# Investigation of exchange and correlation functionals in Density Functional Theory in case of ground and excited state systems

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# 1 Preliminaries and scientific objectives

## Preliminaries

The atomic and molecular physics has greatly improved in the last 80 years, since the birth of quantummechanics. Because of the extremely dynamic improvement of computational technology, the application of the quantum theory turned to be more routinary not only in physics but in modern biology and chemistry too. This field of physics is basically the application of the quantum many-body problem to the N-electron system. As the equation of the N-electron system can be solved analytically just in very limited number of situations, the main purpose of atomic and molecular physics is to develop approximations as accurate as possible.

The idea that the ground state energy of the N-electron system can be investigated as a functional of density first appeared in the Thomas-Fermi model [1], but this theory had several weaknesses. For example, it could not interpret the chemical bindings or according to the model no negative ions could exist. One of the most important corrections to handle these weaknesses was suggested by Dirac, who, in 1930, managed to provide for the homogenous ground state electron gas density expression of the exchange energy suggested purely quantum mechanically [2]. From a different theoretical basis a similar term with a different constant was

proposed by the Hungarian Gáspár Rezső [3] and the American J.C. Slater [4]. It happened already in the 1950s, and then in 1964 Hohenberg and Kohn proved the two theorems [5] which ensured the basis of the modern density funcional theory (DFT). Soon after the basic theorems the so-called Kohn-Sham scheme [6] was worked out, which made it possible to start the calculations. The main problem with the Kohn-Sham method is the lack of the exact form of the exchange and correlation energy functional. In the literature there are several approximations based on different theoretical considerations. Testing and developing these approximations provide for a number of investigations. Another important feature of the original theory is that it is capable of examining only ground state level systems. For this reason the extension of the theory to excited states has been very intensively investigated since the beginning.

The first approximate method for excited state calculation was suggested by Slater, who guessed the excitation energies with the help of half occupation number [7]. A further importance of the method is that it made also possible to calculate the ionization energies. The first theoretically exact method was developed by Theophilou in 1978 [8], which was generalized by Gross, Oliviera and Kohn in the frame of the ensemble Density Functional Theory [9]. The crucial point of the ensemble DFT is

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the form of the exchange and correlation functional, which has an unknown dependence on the $\omega$ ensemble parameter, introduced in the theory.

## Scientific objectives

According to the preliminaries there are two main directions in the researches: First, the effects of the different functionals on the results can be investigated on ground state systems in the frame of the traditional Density Functional Theory, and they can be compared with the results of the Hartree—Fock calculations also developed to ground state level investigations. Secondly, the dependence of the ensemble exchange-correlation on the $\omega$ parameter can be investigated.

I treated the ground state level investigation through two specific problems. First, the 1s, 2s, 2p core level binding energy shifts of the central Aluminium atom in different size of Aluminium clusters (AlAl$_{12}$, AlAl$_{12}$Al$_6$) were investigated with different type of functionals (X$\alpha$ [10], Gunnarsson—Lundqvist [11], Perdew—Wang [12]) and with the HF method. In the second case, dimer and triplex Hydrogen-bonding systems of different natural DNA bases and artificial DNA base-like molecules were investigated. The main question was the binding preference order in all cases (in dimer and triplex systems), and because of this calculations, I could analyze the calculations with different functionals and compare them

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with the results of the HF method. In both cases I also examined the effects of the choice of the Gaussian basis sets.

I wanted to determine the dependence of the exchange-correlation functional on the $\omega$ ensemble parameter with the extension of the local type $X\alpha$ ground state functional. Furthermore, I wanted to investigate how the results are modified in the presence of gradient or correlation corrections.

# 2. Scientific methods

Because of the diversified purposes the applied methods were also very different. In case of the Aluminium binding energy shifts I applied the Slater's type transition state method and the total energies difference calculations according to suggestions in [13] and [14]. I coded different DFT functionals into the Szegedien MS-$X\alpha$ program package [15], which apply the "muffin tin" approximation, known from solid state physics. In the HF case the value of the shifts was determined with the Koopman's theorem and the necessary calculations were performed with the *Gaussian98* code. I also used this code in dimer and triplex system calculations, and I applied the basis counterpoise correction method for the basis set superposition error when the binding energies preference order was determined.

I made fitting in the Xα term of the ground state functionals in such a way that the ensemble energy calculated with experimental data and the ensemble energy from the self-consistent running were made equal. This way I could examine the effects of the different ground state form gradient corrections (Perdew—Wang and Becke [16] corrections) and correlations (Gunnarsson—Lundqvist and Lee—Young—Parr [17]) on the fitted γ(ω) parameter.

# 3. New results

1) I built in exchange functionals (Langreth-Mehl, Perdew-Wang) into the Szegedien MS-Xα program code.

