in exchange-correlation part. [97].

32 Methods of Calculations

In the Kohn-Sham theory [5], which is based on the Hohenberg-Kohn theorem [3] and usually called density functional theory (DFT), the electronic ground state

properties of a system are determined by the electronic density $n(\vec{r})$ via energy density functional. The exchange-correlation part can be treated only numerically using high quadrature for integration.

$$E_{xc}[n] = \int n(\vec{r})\epsilon_{xc}[n(\vec{r})]d\vec{r}, \quad (0.1)$$

where ϵ_{xc} is the exchange-correlation energy density per particle. The Kohn-Sham orbitals are obtained by solving the Kohn-Sham equations [5, 6] (compare with eqs. (1.17)-(1.22)).

$$\left[-\frac{1}{2}\nabla^2 + v_{ext}(\vec{r}) + v_J(\vec{r}) + v_{xc}(\vec{r})\right]u_i(\vec{r}) = \epsilon_i u_i(\vec{r}), \quad (0.2)$$

where $v_{ext}(\vec{r})$, $v_J(\vec{r})$ are the external and Coulomb potentials, respectively. $v_{xc}(\vec{r})$, which unfortunately remains unknown can be expressed as the functional derivative of $E_{xc}[n]$ [45]

$$v_{xc}(\vec{r}) = \frac{\delta E_{xc}[n(\vec{r})]}{\delta n(\vec{r})}. \quad (0.3)$$

The Kohn-Sham equations can be solved in practice by minimizing the total energy expression with respect to the unknown coefficients $c_{\nu i}$ (subject to the orthonormality of the u_i) using a finite set of algebraic secular equations for canonical orbitals.

$$\sum_{\nu} (F_{\mu\nu} - \epsilon_i S_{\mu\nu})c_{\nu i} = 0 \quad (0.4)$$

The quantities ϵ_i are one electron eigenvalues for the occupied orbitals. The Fock-type matrix $F_{\mu\nu}$ is given by

$$F_{\mu\nu} = H_{\mu\nu}^{core} + J_{\mu\nu} + F_{\mu\nu}^{xc}. \quad (0.5)$$

The $S_{\mu\nu}$ and $H_{\mu\nu}^{core}$ are the overlap and bare-nucleus Hamiltonian matrixes, respectively, and $J_{\mu\nu}$ is the Coulomb matrix [161] The exchange-correlation part of the Fock matrix can be given in two different ways. One possible way is to use the functional derivative expression 5.3 of $E_{xc}[n]$, which can be done analitically [6, 161]. This expression is implemented in the program G92-DFT [161, 97]. Then the total energy is expressed as

$$E = \sum_{\mu\nu} P_{\mu\nu} H_{\mu\nu}^{core} + \frac{1}{2} \sum_{\mu\nu\lambda\sigma} P_{\mu\nu} P_{\lambda\sigma} (\mu\nu | \lambda\sigma) + E_{xc}, \quad (0.6)$$

where

$$P_{\mu\nu} = \sum_{i=1}^{MO} c_{\mu i} c_{\nu i}. \quad (0.7)$$

Another possibility of solving eq. 5.4 is to use one-center auxiliary basis sets [8] for fitting the charge density $n(\vec{r})$

$$n(\vec{r}) = \sum_{\mu\nu} P_{\mu\nu} \chi_{\mu}(\vec{r}) \chi_{\nu}(\vec{r}) \simeq \sum_k a_k f_k(\vec{r}). \quad (0.8)$$

The use of this fitting basis set results in computational savings at integral evaluation. This is due to the fact that fitting procedure reduces the four-centered two-electron integrals of eq. 5.4 to three-centered integrals in an analytical, nonvariational least-square fitting procedure. The matrix elements of $J_{\mu\nu}$ are also treated by the functions $f_k(\vec{r})$. Then the $F_{\mu\nu}$ matrix elements of eq. 5.4 can be given by

$$F_{\mu\nu} = H_{\mu\nu}^{core} + \sum_k a_k \int \frac{\chi_{\mu}(\vec{r}) \chi_{\nu}(\vec{r}) f_k(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r} d\vec{r}' + \chi_{\mu}(\vec{r}) \chi_{\nu}(\vec{r}) v_{xc}(\vec{r}). \quad (0.9)$$

The matrix elements of the Fock matrix are calculated with numerical integration [164, 165], in ADF in order to avoid the difficulties which occur when Slater-type orbitals are used for constructing the matrix elements.

$$F_{\mu\nu} = \sum_l w_l \chi_{\mu}(\vec{r}_l) F(\vec{r}_l) \chi_{\nu}(\vec{r}_l), \quad (0.10)$$

where w_l is the integration weight. The recently developed numerical integration technique provides accurate calculation of $F_{\mu\nu}$ matrix elements for reasonable cost [164]. The total energy may be written as

$$E = E^{core} + \sum_{i,val} \langle u_i | T + V^N + V[n^{core}] | u_i \rangle + \frac{1}{2} \int \frac{n^{val}(\vec{r}) n^{val}(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r} d\vec{r}' + E_{xc}[n^{core} + n^{val}] \quad (0.11)$$

$$E^{core} = \sum_{j,core} \langle u_j | T + v_{ext} | u_j \rangle + \frac{1}{2} \int \frac{n^{core}(\vec{r}) n^{core}(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r} d\vec{r}'. \quad (0.12)$$

Note that while E^{core} does not contain any dependence on the valence density, the remainder does depend on the core density ("valence energy"), as the exchange-correlation part is not linear in the density and it can not be splitted into core and valence terms.

In ADF calculations bond energy (BE) is evaluated in one numerical integration for the energy density difference. Therefore, numerical integration errors may be rather similar and cancel to large extent if the same grid is used.

$$\Delta e_{BE}(\vec{r}_i) = e(\vec{r}_i) - \sum_A e_A(\vec{r}_i), \quad (0.13)$$

where $e_A(\vec{r}_i)$ stands for atomic or fragment energy density and $e(\vec{r}_i)$ is the energy density of the whole polyatomic system. The terms, which depend on one fragment only and do not vary with the distance between fragments, cancel against identical expressions in eq. 5.11 and are never calculated. It is not possible to evaluate the Coulomb energy completely analytically over STO functions, therefore analytical expressions are used only to fit charge Coulomb integrals over STO auxiliary functions, and the remaining term is treated as error due to the fitting and calculated numerically. Errors in density and potential due to fitting are usually taken into account as small correction [166, 165].

Becke's nonlocal exchange functional [160] and Perdew's gradient corrected correlation functional [171] (BP86) have been selected for this study. Calculations performed with the Vosko, Wilk and Nusair parametrization of correlation energy of the homogeneous electron gas [110], combined with Slater's exchange [6], will be labeled LDA. BLYP denotes the combination of Becke's exchange with the correlation functional of Lee, Yang and Parr [20], which has the origin in the work of Colle and Salvetti [125]. Combinations of Hartree-Fock and density functional formulation of exchange, based on the recent work of Becke [158], are also considered. Becke's half-and-half theory is based on the linear interpolation approximation of the adiabatic connection formula [170], whereas E_{xc} can be approximated by the mean of noninteracting and fully interacting parts:

$$\int_0^1 E_{xc}[n_\lambda] d\lambda \simeq \frac{1}{2}(E_{xc}^0[n] + E_{xc}^1[n]) \quad (0.14)$$

The noninteracting part E_{xc}^0 is then referred to the pure exchange energy of the Kohn-Sham Slater determinant. Becke's 3-parameter functional represents a general way of mixing Hartree-Fock and DFT exchange combined with correlation correc-

tion,

$$E_{xc}^{B3} = AE_x^{Slater} + (1 - A)E_x^{HF} + BE_x^{Becke} + E_c^{VWN} + CE_c^{NL} \quad (0.15)$$

with the nonlocal correlation provided by the P86 (B3P86). B3LYP denotes the Becke’s 3-parameter functional with the gradient corrected correlation provided by the LYP functional. It has been shown recently [172] that the local part of the LYP is similar to VWN, thus the following combination is implemented instead of the correlation part of eq. (15)

$$CE_c^{LYP} + (1 - C)E_c^{VWN}. \quad (0.16)$$

In the half-and-half theory A=B=1/2 and C=1. Otherwise the constants A, B and C are those determined by Becke by fitting heats of formation [6]. Preliminary studies indicate that these hybrid methods work and perform remarkably well for geometric structures and various properties of molecules [142, 151].

