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**Theory of variational calculation with a scaling correct moment functional to solve the electronic Schrödinger equation directly for ground state one-electron density and electronic energy**

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**Abstract**

The reduction of the electronic Schrodinger equation or its calculating algorithm from 4N-dimensions to a nonlinear, approximate density functional of a 3 spatial dimension one-electron density for an N electron system which is tractable in practice, is a long desired goal in electronic structure calculation. In a seminal work, Parr et al. (Phys. Rev. A, 55 (1997) 1792) suggested a well behaving density functional in power series with respect to density scaling within the orbital-free framework for kinetic and repulsion energy of electrons. The updated literature on this subject is listed, reviewed and summarized. Using this series with some modifications, a good density functional approximation is analyzed and solved via the Lagrange multiplier device. (We call the attention that the introduction of a Lagrangian multiplier to ensure normalization is a new element in this part of the related, general theory.) Its relation to Hartree-Fock and Kohn-Sham formalism is also analyzed for the goal to replace all the analytical gaussian based two and four center integrals ( $\int g_i(\mathbf{r}_1)g_k(\mathbf{r}_2)r_{12}^{-1}d\mathbf{r}_1d\mathbf{r}_2$ , etc.) to estimate electron – electron interactions with cheaper numerical integration. The Kohn-Sham method needs the numerical integration anyway for correlation estimation.

**Keywords**

Density functional theory; power series with correct density scaling; one-electron density; ground state total electronic energy

**1. Introduction**

The non-relativistic spinless fixed nuclear coordinate electronic Schrodinger equation (SE) in free space is capable of describing the electronic motion in molecular systems by providing the anti-symmetric wavefunction  $\Psi(\{Z_A, \mathbf{R}_A\}, \{\mathbf{x}_i\})$  and electronic energy  $E_{\text{total electr}} = E_{\text{electr}}(\{\mathbf{R}_A, Z_A\}) + V_{\text{nn}}$  of the ground and excited states.  $V_{\text{nn}} = \sum_{A=1, \dots, M} \sum_{B=A+1, \dots, M} Z_A Z_B R_{AB}^{-1}$ , where  $R_{Au}$  ( $u = x, y, z$ ) are the M nuclear coordinates with nuclear charges  $Z_A$ , as well as  $\mathbf{x}_i = (\mathbf{r}_i, s_i) = (x_i, y_i, z_i, s_i)$  are the N spin-space electronic coordinates (4N dimensions). For the commonly used *ab initio* calculations as configuration interactions (CI, for ground and excited states) and the faster Hartree-Fock Self Consistent Field (HF-SCF, for ground state) [1] longer time and larger disc space are still demanded, even for ground state  $\Psi_0$  and  $E_{\text{electr},0}$ , as well as convergence problems can rise at about N=10 and 500 respectively. The density functional theory (DFT) method, based on the Kohn-Sham (KS) formulation [2-3] effectively improves the “error” of the HF-SCF method (called correlation energy  $E_{\text{corr}} \equiv E_{\text{electr},0} - E_{\text{HF-SCF/basis}}$  [1, 4-5]), technically with some in-built [6-16] functionals during the SCF algorithm, called “exchange-correlation functionals” – not detailed

here. (On the other hand,  $E_{\text{corr}}$  can be estimated after the HF-SCF routine, for example with Moller-Pleset (MP) and many other methods [1] – also not detailed here.) Another thing, one should not forget about the basis set error and basis set superposition error [12]. However, the kinetic functional in the KS method is still the sum of the  $N$  nabla-square operators, so the computational costs remain similar to the HF-SCF method ( $3N$  dimensional in nature). It has long been desired in DFT, to reduce the dimensionality to 3. While the HF-SCF and KS methods are highly developed, there are still no tractable methods based solely on the 3 spatial dimension one-electron density.

The fascinating idea of moment-based density functionals is seductive: replace the thorny functional analysis that accompanies DFT with “function analysis” by writing the energy as a function (not a functional) of the moments of the electron density. This paper works along those lines. The energy functional for ground state based on scaling correct power series is reviewed and the standard Lagrange multiplier method is introduced in this relation, which ensures the normalization of the density, to solve and analyse these density functionals. We also discuss about the relation of these density functionals with the Kohn-Sham DFT and Hartree-Fock theory.