2)

 a) I successfully applied the DFT method to determine the 1s, 2s, 2p binding energy shifts of the central Aluminium atom in Aluminium clusters ($AlAl_{12}$, $AlAl_{12}Al_6$). I also determined the shifts with Koopmans level HF calculation with the *Gaussian98* program package.

 b) I showed that although the values of the ionization energies were sensitive to the different functionals, while it was less noticeable in the binding energy shifts. The choice of calculation method (ΔSCF or Slater's transition state method) seemed to be more significant. I found that the DFT methods provided a better agreement with the experimental metal data than the Koopmans-level HF calculations.

 c) The HF and the DFT methods led to the same conclusion when the size of the cluster increased: The core level binding energy shift of the central atom was not tending monotonically to the metal's value. I interpreted this as the consequence of the screening effects

of the neighbouring atoms and the charge-transfers between the different shells of atoms.

3)

    a)   Successful and suppletory calculations were performed with DFT and HF methods to the dimer systems of the Hypoxanthine molecule with Adenine, Cytosine, Guanine and Thymine DNA bases with the *Gaussian98* program. I reproduced the experimental results of the binding energy preference order with these simple model systems.

    b)   From the respect of the order of the binding energies all the applied functions (Becke, B3LYP) led to the same result, but from the respect of the length of the H-bondings and consequently in the bonding energies there were differences between the different methods. The results were also sensitive to the size of the Gaussian basis set.

4)

    a)   I pioneered ab initio calculations (HF and DFT) to triplex systems, namely 2-aminopyridin, 2-aminoquinoline, 2-aminopyrrole and 2-aminoindole molecules forming triplexes with the natural DNA bases pairs.

b) I found that if the basis set was the same in the calculations, the DFT (with the B3LYP functional) method always provided shorter bond lengths compared to the HF method. I could see that if I increased the number of the basis functions, the optimum bond lengths were always longer. In connection with the calculation method the result of the two effects is that the HF/3-21 type calculations and the more sophisticated but much more time and memory consuming B3LYP/6-31** calculations led to very similar results.

5)

a) I investigated the dependence of the exchange and correlation functions on the ensemble parameter in the frame of the ensemble DFT developed for excited states. First, I coded the theory into the Hermann-Skilman atomic calculation program, and the necessary exchange and correlation functionals. I extended the ground state form of the functionals as $E_{XC}(n^{\omega}(r);\gamma)=E_{XC}(n^{\omega})+(\gamma(\omega)-1)\cdot E_X^{LDA}(n^{\omega})$ where the $\gamma(\omega)$ parameter was determined by the fact that the ensemble calculation provides the exact ensemble total energy. I presented the results for the 1st, 2nd and 3rd excited states of He, Be and B atoms.

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b)  I found parabolic minimum of the fitted $\gamma(\omega)$ curve in case of the 1st excitation of the He (and according to the calculations for further atoms e.g. F, Na, Cl). The dependence of the fitted parameter was linear for other atoms and for higher excitations, and the slope of the curves was changed from state to state and from atom to atom. Concerning a state of an atom, the features of the fitted curve was not influenced by the presence of the gradient or the correlation corrections. I found that the difference between the fitted parameter and the ground state fitted value ($\gamma_0$) was less than 15% for He at the first three excitations, and in case of the Be and the B it never exceeded 3% .

6)  I determined the dependence (in cases of the X$\alpha$ and the Becke potential) of the highest, non-zero occupation number Kohn-Sham orbital energy dependence on the $\omega$ parameter. I found that in both of the ground state fitted $\gamma_0$ and the fitted $\gamma(\omega)$ cases the orbital energies slightly decreased. Using Levy's formula as a condition, I outlined a possible way to determine the linear type $\gamma(\omega)$ curve by a double self-consistent process.

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## Publications

The thesis is based on the following publications:

1. G. Paragi, I.K. Gyémánt, Zs. Varga
   Advances in Quantum Chemistry 29, 433-439 (1997)

2. G. Paragi, I.K. Gyémánt, V.E. Van Doren
   Chemical Physics Letters 324, 440-446 (2000)

3. G. Paragi, I.K. Gyémánt, V.E. Van Doren
    Journal of Molecular Structure: THEOCHEM, 571, 153-161 (2001)

4. G. Paragi, I. Pálinkó, C. Van Alsenoy, I.K. Gyémánt, B. Penke, Z. Tímár
   New Journal of Chemistry, 26, 1503–1506 (2002)

5. Paragi G., C. Van Alsenoy, Penke B., Tímár Z.
   *Ab initio calculations on simple heterocycles and DNA base-pair triplets*
   accepted for publication in THEOCHEM (in press)

Additional publications:

B. Rousseau, C. Van Alsenoy, A. Peeters, F. Bogár, G. Paragi
*A MIA enhanced linear scaling approach to the computation of the echange-correlation terms in DFT/LDA*
accepted for publication in THEOCHEM (in press)

I. Mándity, G. Paragi, F. Bogár, I.G. Csizmadia
*A conformational analysis of histamine, and its protonated or deprotonated forms: an ab initio study*
accepted for publication in THEOCHEM (in press)