We determined the interaction energies as well as the equilibrium geometries of selected conformers of the $HCOO^- . HCOOH$ system. The obtained results are compared with the available experimental observation. The standard 6-311G(d,p) basis is used with and without diffuse functions. MP2/6-311G(d,p) geometry optimization is performed for all the isomers. The numerical integration was carried out with the method of te Velde and Baerends [164], in the ADF calculations and with Becke’s fuzzy-cells method, as it was implemented in the G92-DFT code [160]. Auxiliary functions are used as it was put in eq. 5.8 by means of ADF code [165]. Slater-type basis functions of double- ζ quality are employed and polarization functions are added to each atom. For comparative purpose, large standard Slater-type basis sets as triple- ζ in valance (TZ) are employed. In certain cases we used TZ augmented with two polarization functions (TZDF) and nonstandard quadruple splitted basis with polarization functions (QZDF) [167, 168]. DZD and TZDF basis sets augmented with diffuse functions (DZD++ , TZDF++) as well [168]. A set of auxiliary s, p, d, f and g STO functions centered on all nuclei, is used to fit molecular density, the Coulomb and exchange potentials accurately in each SCF cycle [169]. These basis sets are specifically designed for Kohn-Sham formalism, whereas the

basis sets for calculations by means of G92/DFT code were taken from conventional *ab initio* MO theory. Core electrons were kept frozen in ADF calculations [166, 165]. We performed complete geometry optimization for each of the considered systems using various xc-functionals selfconsistently. In certain cases zero-point energy correction has been taken into account in the complexation energies to ΔH association enthalpies and the counterpoise (CP) estimation of basis set superposition error (BSSE) [25a,b] has also been evaluated. The CP calculations have been carried out at the level of MP2/6-311G(*d,p*) with and without diffuse functions in the same way as in ref [155]. In addition, BSSE has been estimated at BP/DZD level of the density functional theory, using the ADF code. The substantial effect of correlation on optimized geometry has been reported previously [149, 155, 157] thus we do not present Hartree-Fock results.

33 Structure and dipole moment of formic acid

The structure of the H-bonded complex will depend on the structure calculated for formic acid and formate anion. Therefore, in *Table 5.1-5.2* we present the optimized geometry of "monomers" and the dipole moment (DM) of formic acid, calculated using various exchange-correlation (xc) density functionals as implemented in G92-DFT and ADF. For comparison, results of second and higher order Moller-Plesset (MP) calculations, the experimentally obtained structure [175] and DM [177] are also given. It can be seen that DF methods seem to be superior to MP results, especially when calculating DMs. Extending the basis set with diffuse functions, a slightly worse value is obtained both in MP and DF calculations. The 6-311G(*d,p*) and DZP Slater-type bases provide accurate values of DM and bond lengths at a reasonable cost. Recently Rashin et al. concluded that the use of the larger triple- ζ basis set does not lead to better agreement with experimental data, and the double zeta basis with polarization and diffuse functions provides the best available choice for accurate DF calculations [180]. Using a basis set as large as TZDF++, we got the same DM as with the smaller DZD basis. The best agreement was obtained by BP and B3LYP xc-functionals.

Table 10: Total energies , bonding energies and structural parameters for HCOOH (formic acid) obtained by various $E_{xc}[n]$.

Total energies and bonding energies (ADF) are in a.u. and bond lengths are in Å. All the calculations are carried out at the following levels of theory including complete geometry optimization using the notations : ++ , ** and ++dfp are 6-311++G(d,p), 6-311G(d,p) and 6-311++(3df,2p) basis sets, respectively. LDA denotes the Slater's exchange [6] combined with VWN correlation [110]. G92 and ADF refer to G92-DFT [97] and ADF [165] calculations respectively. LDA calculations employed the DZD and 6-311G(d,p) bases. ADF calculations employed the DZD (III), TZ (IV) and TZDF (V) Slater-type bases [16b], DZD and TZDF with diffuse functions on each atoms (DZD++, TZDF++) [167, 168]] (see text). EXP denotes the experimental observation [177, 175]. The bond lengths and angles were taken from ref [177] and experimental dipole moment was taken from ref [178]. μ is the calculated dipole moment in Debye.

	Energy	μ (D)	H-C	C=O	C-O(H)	O-H	H-C=O	H-C-O	C-O-H
MP2/++	-189.362298	1.67	1.096	1.205	1.348	.969	125.3	109.3	106.3
MP2/**	-189.351729	1.60	1.097	1.203	1.347	.968	125.6	109.2	105.6
MP4/**	-189.383842	1.60							
BLYP	-189.797920	1.43	1.105	1.211	1.365	.982	125.6	109.1	107.4
B3LYP**	-189.819486	1.42	1.099	1.197	1.347	.970	125.7	109.2	107.1
B3LYP++	-189.827781	1.50	1.098	1.199	1.346	.971	125.3	109.6	108.0
BP**	-189.824185	1.40	1.109	1.209	1.358	.981	125.9	108.8	106.0
BP++	-189.832633	1.45	1.108	1.210	1.359	.981	125.6	109.1	106.8
B3P**	-190.241331	1.47	1.099	1.196	1.339	.969	125.5	109.4	107.0
B3P++	-190.247889	1.52	1.098	1.197	1.339	.969	125.2	109.7	107.6
BP3P++dfp	-190.260919	1.57							
G92/LDA	-188.874924	1.50	1.098	1.197	1.339	.969	125.3	109.7	107.6
ADF/LDA	-1.165173	1.45	1.110	1.200	1.337	.993	125.5	109.1	106.1
ADF/BP III	-1.082843	1.43	1.109	1.207	1.359	.993	125.5	108.7	106.5
ADF/BP DZD++	-1.087236	1.44	1.109	1.204	1.356	.988	125.4	108.7	106.5
ADF/BP IV	-1.084610	1.46	1.111	1.210	1.362	.985	125.5	109.2	106.2
ADF/BP V	-1.093321	1.48	1.110	1.206	1.357	.982	125.5	108.9	107.0
ADF/TZDF++	-1.098200	1.43	1.111	1.203	1.356	.980	125.8	108.9	107.1
EXP		1.41	1.097	1.204	1.342	0.972	124.8	112.0	106.3

The experimental bond lengths are reproduced by various DFs within 0.005 Å. The most precise agreement is obtained by means of hybrid functionals, which is in accordance with recently published results [142, 151, 158]. Contrary to this, BP and BLYP functionals tend to overestimate the bond lengths. The extension of basis set by means of diffuse functions and/or the major expansion of the polarization space result only in a very modest change in bond lengths and angles. The Slater-type DZD basis seems to be equivalent to the 6-311G(*d, p*) basis when DMs and geometry are compared. The bond lengths and angles, obtained by DFs and using gaussian or Slater-type basis sets, are also in good accordance, especially when the largest basis sets are compared. It is worth mentioning that LDA provides results very close to the gradient corrected values.

34 Formate anion

While experimental H-C and C=O bond lengths [177] indicate C=O lengthening, almost unaltered H-C was found with respect to the corresponding values of the formic acid (Table 5.1-5.2). The H-C-O bond angle is larger compared to that of HCOOH. This observed trend is well-reproduced by all the xc-functionals and MP2 calculations, except for the H-C bond, where the calculated values are too long.

The hydrogen-centered diffuse function set has negligible effect on geometry and usually may be omitted with little loss of accuracy [156, 155]. To the best of our knowledge there is no available experimental DM for $HCOO^-$ with which to make a comparison, thus we indicate only that the MP results predict values between 1.5 and 2.0 Debye, whereas DF calculations provide somewhat lower values between 1.3 and 1.7 Debye at the experimental geometry. Just to cite examples using B3P and 6-311++G(3df,2p) basis set, we found a value of 1.68 D, whereas using the 6-311G(*d, p*) basis the value of 1.37 D is obtained. $MP2/6-311G(3df, 2p)$ calculation gives 1.82D.