## 2. Review of the Energy Functional for Ground State Based on Scaling Correct Power Series

### 2.a The N-electron density functional and density integro-differential operator

The ground state  $N$ -normalized one-electron density,  $\rho_0(\mathbf{r}_1)$ , is the central variable in DFT. Since the density functional for  $\rho_0(\mathbf{r}_1)$  is non-linear, its solution generally requires numerical integration as described and cited in refs.[14-15], not only in the correction terms as in KS formalism, but also in the main terms as well. In the one-electron density formulation of DFT, the energy functional (in the absence of external field other than the molecular frame) comes from

$$\begin{aligned} E_{\text{electr}}[\rho] &= N^{-1} [\int D_{\nabla}(\rho(\mathbf{r}_1)) d\mathbf{r}_1 + \int D_{\text{rr}}(\rho(\mathbf{r}_1)) d\mathbf{r}_1] - \sum_{A=1, \dots, M} Z_A \int \rho(\mathbf{r}_1) r_{A1}^{-1} d\mathbf{r}_1 \equiv \\ &\equiv N^{-1} \int D[\rho] d\mathbf{r}_1 \equiv F[\rho(\mathbf{r}_1)], \end{aligned} \quad (\text{Eq.1})$$

where  $r_{A1} \equiv |\mathbf{R}_A - \mathbf{r}_1|$  and the kinetic-, electron-electron-, and nuclear-electron energy terms [14-19] can be identified. (In the literature [2] the notation  $F$  is sometimes used in another way i.e. the energy functional of nuclear-electron attraction is not included in it, but added after as  $F[\rho(\mathbf{r}_1)] - \sum_{A=1, \dots, M} Z_A \int \rho(\mathbf{r}_1) r_{A1}^{-1} d\mathbf{r}_1$ .) For ground state electronic energy, the 2<sup>nd</sup> Hohenberg – Kohn (HK) theorem [2, 20] referring to the energy variation principle demands, the true electronic DFT functional satisfies the relation  $E_{\text{electr},0}[\rho_0] \leq E_{\text{electr},0}[\rho_{0,\text{trial}}]$  for a trial,  $N$ -normalized, everywhere positive density  $\rho_{0,\text{trial}}(\mathbf{r}_1)$ , where  $\rho_0$  is the true solution. The  $N$ -norm is

$$\int \rho_{0,\text{trial}}(\mathbf{r}_1) d\mathbf{r}_1 = N. \quad (\text{Eq.2})$$

The terms of  $N$ -electron DFT (differential or integro-differential [14]) operator ( $D$ ) come from integrating both sides of the electronic SE containing the Hamiltonian  $H$  for all  $\mathbf{x}_i$  except  $\mathbf{r}_1$  after multiplying by the complex conjugate of the same  $j^{\text{th}}$  excited state wave function from the left:

$$D[\rho] \equiv D_{\nabla}[\rho] + D_{\text{Rr}}[\rho] + D_{\text{rr}}[\rho] = \rho E_{\text{electr}} \quad (\text{Eq.3})$$

The disadvantage of  $D$  is its non-linearity. Notice that  $N^{-1}$  in Eq.1 comes from integrating both sides of Eq.3 for the 3 dimensional space and the normalization  $\int \rho d\mathbf{r}_1 = N$ . (In detail, one must be careful with the normalization when manipulating for Eq.1: while  $\int \Psi_0^* \Psi_0 d\mathbf{x}_1 \dots d\mathbf{x}_N = 1$  stemming from “ $N$  over  $N$  is 1 in combinatorics for HF-SCF”, the  $\int \rho_0 d\mathbf{r}_1 = \int (\int \Psi_0^* \Psi_0 ds_1 dx_2 \dots dx_N) d\mathbf{r}_1 = \int \Psi_0^* \Psi_0 d\mathbf{x}_1 \dots d\mathbf{x}_N = N$  stemming from “ $N$  over 1 is  $N$  for DFT.”) The peculiarity of  $D$  is that some of its terms can have zero integral [14] in the form of Eq.1, although it plays a part in shaping the  $\rho$  via Eq.3. For H-like atoms (or an unstable system of a molecular frame with one electron) the sub-case of Eq.3 is the partial differential equation,  $D[N=1, \rho(\mathbf{r}_1)] \equiv -(1/4) \nabla_1^2 \rho(\mathbf{r}_1) + (1/8) \rho(\mathbf{r}_1)^{-1} |\nabla_1$

$\rho(\mathbf{r}_1)|^2 + \rho(\mathbf{r}_1)v(\mathbf{r}_1) = E_{\text{electr}} \rho(\mathbf{r}_1)$ , for ground and excited states [14]. In practice, the main problem with D or F is that their exact analytical formula are unknown, there are only approximations for them, the latter are problematic in programming, and more importantly in chemical accuracy (i.e. to reach the 1 kcal/mol even in energy differences).