Table 11: **Total energies , bonding energies and structural parameters for HCOO^- (formate anion) obtained by various \mathbf{E}_{xc} [n].**

The notations are the same as it was put in Table 1.

	Energy	H-C	C=O	H-C-O
MP2/++	-188.802606	1.134	1.258	114.7
MP2/+**	-188.802455	1.134	1.258	114.8
MP2/**	-188.769191	1.150	1.252	114.3
BLYP	-189.247793	1.149	1.266	114.7
B3LYP	-189.272801	1.139	1.252	114.7
BP**	-189.251410	1.173	1.260	114.3
BP++	-189.280241	1.152	1.263	114.7
B3P**	-189.665193	1.153	1.246	114.4
B3P++	-189.689990	1.139	1.249	114.7
ADF/LDA++	-1.066098	1.157	1.249	114.4
ADF/BP (DZP)	-.994806	1.157	1.259	114.5
ADF/BP (DZD++)	-.999064	1.158	1.260	114.5
ADF/BP (TZ)	-1.001552	1.158	1.264	114.5
ADF/BP (TZDF)	-1.001552	1.158	1.259	114.5
ADF/BP86 (QZDDF)	-1.004680	1.163	1.257	114.5
ADF/BP86 (TZDF++)	-1.006462	1.157	1.262	114.3
<i>EXP</i> ^[177]		1.090	1.250	117.0

35 Structure of formate-formic acid complex

Four energy minimum structures have been identified on the potential energy surface (PES). Two of them are nonsymmetrical doubly-bonded isomers (closed and opened syn-anti), the others represent symmetrical single- and triple-bonded structures (anti-anti and syn-syn, respectively). The number of possible torsional isomers is enormous, however, only few of them have thermodynamical relevance. It has immediately turned out, that single-bonded structures provide thermodynamical data in the worse agreement with available experimental results. Nusser et al. have selected four structures based on mainly X-ray structure analysis of aspartyl-proteases and acid salts [173]. All the structures we have taken into account are found to be planar systems. However, during geometry manipulation steps it turned out that this complex has low out-of-plane bending barrier. The experimentally observed non-planar structure of carboxylate-carboxyl systems may well be due to this torsional flexibility [173], since the PES is very flat with respect to the characteristic torsional variations, and those planar structures represent the energy minimum. The experimental structural information is based on the neutron diffraction study of potassium hydrogen diformiate ($KH(HCO_2)_2$) [179]. Nevertheless, one has to be careful when comparing "gas phase" calculations with this neutron diffraction experiment, since it is not easy to consider packing effects as well as the effect of counter ion on hydrogen diformiate geometry in crystals. On the other hand, it has been shown recently that transferability is fair allowing to use experimental crystal structure data as reference for quantum chemical calculations in "gas phase" [173], especially when only the qualitative comparison is given.

Previous experimental study based on thermochemical examination proposed doubly hydrogen-bonding, but only one possible conformer was suggested [136]. Recently Gilli et al. [138] have investigated the covalent nature of strong homonuclear H-bonds by crystal structure correlation methods. They have used the strong H-

bond expression for the class of O-H...O bonded systems, which have been found to be able to form short ($2.5 \leq R \leq 2.65 \text{ \AA}$) or very short ($R \leq 2.50 \text{ \AA}$) O-O contact. In weakly bonded systems, as e.g. the water dimer, the O-O distance is 2.98 \AA [24]. In carboxyl-carboxylate systems the average O-O distance is found to be about 2.45 \AA based on extensive crystal structure comparative study [173, 179].

Despite its theoretical significance there are only a few publications concerning the quantum chemical treatment of hydrogen-diformiate [147, 173, 174]. These studies are confined to only semiempirical or Hartree-Fock approaches. Nusser et al. performed full geometry optimization on selected conformers at the $6-31G++(d,p)$ level of theory without any correlation effect. However, they did not note the multiple H-bonded character of this complex [173]. Hadzi et al. modelled the active site of aspartyl proteases with hydrogen diformiate, and set the geometry in the corresponding X-ray structure [174]. Their calculations were limited to the very poor level of $STO-3G$ and $4-31G$ basis sets. The best theoretical results up to date have been obtained by Steven and Basch [147, 148]. The comparison between our and their results will be given later during the discussion session.

The calculated complexation energies as well as the calculated association enthalpies using zero point correction and entropies are collected in Table 5.4a, b. Some of the abovementioned data are also displayed for the closed syn-anti conformer in a more detailed way reflecting the basis set dependence in Table 5.3. The molecular graphics of the various conformers are given in figure 5.1 – 5.4. The characteristic structural parameters can be found in Table 5.4a,b as well. The measured energetics is based on Meot-Ner et al.'s experimental work [136]. The symmetrical and nonsymmetrical conformers are tabulated separately.

The most obvious conclusion concerning Table 5.4a, b is that closed syn-anti and syn-syn structures represent suitable candidates for quantitative comparison with available experiment. The obtained complexation energies (ΔE) are comparable within 1-2 kcal/mol with the experimental 36.8 kcal/mol association enthalphy [136]. The syn-syn structure was found by the neutron diffraction study of $KH(HCO_2)_2$. Our gas-phase MP2 and DF calculations slightly favour the two-H-bonded closed

Table 12: Complexation energies and characteristic interatomic distances as calculated by various density functionals for hydrogen-diformiate system. The planar two hydrogen-bonded closed syn-anti system.

E denotes the calculated energy in vacuum (a.u.). ΔE denotes the complexation energy (kcal/mol) (the corresponding experimental association enthalpy is 36.8 kcal/mol [1b]), $\Delta E = E_{complex} - (E_{HCOO^-} + E_{HCOOH})$. d_{O-O} is the bridge oxygen atom distance in the hydrogen-bond. EXP denotes the structural information derived by neutron diffraction study for potassium hydrogen diformate ($KH(HCO_2)_2$) [179].

	E	ΔE	d_{O-O}
MP2/++	-378.214020	30.8	2.52
MP2/6-311G(d,p)	-378.178137	35.9	2.51
MP3/6-311G(d,p)	-378.165258	34.9	
MP4/6-311G(d,p)	-378.239285	35.6	
BLYP/6-311++G(d,p)	-379.091932	29.0	2.58
BP/6-311G(d,p)	-379.135176	37.0	2.52
BP/6-311++G(d,p)	-379.160468	30.8	2.53
B3LYP**	-379.965963	36.4	2.53
B3LYP/++	-379.146966	30.4	2.54
B3P**	-379.965963	37.3	2.50
B3P/++	-379.988778	31.9	2.51
B3P/++(3df,2p)	-380.013010	32.1	
G92/LDA	-377.272238	41.2	2.51
ADF/LDA (DZP)	-2.303828	45.1	2.46
ADF/BP (DZP)	-2.134622	35.8	2.49
ADF/BP (TZ)	-2.129477	32.5	2.48
ADF/BP (TZDF)	-2.145258	32.1	2.49
EXP		36.8	2.45

syn-anti conformer as well as Steven and Basch obtained similar results [147]. This preference still remains when zero point energy correction is taken into account to ΔE . The experimental measurements were carried out under gas phase conditions in a pulsed electron beam mass spectrometer [136], thus the comparison can be made directly between our calculations and the experiment. It has been concluded recently that due to packing effects the carboxyl-carboxylate conformations, preferred in gas phase, are poorly populated in crystals [173]. In liquid phase or in solution the closed syn-anti form may be the most significant conformer, if we take into account that the closed syn-anti conformer provides the best agreement with experiment for the calculated ΔS entropy as well. The experimental d_{OO} distance in $KH(HCO_2)_2$ is 2.45 \AA [179], while the calculated values are within the range of $2.40 - 2.45 \text{ \AA}$ for the syn-syn isomer. The H-bonds in formic acid and acetic acid are considerably longer, 2.58 and 2.61 \AA , respectively [179]. This is, of course, to be expected as the H-bond accepting power of an ionized carboxyl group is considerably greater than that of the corresponding acid. The longer d_{OO} distance ($2.65 - 2.70 \text{ \AA}$) in the active site of enzymes [143] is clearly due to the stronger constraint put on geometry of the carboxyl-carboxylate moiety by the environment of the active center in proteins. We should emphasize here that this longer observed d_{OO} distance in aspartyl-proteases may well be important when the mechanism of the catalysis is interpreted [135]. Probably the d_{OO} distance goes through moderate variations during the catalysis and its energetical change can contribute significantly to the stabilization of the reaction intermedier. The role of strong H-bonding versus electrostatic stabilization in transition state during enzyme catalysis is still not clear [135, 141] and we hope this paper can contribute to further understanding.

Table 13: Complexation energies and characteristic interatomic distances as calculated by various density functionals for hydrogen-diformate. The closed (C) and opened (O) form of the syn-anti hydrogen-bonded systems.

	MP2	BP (G92)	BP (ADF)	B3P	B3LYP
E syn-anti (C)	-378.178137	-379.135176	-2.134622	-379.965963	-379.120753
ΔE	35.9	37.0	35.8	37.3	36.4
ΔH			35.7	35.5	34.9
ΔS			42.0	40.3	40.7
O...O	2.510	2.517	2.490	2.497	2.528
O...H(1)	1.476	1.439	1.392	1.443	1.483
O...H(2)	2.410	2.434	2.514	2.382	2.427
C=O	1.241	1.246	1.243	1.233	1.237
C-O(H)	1.272	1.284	1.287	1.267	1.270
H-C(1)	1.124	1.137	1.133	1.125	1.126
H-C-O	117.1	117.6	118.0	117.4	117.2
O-C-O	124.2	124.3	124.7	124.3	124.2
C-O-O		112.9	114.1	113.0	117.3
E syn-anti (O)	-378.174290	-379.131958	-2.133317	-379.962300	
ΔE	33.5	35.0	34.9	35.0	
ΔH			28.3	31.2	
ΔS			45.5	45.6	
O...O	2.470	2.477	2.474	2.452	
O...H(1)	1.420	1.371	1.336	1.381	
O...H(2)	2.600	2.714	2.765	2.661	
C=O	1.234	1.238	1.238	1.225	
C-O(H)	1.279	1.292	1.294	1.275	
H-C(1)	1.124	1.138	1.132	1.125	
H-C-O	118.1	118.7	118.6	118.4	
O-C-O	125.8	126.0	126.0	125.9	
C-O-O		103.7	105.4	103.0	

Table 14: **Complexation energies and characteristic interatomic distances as calculated by various density functionals for hydrogen diformate. The syn-syn and anti-anti hydrogen-bonded systems.**

	MP2	BP (G92)	BP (ADF)	B3P
E (syn-syn)	-378.173616	-379.132058	-2.135311	-379.962333
ΔE	33.1	35.0	36.2	35.0
ΔH			34.9	34.2
ΔS			45.3	35.6
O...O	2.397	2.441	2.455	2.404
O...H(1)	1.200	1.226	1.230	1.197
O...H(2)	2.822	2.932	2.947	2.901
H(1)...H(2)	2.141	2.212	2.223	2.181
C=O	1.227	1.234	1.235	1.220
C-O(H)	1.293	1.303	1.303	1.287
H-C(1)	1.117	1.131	1.125	1.119
H-C-O	119.2	119.4	119.5	119.4
O-C-O	127.3	126.9	126.7	127.1
C-O-O	109.5	111.5	112.2	112.2
E (anti-anti)	-378.171010	-379.129715	-2.130460	-379.959339
ΔE	31.4	33.6	33.1	33.1
ΔH			31.1	
ΔS			41.4	
O...O	2.413	2.452	2.466	2.424
O...H(1)	1.193	1.264	1.233	1.261
O...H(2)	2.583	2.705	2.659	2.631
C=O	1.227	1.236	1.235	1.223
C-O(H)	1.290	1.296	1.300	1.279
H-C(1)	1.118	1.135	1.130	1.127
H-C-O	119.4	119.3	119.3	119.2
O-C-O	129.7	129.8	129.9	129.5
C-O-O	115.2	116.8	117.1	117.6

E is responsible for the total (G92-DFT) and bonding (ADF) energies in a.u. ΔE denotes the complexation energy (the experimental one is 36.8 [1b] kcal/mol); ΔH and ΔS denote the calculated zero point energy correction and entropy in kcal/mol and kcal/mol K, respectively. The experimentally obtained entropy is 39.1 kcal/mol K [1b]. The experimental C=O, C-O(H) distances and the O-C-O, C-O-O angles are 1.24 and 1.26 Å, 125.3° and 113.4°, respectively [21]. O-O is the bridge oxygen atom distance in the hydrogen-bond, O...H (1) is the hydrogen bond distance (O-H-O), O...H (2) is the second hydrogen bond in the system (C-H-O). All the calculations employ the 6-311G(d,p) basis

(triple zeta quality in valance augmented with two sets of polarization functions). ADF calculations employed the DZD Slater-type basis.

Figure 5.1 The molecular structures of various hydrogen-diformiate complexes obtained by the MOLPLT molecular graphics program [82].

The calculations predict longer O-H-O bond for the closed syn-anti isomer and consequently slightly weaker H-bond, but stronger second H-bond when compared

with the syn-syn conformer. In order to emphasize the importance of the second H-bond we performed BP/DZD calculation on the *hydrogen-diacetate* anionic system, which is a typical single-H-bonded complex. The values of 27.3 kcal/mol and 2.41 Å are calculated at the level of BP/DZD for the complexation energy and d_{OO} , respectively. The shortest d_{OO} distance implies stronger hydrogen-bonding with a more deeply buried proton in the interaction site than in the hydrogen-diformiate. However, due to steric repulsion effects and the lack of C-H...O contacts, lower ΔE is found both by experiment and theory. The experimentally observed ΔH value (29.3 kcal/mol) [1b] is reproduced quite well indicating the correctness of our theoretical model. Compared with $CH_3COO^- \cdot CH_3COOH$, the experimental ΔH and ΔS of $HCOO^- \cdot HCOOH$ increased by 7.5 kcal/mol and 9.5 kcal/mol.K, respectively, both in the range characteristic of the formation of a second H-bond. The second H-bond represents short C-H...O contact. This type of H-bond was previously proposed by crystallographic [186] and by *ab initio* calculations [147]. The (C)O...H distance is found in the range of 2.4-2.5 Å (Table 5.4a) in the syn-anti closed isomer, which is well comparable with microwave experimental results obtained for other molecular complexes like the oxirane-acetylene "C-H...O" H-bonded system [187]. The O-O distance is slightly sensitive to the quality of the xc-functional (see Table 3). Usually the longest d_{OO} is obtained by the BP functional. The shortest H-bond is the strongest conclusion [138, 139] supported by the B3P functional in the case of the closed syn-anti structure. In most cases, MP2 predicts lower ΔE values in worse agreement with experiment than DF methods. The experimental [179] (see the text under Table 5.4a,b), MP2 and DF methods predict significant C=O bond lengthening and C-O(H) shortening compared to those of HCOOH. However, C-O(H) shortening is reproduced relatively poorly, which is probably due to the exclusion of the effect of the counter K^+ ion. The experimental structure of $KH(HCOO)_2$ is of less help when its unsymmetrical structure is taken into account [179], since in "gas phase" symmetrical molecular complex is obtained. The BP functional gives values within 0.005 Å, while MP2 and B3P methods slightly underestimate the length of C=O bond. The experimental C-O-O and O-C-O angles (Table 5.4b) [179] are pretty well reproduced by all DF methods in the syn-syn conformer within $1^\circ - 2^\circ$. Com-

paring the ΔE and ΔH values of the anti-anti one-H-bonded complex, the second and third H-bonds represent at least 3-4 kcal/mol energy-lowering and contribute significantly to the thermodynamic stability of the multiple-bonded structures. In fact, in the anti-anti conformer the proton in the O-H-O bond is shared slightly by the other oxygens as well, which leads to the formation of second H-bond. However, it represents a weaker contact than in C-H...O interactions. The opened form of the syn-anti complex, which represents double-H-bonded conformer, seems to be thermodynamically the least stable system when the ZPE correction is taken into account. This is probably due to the longer and weaker second H-contact.