While the DFT formula for the nuclear–electron energy term (using notation  $v(\mathbf{r}_1) \equiv -\sum_{A=1,\dots,M} Z_A r_{A1}^{-1}$  for “external potential”),

$$V_{\text{ne}}[\rho(\mathbf{r}_1)] \equiv N^{-1} \int D_{\text{Rr}}(\rho(\mathbf{r}_1)) d\mathbf{r}_1 = -\sum_{A=1,\dots,M} Z_A \int \rho(\mathbf{r}_1) r_{A1}^{-1} d\mathbf{r}_1 = \int v(\mathbf{r}_1) \rho(\mathbf{r}_1) d\mathbf{r}_1 \quad (\text{Eq.4})$$

in Eq.1, is extremely simple and analytically 100% accurate, the other two in F are very difficult algebraically and only approximations are known. (In. ref.[14] the integral formula,  $D_{\text{Rr}}[\rho] = \rho(\mathbf{r}_1)v(\mathbf{r}_1) + (N-1) \int d_2(\mathbf{r}_1, \mathbf{r}_2)v(\mathbf{r}_2) d\mathbf{r}_2$ , is reported for the intergo-differential equation in Eq.3, where  $d_2$  is the N-normalized two-electron density. There exists another equation which compares to Eq.4 with respect to its simplicity and also its importance “at the same time” in DFT, the famous electrostatic theorem of Feynman as a subcase of Hellmann–Feynman theorem [2, 21]:  $\partial E_{\text{electr}}/\partial R_{\text{Au}} = \int \rho(\mathbf{r}_1)(\partial v(\mathbf{r}_1)/\partial R_{\text{Au}}) d\mathbf{r}_1 = -Z_A \int \rho(\mathbf{r}_1)(u_1 - R_{\text{Au}}) r_{A1}^{-3} d\mathbf{r}_1$  with  $u=x, y$  or  $z$  to be used in  $\partial E_{\text{total electr}}/\partial R_{\text{Au}} = \partial E_{\text{electr}}/\partial R_{\text{Au}} + \partial V_{\text{nn}}/\partial R_{\text{Au}}$  with straightforward partial derivative for  $V_{\text{nn}}$ .)

## 2.b Scaling correct power series for kinetic and electron-electron repulsion density functionals

Parr et al. reported a power series [22] based on the rules of density scaling [2] for the other two terms than the nuclear-electron one in F: for kinetic energy in Eq.1 the series of coordinate homogeneous functional of degree two is

$$T[\rho(\mathbf{r}_1)] \equiv N^{-1} \int D_{\nabla}(\rho(\mathbf{r}_1)) d\mathbf{r}_1 = \sum_{j=1,\dots,n} A_j [\int \rho^{[1+2/(3j)]} d\mathbf{r}_1]^j \quad (\text{Eq.5})$$

, while the electron-electron repulsion energy term, the functional is of a degree one

$$V_{\text{ee}}[\rho(\mathbf{r}_1)] \equiv N^{-1} \int D_{\text{rr}}(\rho(\mathbf{r}_1)) d\mathbf{r}_1 = \sum_{j=1,\dots,n} B_j [\int \rho^{[1+1/(3j)]} d\mathbf{r}_1]^j \quad (\text{Eq.6})$$