MP2/6-311++G(*d,p*) geometry optimization was carried out only for the closed syn-anti conformer. Comparison of ΔE values obtained for the closed syn-anti conformer (Table 3) clearly shows that diffuse functions in the basis set result in values which seem to be too small. The extension of the valence region by means of additional d and f functions does not produce any improvement, thus still significant BSSE remains. This poor predictive power of diffuse functions is well-reflected in the long d_{OO} distances, and that is the reason for the weaker calculated H-bond. Unfortunately, in practice it is no use making further extension in the basis, and it is better to estimate the magnitude of BSSE (see next section). LDA provides too high ΔE value, and one of the shortest value for d_{OO} , owing to the well-known overbinding behaviour of LDA [180]. By means of gradient corrected xc-functionals fair agreement was obtained with thermochemical experiment, especially when hybrid functionals were employed.

36 BSSE

The almost perfect agreement observed for calculations of binding energy with various gradient corrected DFs with 6-311G(*d,p*) basis has to be considered as due to accidental cancelation of errors. However, there still remains significant basis set superposition error. Nevertheless, this choice of basis, combined with B3P or B3LYP functionals seems to be efficient for treating strong hydrogen-bonded sys-

tems, whereas relatively poor binding energy is obtained (Table 5.3.) using diffuse functions. The DF and $MP2/6-311G(d,p)$ complexation energies went in the wrong direction when the basis set was enlarged to $6-311++G(d,p)$. The total energy of $HCOO^-$, $HCOOH$ and the complex is lowered by means of diffuse functions with 25, 7 and 23 mH , respectively when B3P functional is used. Values of 34, 10 and 36 mH are obtained, respectively when $MP2/6-311++G(d,p)$ geometry optimization was performed. The difference between the monomers and complex energy lowering accounts well for the deviation from experimental association enthalphy. In order to give more sophisticated explanation of this basis set problem we have calculated the counterpoise correction to BSSE, and it was found that the ghost functions of $HCOO^-$ contribute significantly to the BSSE of the complex with the magnitude of 4.6 kcal/mol, while in the reverse case almost zero contribution is found. At the level of $MP2/6-311G(d,p)$ and BP/DZD, 5.4 and 4.8 kcal/mol BSSE were found, respectively, with opposite sign. In this latter case the BSSE provides excess energy on ΔE and brings close the calculated properties to the measured values. These values were obtained by means of the corrected Boys-Bernardi scheme [183]. The relaxation of the monomers, upon formation of the dimer has been taken into account [155, 157, 185]. Still, one has to be careful at the interpretation of the BSSE of strong complexes [155]. It was pointed out that problems associated with correlated counterpoise calculations can occur, especially when strong complexes are treated, [5g,23] thus we use our BSSE calculations only for qualitative explanation.

37 Bonding energy analysis

In order to get more information in connection with the covalent vs. electrostatic character of strong H-bonded systems like the $HCOO^- \cdot HCOOH$ an energy decomposition has been performed, which allows one to make bonding energy analysis (BEA). Following the way as it was put by Umeyama and Morokuma [182] and using the ADF code, which was originally programmed to offer BEA [165], we determined the various components of the calculated binding energy (BE). We decomposed BE

Table 15: **Bonding energy analysis of different conformers of hydrogen-diformiate at the level of BP/DZD.**

Syn-anti (C) and (O) denote the closed and opened forms of this conformer (see molecular graphics on figure 1-2). EX, ES and EO denote the Pauli, electrostatic and orbital interaction terms, respectively (see text for further explanation). The corresponding EX, ES and EO terms of HCOOH are as follows: 3.9116, -0.8551 and -4.1394 and for HCOO⁻: 3.3493, -0.7415 and -3.6025, while for CH₃COOH the values of 5.8471, -1.2349 and -6.3017, for CH₃COO⁻ 5.2419, -1.1008 and 5.7386 are obtained. dEX, dES and dEO stand for bonding energy terms as computed by subtracting the corresponding terms of HCOOH and HCOO⁻. % is the percentage contribution of EO term to the complexation energy. All these quantities are in a.u. CE denotes the sum of the terms in kcal/mol. The corresponding EX, ES and EO terms of (H₂O)₂ are taken from ref 24, while the experimental CE of water dimer is from ref 5e.

terms	syn-anti (C)	syn-anti (O)	syn-syn	anti-anti	$H(CH_3COO)_2^-$	$(H_2O)_2$
EX	7.4733	7.4827	7.4886	7.4693	11.4726	0.0069
ES	-1.6535	-1.6593	-1.6617	-1.6574	-2.4120	-0.0100
EO	-7.9546	-7.9567	-7.9622	-7.9423	-12.3928	-0.0038
dEX	0.2124	0.2218	0.2277	0.2084	0.3836	
dES	-0.0569	-0.0627	-0.0651	-0.0608	-0.0763	
dEO	-0.2127	-0.2148	-0.2203	-0.2004	-0.3489	
CE	35.8	34.9	36.2	33.1	27.3	5.44
%	78.9	77.4	77.2	76.7	83.7	27.5

into three parts:

Electrostatic interaction (ES) which accounts for the interaction between the undistorted electron distribution of monomer A and that of monomer B. This component includes the interaction between all permanent charges or multipoles. This is a purely attractive term.

Exchange repulsion (EX) caused by exchange of electrons between A and B. Physically it means short-range repulsion due to the overlap of electronic distribution of A with that of B, thus this is a purely repulsive term.

The name *orbital interaction* (EO) is given to the third term in BEA following the nomenclature in the ADF code. The third term includes all the rest of the contributions from charge-transfer (electron delocalization effect) and polarization interaction. The remaining part is frequently called the mixing term.

The decomposed terms are collected and presented in Table 5.5 for all the conformers. In all cases EO has the largest contribution to the attractive terms. *Thus the covalent character in the binding energy is between 75 – 80 per cent, while the remaining part is electrostatic.* In weakly-bonded systems, such as the water dimer, an almost purely electrostatically dominant H-bond is found (Table 5.5) [182]. In other neutral H-bonded systems again the electrostatic term is found to be the leading term in the interaction energy [182]. The most pronounced covalent character is found in the closed syn-anti conformer when the percentage of EO contributions is compared. However, if we take into account, that covalency can be assigned only to the O-H-O hydrogen-bond, while the second C-H.O H-bond is rather electrostatic-like weak interaction, one can get higher than 80.0 per cent degree of covalency in the O-H-O bond. Umeyama and Morokuma[182] found significant EO contributions in $H_3N - H^+$ and $H_2O - H^+$ protonation complexes, however, those account for only 50 percent of the interaction energy.

In C-H.O bond, which can be written as $C - H.O^-$, the distance d_{HO} is found to be $2.4 - 2.5 \text{ \AA}$, which is longer by 1.0 \AA than in the O-H-O "three-center" bond. The strong electrostatic character in $(H_2O)_2$ is found at the equilibrium distances ($d_{OO} = 2.98$ and $d_{HO} = 1.95 \text{ \AA}$), respectively. Consequently, electrostatic character must be attached to C-H.O bond as well.

To give a clearer picture of covalency in O-H-O bond an energy decomposition of hydrogen-diacetate was performed as well. As it was noted previously, the $CH_3COO^- . HOOCCH_3$ system contains no other H-bond due to the lack of C-H.O contacts, therefore it provides the possibility of pure BEA in O-H-O bond. The distance d_{OO} being shorter than in $H(HCOO)_2^-$ implies again a more significant contribution of EO term to the interaction energy. The value of 83.7 percent is found.