(The density scaling, which is the base of Liu and Parr's work [22], is well discussed in the book of general theory in ref. [2], and will not be detailed here.) In ref.[14] the 100% accurate integral formula,  $D_{\text{rr}}[\rho] = (N-1) \int d_2(\mathbf{r}_1, \mathbf{r}_2) r_{12}^{-1} d\mathbf{r}_2 + [N(N-1)/2 - (N-1)] \int d_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) r_{23}^{-1} d\mathbf{r}_2 d\mathbf{r}_3$ , is reported for the intergo-differential equation in Eq.3, where  $d_2$  and  $d_3$  are the N-normalized two- and three-electron densities. These are symmetric (called r-symmetric) in exchange of  $\mathbf{r}_i$  and  $\mathbf{r}_j$ . Furthermore, the two-electron density functional,  $V_{\text{ee}} \equiv (1/N) \int D_{\text{rr}}[d_2] d\mathbf{r}_1 d\mathbf{r}_2 = ((N-1)/2) \int d_2 r_{12}^{-1} d\mathbf{r}_1 d\mathbf{r}_2$ , is also 100% accurate analytically [14]: however, the N- representability is not so simple for  $d_2$  and for  $d_3$ . The latter means that, when  $d_2$  or  $d_3$  is expanded into a series of e.g. Gaussian type orbital (GTO) in 6 or 9 dimensional  $(\mathbf{r}_1, \mathbf{r}_2)$  or  $(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$  space as r-symmetric function, one must ensure that it can be de-convoluted into an anti-symmetric  $4N$  dimensional wavefunction (generally it is not necessarily possible). Furthermore,  $\int d_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) d\mathbf{r}_3 = d_2(\mathbf{r}_1, \mathbf{r}_2)$  and  $\int d_2(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 = \rho(\mathbf{r}_1)$  hold.

Before we analyze Eqs.5-6 and their consequences further, we mention that while there has always been some work on “moment expansions” of the electron density, the work really started in earnest with the work of Agnes Nagy in the mid-1990's, and the subsequent work from the Parr group that this stimulated. The idea is incredibly attractive: one can rewrite every density functional as a function of the moments of the density. (In practice, it is a bit tricky, because one has to make sure the moments are complete; cf. ref. [23].) This allows one to replace the functional analysis in DFT with simple multivariate calculus, which is a huge formal advantage. Most of the work (the only exception we know of is a tiny bit of work from Parr [23]) assumes that quantities can be written as a linear function of the moments, though that is obviously an incorrect assumption, though it is perhaps a useful approximation. The biggest drawback of these approaches is that most moment expansions (and especially most nonlinear moment expansions)

are not size consistent. The biggest advantage of this approach is that it works well (if not excellently) and that there are beautiful mathematical results, including an explicit method for finding the exact universal density functional from the form of the density functional for one specific system [23-24]. Our contribution here fits into this context.

## 2.c Truncation opportunities and the series constants in scaling correct power series for density functionals

Truncation  $j=1$  in Eq.5 provides the classical Thomas-Fermi (TF) formula ( $T \approx A_1 \int \rho^{5/3} d\mathbf{r}_1$ ) as the main term for  $T$  with TF constant [2]  $c_F = (3/10)(3\pi^2)^{2/3} = 2.871234 \approx A_1$ . The rest, mostly in KS formalism, is approximated in the literature: with local, non-local, spin and spinless, gradient corrected DFT functionals for ground state. These contain the derivatives of  $\rho_0$ , and have completely different forms than Eq.5. For example,  $T[\rho_0(\mathbf{r}_1)] \approx \int [c_F \rho_0^{5/3} + (\lambda/8)|\nabla_1 \rho_0|^2/\rho_0 + \text{corr.terms}] d\mathbf{r}_1$  form is the so-called Weizsacker gradient correction [2, 16]. (In the TF+ $\lambda W$  theories, the estimation for  $\lambda$  is between 1/9 and 1/5 [2, 16], however, a very popular choice, early on, was  $\lambda=1$  [25-28].) We will not summarize the vast literature about it here, but as analyzed below, we mention that Eqs.5-6 have reality via the general property of functions capable to be expanded into series. The constants  $A_j$  in Eq.5 can be subdivided as

$$A_1 \equiv c_{10} c_F \text{ and } A_j = c_{10} c_F a_j = A_1 a_j \quad \text{for } j=2,3,4,\dots \quad (\text{Eq.7})$$

where the  $c_{10}$  is supposed to correct the TF constant, and the others ( $a_j$ ) are ‘‘behind’’  $A_1$  for higher terms without  $N$ -dependence. The  $c_{10}$ ,  $a_2$ ,  $a_3$ ,  $a_4$ , ... can come from parameter fitting, ( $c_{10} > 0$  is not far from unity, and  $|a_j| < c_{10}$  for  $j=2,3,4, \dots$ ).

Truncation  $j=1$  in Eq.6 gives the main term as  $V_{ee} = B_1 \int \rho^{4/3} d\mathbf{r}_1 + \text{corr}_1$  with  $B_1 \approx 2^{-1/3}(N-1)^{2/3}$ , mentioned and analyzed in ref.[2], however, it can also only be the main term of correction (Dirac exchange functional approximation [6, 18] with constant  $B_{\text{Dirac}}$ ) if the main term is taken as the classical Coulomb repulsion energy as  $V_{ee} = (1/2) \int \rho_0(\mathbf{r}_1) \rho_0(\mathbf{r}_2) r_{12}^{-1} d\mathbf{r}_1 d\mathbf{r}_2 + \text{corr}_2$  with  $\text{corr}_2 = B_{\text{Dirac}} \int \rho_0^{4/3} d\mathbf{r}_1$ . The latter is a more accurate approximation, i.e. generally  $|\text{corr}_2| < |\text{corr}_1|$ , however, both  $\text{corr}_i$  are necessary for accuracy. This coincidence is not accidental, since the Dirac formula is also a scaling correct power series truncated after the first term.  $V_{ee}[\rho(\mathbf{r}_1)]$  scales one, but the classical Coulomb repulsion energy approximation, scales two, which is incorrect. It is the main source of correlation energy ( $E_{\text{corr}}$ ), which is the major problem with respect to chemical accuracy in HF-SCF (due to the lack of formula) or KS (which does have a suitable but yet not perfect formula) methods, stemming from using only a single Slater determinant to approximate  $\Psi_0$ .

We also mention that, the classical Coulomb repulsion energy as the main algebraic term contains only the first (in fact second) powers of  $\rho_0$ , good for HF-SCF routine where a GTO basis set is used to make the integrations analytical in the approximation. The Dirac formula is one trial of the many which is designed to estimate its error ( $\text{corr}_2$ ). It is considered in great detail in the literature. Recall again the local, non-local, spin and spinless, gradient corrected, hybrid, etc. exchange-correlation functionals in KS formalism. Historically, the promising approximations of  $\text{corr}_2$  have made DFT successful in practice, but there is still no total control over its accuracy in different systems. The exact analytical form is unknown at the present time, there are only empirical formulas, parameterized and optimized mainly for ground states.

The constants  $B_j$  in Eq.6 can be treated as

$$B_1 \equiv c_{20} (2^{-1/3}(N-1)^{(2/3)c_{200}}) \text{ and } B_j = B_1 b_j \text{ for } j=2,3,4,\dots \quad (\text{Eq.8})$$

where the  $c_{20}$  is supposed to correct the expression  $2^{-1/3}(N-1)^{(2/3)c_{200}}$ , and the others ( $b_j$ ) are ‘‘behind’’  $B_1$  for higher terms without  $N$ -dependence. In ref.[2]  $c_{200} = 1$ , leaving the power simply

as  $2/3$ , but we are trying to correct this part too by tuning with the factor  $c_{200}$  in later work. The  $c_{200}$ ,  $c_{20}$ ,  $b_2$ ,  $b_3$ ,  $b_4$ , ... can come from a parameter fitting as well, ( $c_{20}$ ,  $c_{200} > 0$  are not far from unity, and  $|b_j| < c_{20}$  for  $j=2,3,4,\dots$ ).

We call the attention that it isn't strictly true that the exact form of the functional isn't known for these sorts of moment expansions. The exact form is known, but it is hopelessly complicated and, as pointed out by Ayers, contains terms that are not included in the simple series expansion in Eqs.5-6. Specifically, increasingly complicated ratios of moments appear [23-24]. While the approach is very elegant, the results in those papers [23-24] are much less favorable than those of Liu, Nagy, and Parr [29-30], probably because much the dataset being fit was much larger. The modern literature on density moments in DFT is quite small, with only a few important researchers (Nagy, Parr, and some others) have published yet results [23-24, 29-43].