Table 16: **CPU time required to perform one SCF calculation on a single SGI Power Challenge (R8800) processor at the MP2, LDA and BP level of theory.** *Notations are the same as it was put in Table 1.*

	CPU/SCF (sec)
MP2/6-311G(d,p)	1518
MP2/6-311++G(d,p)	5711
LDA/DZD	681
BP/DZD	1320
BP/TZDF	2691
LDA/6-311G(d,p)	490
BP/6-311G(d,p)	548
BP/6-311++G(d,p)	1318
BP/6-311++G(3df,2p)	2603

38 Timings

For further analysis, in Table 5.6 the time required to perform a single SCF calculation on hydrogen-diformiate (syn-anti closed form) at the LDA and BP gradient corrected levels with the programs ADF and G92-DFT is compared to that required to perform the same at the MP2 level. These timings were done on a single R8800 processor of SGI Power Challenge workstation. All the calculations employed direct SCF. The MP2 calculations were limited to maximum of 300 megabyte disk space, while the disk space requirement for integral storage, for even the largest basis set, was under 40 megabyte for DF calculations.

The efficiency of DF methods is higher than that of MP2, is the clearest conclusion, however, when ADF and G92-DFT is compared a more diffuse picture has been obtained. In these cases timing roughly depends on the employed accuracy at numerical integration. In G92-DFT calculations the standard accuracy has been used, while the parameter ACCINT in ADF has been set in 3.0, which results in at least 4 digit accuracy in bonding energy [164]. Using these settings, ADF seems to be slower, especially when the timing of gradient corrected level is compared, whereas the ADF calculation is roughly 1.5 to 2.0 times longer than its G92-DFT counterpart. However, one has to be careful when this test is taken into account,

since it is not easy to compare calculations which are based on Slater or Gaussian-type basis sets. Gaussian-type basis sets exhibit poorer characteristics at the nucleus and in the long range regions, and consequently provide poorer local behaviour of exchange-correlation potential and energy density. The most recent finding suggests the increased importance of correct local characteristics in density functional calculations [98]. The price one has to pay for correct description of $\epsilon_{xc}[n(\vec{r})]$ in eq. 1 is the longer time requirement during SCF calculations when Slater-type basis is used.

39 Conclusions

The overall conclusion, which can be drawn on the basis of the results presented here, is that current implementations of gradient corrected density functionals both in the program G92-DFT and ADF are capable of describing hydrogen-bonding in this strongly bonded $HCOO^- \cdot HCOOH$ system. Hybrid exchange-correlation functionals provide a somewhat better agreement with experiment. The observed complexation energy is reproduced within almost chemical accuracy.

The double hydrogen-bonded nonsymmetrical closed syn-anti conformer is found to be in the best accordance with the available gas-phase experiment, while the symmetrical triple hydrogen-bonded syn-syn system provides the best agreement with the neutron diffraction experiment. The calculations on the closed syn-anti and syn-syn isomers provide values of 35.7 and 34.9 kcal/mol for the ΔH association enthalpy and the values of 2.49 and 2.46 Å for the distance of the oxygens in hydrogen-bridge, respectively. The corresponding experimental values are 36.8 [136] kcal/mol and 2.45 Å [21]. MP2 calculations predict complexation energy too low and O-O distance too short when compared to the corresponding values of syn-syn conformer obtained by density functional methods. The multiple hydrogen-bonded character of these complexes is due to the second and/or third short C-H...O contacts. The presence of this weak interaction can cause 3 – 4 kcal/mol binding energy lowering and significant enlargement of the entropy.

On the basis of bonding energy analysis significant covalent character is found

in this O-H-O type strong hydrogen-bond. At least 78 per cent of the decomposed binding energy is orbital interaction-like contribution in attractive terms, the rest is electrostatic. In weakly bonded complexes as the water dimer a reverse proportion is found.

APPENDIX A The equivalency of different definitions of $T_c[n]$.

According to Savin [42] the correlation energy can be written in terms of scaled first order density matrices as follows:

$$E_c[\rho] = \frac{1}{2} \int_0^1 d\lambda \int dr \nabla_{r'}^2 [\gamma_{\rho_{1/\lambda}}^{\lambda=1}(r, r') - \gamma_{\rho_{1/\lambda}}^{\lambda=0}(r, r')] \Big|_{r=r'}. \quad (\text{A1})$$

In a similar way using eq. 3 and eq. A1 $T_c[n]$ can be given in terms of first order density matrices (eq. 5). Another possibility for giving T_c is the Levy-Perdew formulation of the virial theorem (eq. 14) [78]. Since the kinetic energy contribution to the correlation energy is not unique quantity, it is not immediately follows, that definitions are given by eq. 14 and eq. 5 are equivalent with each other. In several steps we give the proof of the equivalency.

E_c can be decomposed into potential and T_c parts [98]:

$$E_c[\rho] = W_c[\rho] + T_c[\rho], \quad (\text{A2})$$

as well as E_c can be given in term of W_c using the adiabatic connection scheme [102]

$$E_c[\rho] = \int_0^1 d\lambda W_c[\rho_\lambda]. \quad (\text{A3})$$

Using eqs. A1-A2-A3 we get for $W_c[\rho]$

$$W_c[\rho] = \frac{1}{2} \int dr \nabla_{r'}^2 [\gamma_{\rho_{1/\lambda}}^{\lambda=1}(r, r') - \gamma_{\rho_{1/\lambda}}^{\lambda=0}(r, r')] \Big|_{r=r'}. \quad (\text{A4})$$

Comparing eqs. A1 with A4 together with the equality

$$\frac{1}{2} \int_0^1 d\lambda \int dr \nabla_{r'}^2 \gamma_{\rho_{1/\lambda}}^{\lambda=0}(r, r') \Big|_{r=r'} = \frac{1}{2} \int dr \nabla_{r'}^2 \gamma_{\rho_{1/\lambda}}^{\lambda=0}(r, r') \Big|_{r=r'} \quad (\text{A5})$$

we obtain for $T_c[\rho]$

$$T_c[\rho] = \frac{1}{2} \int_0^1 d\lambda \int dr \nabla_{r'}^2 \gamma_{\rho_{1/\lambda}}^{\lambda=1}(r, r') \Big|_{r=r'} - \int dr \nabla_{r'}^2 \gamma_{\rho_{1/\lambda}}^{\lambda=1}(r, r') \Big|_{r=r'}. \quad (\text{A6})$$

Eq. A5 follows from the fact that we have a noninteracting first order density matrix [1],

$$-\frac{1}{2} |\gamma_{\rho_{1/\lambda}}^{\lambda=0}(r, r')|^2 = \rho(r)\rho(r') [1 + g_s^{\lambda=0}([\rho]; r, r')], \quad (\text{A7})$$

where the noninteracting pair-correlation function $g_s^{\lambda=0}([\rho]; r, r')$, will be λ - independent and eq. A5 holds. Then T_c can be expressed in terms of W_c parts only (eq. A2-A3):

$$T_c[\rho] = \int_0^1 d\lambda W_c[\rho_\lambda] - W_c[\rho] \quad (\text{A8})$$

Using eqs. A4 ,A5 and A8 we obtain eq. A6 and thus the equivalency is proved.

In the proof one can find only integral quantities, however, the equivalency also holds for local quantities such as $t_c([\rho], \vec{r})$ kinetic energy density in local density approximation (LDA) [78]. This is due to the fact that the above-mentioned equalities are true for the quantities under the integration sign as well. On the basis of eq. A6 we have in hand the expression for the kinetic energy density $t_c([n]; \vec{r})$ in terms of first order density matrices.

$$t_c([\rho; \vec{r}]) = \frac{1}{2\rho(r)} \left(\int_0^1 d\lambda \nabla_{r'}^2 \gamma_{\rho_{1/\lambda}}^{\lambda=1}(r, r') \Big|_{r=r'} - \nabla_{r'}^2 \gamma_{\rho_{1/\lambda}}^{\lambda=1}(r, r') \Big|_{r=r'} \right). \quad (\text{A9})$$

Using the local forms of the formulas of this Appendix one can readily obtain A9 starting from the local form of the virial relation (eq. 18). Using eqs. 2 and 14 (correlation part only) we have the following integral equation:

$$\frac{\partial E_c^{\lambda, mod}([\rho_\lambda]; \vec{r})}{\partial \lambda} = \int d\vec{r}' \rho(\vec{r}') \vec{r}' \nabla v_c([\rho]; \vec{r}). \quad (\text{A10})$$

Eq. 14 is derived in ref 2a on the basis of eq. A10 and for local quantities A10 as well as eq. 14 holds approximately only in LDA. Consequently the local form of eq. A6 and eq. 18 are must be the same point by point in the space only in LDA with slowly varying densities .

APPENDIX B: New $T_c[n]$ functionals obtained by Levy-Perdew relation and Stoll's correction

Without any derivation we give the explicit form of the following functionals:

$$t_c^{mod}([\rho]; \vec{r}) = \frac{\partial \epsilon_c^{\lambda, mod}(n_{\alpha, \beta})}{\partial \lambda} \Big|_{\lambda=1} - \frac{\partial \epsilon_c^{\lambda, mod}(n_{\alpha; 1})}{\partial \lambda} \Big|_{\lambda=1} - \frac{\partial \epsilon_c^{\lambda, mod}(n_{\beta; 1})}{\partial \lambda} \Big|_{\lambda=1} - \epsilon_c^{mod}(\rho_\alpha, \rho_\beta) + \epsilon_c^{mod}(\rho_\alpha; 1) + \epsilon_c^{mod}(\rho_\beta; 1) \quad (B1)$$

where "mod" denotes two possibilities: VWN correlation functional [110] in the parametrization of Perdew and Wang [106], and functional Bc95 [14].

$$\frac{\partial \epsilon_c^{VWN}}{\partial \lambda} \Big|_{\lambda=1} = 2a_{01} [a_{11} r_s \ln(1 + [-2a_{01}(b_{11} r_s^{1/2} + b_{21} r_s + b_{31} r_s^{3/2} + b_{41} r_s^2)]^{-1}) + \frac{(1 + a_{11} r_s)}{1 + [2a_{01}(b_{11} r_s^{1/2} + b_{21} r_s + b_{31} r_s^{3/2} + b_{41} r_s^2)]^{-1}} A] \quad (B2)$$

where

$$A = \frac{1/2 b_{11} r_s^{1/2} + b_{21} r_s + 3/2 b_{31} r_s^{3/2} + 2b_{41} r_s^2}{(b_{11} r_s^{1/2} + b_{21} r_s + b_{31} r_s^{3/2} + b_{41} r_s^2)^2} \quad (B3)$$

Parameters $\alpha_{11}, b_{11}, b_{21}, b_{31}, b_{41}$ and a_{01} can be found in ref 13a. The gradient corrected form of the above-mentioned functional is as follows (Bc95) [14]:

$$\frac{\partial \epsilon_c^{opp}(n_{\alpha, \beta})}{\partial \lambda} \Big|_{\lambda=1} = [1 + (c_{opp} (\frac{|\nabla \rho_\alpha|^2}{\rho_\alpha^{8/3}} + \frac{|\nabla \rho_{\beta; 1}|^2}{\rho_\beta^{8/3}}))]^{-1} (\frac{\partial \epsilon_c^{VWN}(\rho_{\alpha, \beta})}{\partial \lambda} \Big|_{\lambda=1} - \frac{\partial \epsilon_c^{VWN}(\rho_{\alpha; 1})}{\partial \lambda} \Big|_{\lambda=1} - \frac{\partial \epsilon_c^{VWN}(\rho_{\beta; 1})}{\partial \lambda} \Big|_{\lambda=1}) \quad (B4)$$

$$\frac{\partial \epsilon_c^{\sigma\sigma}(\rho_\alpha)}{\partial \lambda} \Big|_{\lambda=1} = [1 + (c_{\sigma\sigma} \frac{|\nabla \rho_\sigma|^2}{\rho_\sigma^{8/3}})]^{-2} \frac{\sum_i |\nabla u_{i\sigma}|^2 - 1/4 \frac{(\nabla \rho_\sigma)^2}{n_\sigma}}{3/5 (6\pi^2)^{2/3} \rho_\sigma^{5/3}} \frac{\partial \epsilon_c^{VWN}(n_\sigma)}{\partial \lambda} \Big|_{\lambda=1} \quad (B5)$$

$$\frac{\partial \epsilon_c^{Bc95}(n_\alpha)}{\partial \lambda} \Big|_{\lambda=1} = \frac{\partial \epsilon_c^{opp}(n_{\alpha, \beta})}{\partial \lambda} \Big|_{\lambda=1} + \frac{\partial \epsilon_c^{\alpha\alpha}(n_\alpha)}{\partial \lambda} \Big|_{\lambda=1} + \frac{\partial \epsilon_c^{\beta\beta}(n_\beta)}{\partial \lambda} \Big|_{\lambda=1} \quad (B6)$$

The explicit formula of $\epsilon_c^{Bc95}([n]; \vec{r})$ and the parameters c_{opp} and $c_{\sigma\sigma}$ can be found in ref 11.

40 The main conclusions of this thesis

In the second and third chapters the view is developed that on the one hand the electron correlation is fairly nonlocal, on the other hand it is possible to obtain the exact correlation energy density $e_c([\rho]; \vec{r})$ via a constrained search procedure using the best available full-CI electronic density. The systematic study of the nearly exact correlation energy density provides new constraints for developing model functionals. Ususally the short range tail near the nuclei as well as the bonding region of $e_c([\rho]; \vec{r})$ in molecules are poorly represented by model energy densities $e_c^{model}([\rho]; \vec{r})$. The present results show that, in spite of some success of the gradient models, further improvement of the DFT approximations to $e_c(\vec{r})$ is desirable, especially, to describe properly the correlation in molecular systems. The "errors" of the GGA exchange-correlation functionals in molecules with strong near-degeneracy correlation seem to be compensated systematically by opposite "errors" in the GGA exchange functionals explaining the success of the molecular applications of the generalized gradient approximation (GGA) reported recently. In those cases a combined treatment of exchange and correlation may be more useful (Chapter 2). Furthermore, the improvement of model functionals by means of gradient expansion can be debated since in molecules in the bond midpoint $|\nabla\rho|=0$ and higher order terms oscillates heavily. Present results provides characteristic local behaviour for kinetic contributions to the correlation energy density, especially in the bonding region of molecules.

As for correlation models, the functions $\epsilon_c(\vec{r})$ obtained from the correlated $\rho(\vec{r}', \vec{r})$ and $\rho_2(\vec{r}_1, \vec{r}_2)$ can serve as a benchmark for successful models $e_c^{mod}(\vec{r})$. The procedure presented in Section 13 allows to construct $\epsilon_c(\vec{r})$ and $e_c(\vec{r})$ for an arbitrary many-electron system, which opens new possibilities for the DFT modelling. When developing a new $\epsilon_c^{mod}(\vec{r})$, one can take into account not only E_c estimates or the scaling and asymptotic properties of the E_c functional, but also the local behavior of the essentially accurate $\epsilon_c(\vec{r})$ obtained from *ab initio* wavefunctions for a representative set of atomic and molecular systems. A promising option is to approximate directly the potential $\frac{1}{2}w_c(\vec{r})$ and kinetic $v_{kin}(\vec{r})$ components which, as has been shown in the present thesis, have a characteristic form. The corresponding work as

well as the application of the proposed procedure of $\epsilon_c(\vec{r})$ construction to systems with more than two electrons is in progress.

The complexity of virial theorem in DFT which is due to the localization effect introduced in the Kohn-Sham equations, gives the ground for the modelling of the kinetic energy contribution to the correlation energy. The decomposition of the correlation energy E_c into potential W_c and kinetic T_c parts (Chapter 2) allow one the modelling of the constituents distinctly. Using the same constrained search methodology, as it was proposed in chapter 2, the kinetic energy density $t_c([\rho]; \vec{r})$ is obtained for small molecules, and its local characteristics is studied. One of the most interesting findings was that $t_c([\rho]; \vec{r})$ exhibits bond midpoint peak in H_2 which is reproduced by none of the model functionals. It was concluded that this is due to the lack of the explicitly treated nondynamical correlation in these model functionals (Chapter 3). The most widely used correlation functionals are usually parametrized for atoms, however, near-degeneracy correlation usually appears in molecular systems, and consequently represents great challenge for the new generation of correlation energy functionals (Chapters 2,3 and 4).

It is said that the applications are the greatest challenge for theory. To keep this in mind we have been conducted density functional calculations for the strong hydrogen-bonded system, called hydrogen diformiate. This system is one of the strongest known low-barrier hydrogen bonded anionic molecular complex with the experimental binding energy of 36.8 kcal/mol. This system can be used as a model system for biophysical problems like enzyme catalysis. In Chapter 5 the overall conclusion, which can be drawn, is that current implementations of gradient corrected density functionals are capable of describing hydrogen-bonding in this strongly bonded $HCOO^- \cdot HCOOH$ system. Hybrid exchange-correlation functionals provide a somewhat better agreement with experiment. The observed complexation energy is reproduced within almost chemical accuracy.

41 A disszertáció rövid összefoglalója

A második és harmadik fejezetben azt vizsgáltuk meg, hogy bár az elektronkorreláció tisztán nemlokális sajátosság, ugyanakkor lehetséges az egzakt korrelációs energiasűrűség előállítására egy ún. korlátozott keresést alkalmazó módszerrel keresztül teljesen korrelált elektronsűrűséget használva. Közel egzakt $e_c(\vec{r})$ korrelációs energiasűrűség szisztematikus tanulmányozása lehetőséget teremt új megközelítések bevezetésére a model funkcionálok fejlesztésekor. Rendszerint az $e_c(\vec{r})$ maghoz közeli viselkedése gyengén reprodukált a modellfunkcionálok által. A jelenlegi eredmények az mutatják, hogy a gradiens korrekciót alkalmazó modellek utóbbi években tapasztalt sikere ellenére a közelítések további finomítására van szükség, különösen molekulák esetében. A GGA (generalized gradient approximation) korrelációs funkcionálok terhelő hibák molekulákban szisztematikusan kompenzálódnak az ellenkező irányú hibák által ami jól értelmezi a GGA modell széleskörű alkalmazhatóságát. Ilyen esetekben a kicserélődési és korrelációs funkcionálok kombinált alkalmazása már jól bevált megoldásnak tekinthető és ennek megfelelően gyakran használják is az irodalomban (2. fejezet). A modellfunkcionálok gradiens korrekciók általi további javítása azonban megkérdőjelezhető, mivel molekulákban a kémiai kötést felezőpontban az elektronsűrűség gradiense zérus, $|\nabla\rho|=0$ és az ún. kötési régióban alacsony értéket vesz föl ill. a magasabb rendű tagok viszont erősen oszcillálnak. A jelen dolgozatbeli eredmények jellegzetes lokális viselkedést mutatnak a korreláció kinetikus energia járuléka esetében is, különösen a kötési régióban.

Az elsőrendű és másodrendű sűrűségmátrixokból előállított $e_c(\vec{r})$ függvények komoly alapként szolgálhatnak a különböző korrelációs modellek és $e_c^{mod}(\vec{r})$ modell energiasűrűségek fejlesztéséhez. A 2.3 alfejezetben bemutatott módszer lehetővé teszi $e_c(\vec{r})$ előállítását tetszőleges rendszerre, amely új lehetőségeket teremt a DFT-modellezésben. Ezután nem elég csak aszimptotikus és skálázási sajátosságokat figyelembe venni, hanem a lokális tulajdonságok részletes tanulmányozása is elengedhetetlen. Ígéretesnek tűnő választás a potenciális $w_c(\vec{r})$ és kinetikus $v_{kin}(\vec{r})$ járulékok direkt modellezése amelyeknek jellegzetes lokális viselkedése szintén a 2. fejezetben került bemutatásra. A módszer kiterjesztése több mint két elektront tartalmazó rendsz-

erekre folyamatban van.

A viriál tétel összetettsége a sűrűségfüggő elméletekben a Kohn-Sham egyenletekben bevezetett lokalizációs effektusoknak köszönhető. Az E_c korrelációs energia felbontása potenciális W_c és kinetikus T_c részekre (2. fejezet) lehetővé teszi ezen részek elkülönített modellezését. A 2. fejezetben használt feltételes keresés módszerével $t_c([\rho]; \vec{r})$ kinetikus energiasűrűséget számítottuk ki kis molekulákra és a lokális karakterisztikát vizsgáltuk a kötéstengely mentén. Az egyik legérdekesebb eredmény szerint $t_c(\vec{r})$ energiasűrűség a kötés felezőpontbeli csúccsal jellemezhető a hidrogén molekulában, azonban egyik $T_c^{mod}[\rho]$ funkcionál sem reprodukálta ezt a jellegzetes topológiát. Ez annak tulajdonítható, hogy a nemdinamikus korreláció, amely a erős degenerációs effektusokkal is kapcsolatba hozható, nincs figyelembe véve a leginkább használt korrelációs funkcionálokban (2.,3. és 4. fejezetek). A manapság használatos funkcionálok csak az atomi korrelációt írják le a molekulákban is (dinamikus korreláció), következésképpen az elkövetkező évek újgenerációs korrelációs funkcionáljai számára a legnagyobb kihívást a nemdinamikus korreláció eredményes modellezése jelenti (lsd. szintén az 1. fejezetet).

Gyakorta hangoztatott vélemény, hogy egy elmélet számára a legnagyobb kihívást annak széleskörű alkalmazása jelenti hiszen ilyenkor derülhet fény az esetleges hiányosságokra. Ezt szem előtt tartva sűrűségfunkcionál számításokat végeztünk egy erős hidrogénhidas rendszerre, a hidrogén-diformiátra. Ez az anionos komplex nem várt módon az egyik legerősebb alacsony potenciális energiagáttal rendelkező hidrogénhidas (LBHB) molekulakomplexnek bizonyult 36.8 kcal/mol kísérleti asszociációs energiával. A hidrogén-diformiát jól használható modellként olyan biofizikai problémákhoz, mint az enzimkatalízis. Az alkalmazott gradiens korrigált kicserélődési-korrelációs funkcionálok alkalmasnak bizonyultak az LBHB leírására a $HCOO^- \cdot HCOOH$ molekulában. Az ún. hibrid kicserélődés-korrelációs funkcionálok némileg jobb eredményeket adtak közel kémiai pontossággal reprodukálva a kísérleti adatokat (5. fejezet).

42 The documentation of publications

P. Süle and Á. Nagy, Acta Phys. Chim. Debr. **29**, 1 (1994) Comparative test of local and nonlocal Wigner-like correlation energy functionals

P.Süle, O. Gritsenko, Á. Nagy and E. J. Baerends, J. Chem. Phys. **103**, 10085. (1995), Correlation energy density from *ab initio* first- and second-order density matrices: A benchmark for approximate functionals

P. Süle and Á. Nagy, J. Chem. Phys., J. Chem. Phys. **104**, 8524. (1996)
Density functional study of strong hydrogen bonding. The hydrogen-diformiate complex

P. Süle, Chem. Phys. Lett., **259**, 69. (1996)
Kinetic contribution to the correlation energy density: A benchmark for $T_c[n]$ functionals

S. Liu, P. Süle, R. López-Boada, Á. Nagy, Chem. Phys. Lett. **257**, 68. (1996)
Application to atoms, ions, and molecules of a novel form of the correlation energy density functional

P. Süle, Low-barrier hydrogen bonding in dielectric continuum: Density functional study of hydrogen-diformiate in self-consistent reaction field, submitted

Posters, Lectures

Wigner-type local and nonlocal correlation functionals, lecture at the Dept. of Theoret. Physics of Kossuth Lajos University (1995)

Thirty Years of Density Functional Theory: Concepts and Applications, Cracow, Poland 1994. Book of abstracts, *poster and lecture*

8th International Congress of Quantum Chemistry, Prague 1994, Book of abstracts, *poster*

6th International Conference on the Applications of Density Functional Theory in Chemistry and Physics, Paris 1995, Book of abstracts, *poster*

Electronic structure of atoms and molecules, summer school, Debrecen 1995, *poster*

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