## 2.d The magnitude of the series constants of scaling correct power series for density functionals

In ref.[22], the series on the right hand side of Eq.6 is used for exchange energy [2] (as a part of  $E_{\text{corr}}$  in HF-SCF formalism) or the similar magnitude exchange correlation energy [3] (to describe Coulomb and Fermi holes in KS formalism), however, here we use it to estimate the entire  $V_{\text{ee}}$ . In this way, if we do not truncate too soon, Eqs.5-6 help to avoid the problem of  $E_{\text{corr}}$ , as well as the algorithm becoming simpler since one does not have to deal with messy derivatives and non-local integrals. In ref.[22] the formulas in Eqs.5-6 were tested with HF-SCF one-electron densities,  $\rho_{0,\text{HF-SCF}}$ , and among many conclusions, the most important thing for us now is that 3-4 terms may be enough for chemical accuracy, and in accord, the absolute value of the coefficients decrease rapidly. Here we use these formulas as direct substitution into Eq.1 and solve them for ground state, but we emphasize that Eqs.4-6 hold for excited states as well. The rapid decrease of  $A_j$  and  $B_j$  are not surprising if one recognizes that a crude and more precise estimation (see Appendix) for the magnitude of power terms in Eqs.5-6 is  $[\int \rho^{[1+a/(3j)]} d\mathbf{r}_1]^j \sim [\int \rho d\mathbf{r}_1]^j = N^j$  and

$$[\int \rho^{[1+a/(3j)]} d\mathbf{r}_1]^j \approx G^j \text{ with } G(x) \equiv N^x(N^3/\pi)^{x-1}/x^3 \text{ and } x \equiv 1+a/(3j), \quad (\text{Eq.9})$$

respectively, where  $a = 1$  or  $2$  and  $j > 1$ , as well as notice that  $G(1)=N$ , - i.e. these increase rapidly with  $N$ , which is large in calculations for molecules. Another hypothesis is that a replacement of  $a_j$  and  $b_j$  in Eqs.7-8 with  $a_j N^{1-j}$  and  $b_j N^{1-j}$  for  $j=2,3,4, \dots$  may be better (i.e. in this way  $a_j$  and  $b_j$  are more independent from  $N$ ), because Eqs.5-6 contain larger powers of  $N$  in view of Eq.9. (View in the perspective of dimensional analysis that functional  $\int \rho^{5/3} d\mathbf{r}_1$  approximates  $T$  and  $\int \rho^{4/3} d\mathbf{r}_1$  approximates  $V_{\text{ee}}$ , while functional  $\int \rho d\mathbf{r}_1$  gives  $N$ .) An answer for this will be given via tests on real systems. Also, we must mention that  $N$ -dependent functionals are not size consistent. Hard to find a good reference for that (though it is obvious), for example, it was mentioned by Parr in his work on the Fermi-Amaldi model [44].

## 2.e Density functionals in scaling correct power series form versus partial differential equation to describe molecular systems

Replacing a partial differential eigenvalue equation with a functional containing algebraic equation can be perilous, but recall the truth that  $E_{\text{electr}}$  in SE depends only on the  $\{\mathbf{R}_A, \mathbf{Z}_A\}_{A=1,2,\dots,M}$  molecular frame (the basic, original inspiration of the HK theorems). In this way, for a power series expansion, e.g. with  $\rho$  (in which DFT states that it contains all the properties), it is just a question of the quality of the power series that has been chosen. We point out that the HF-SCF and CI methods (see Fock matrix, secular equation, or advanced devices based on series expansion, etc.) obtain roots (energy values) from a  $k^{\text{th}}$  order determinant transformed from SE.

This also corresponds to a  $k^{\text{th}}$  order algebraic equation, so from this view the form examined here should not be considered unusual. We mention that Parr et al. [2, 45] recognized that in F for ground state, the problem of finding the electronic structure of molecules reduces to treat some algebraic expressions for the 2<sup>nd</sup> HK theorem back in 1979. However, due to the early stages of computers, problems of accuracy and finding a convenient method to locate the extremum, it has not moved into a focus of interest. Mostly, HF-SCF level  $\rho_{0,\text{HF-SCF}}(\mathbf{r}_1)$  functions were used to test these kinds of DFT functionals.

Expanding with the Weizsacker term, Handy et al. [18] have tested the non-KS formalism DFT functionals by expanding the  $\rho_0(\mathbf{r}_1)$  with a gaussian basis set. Before and more generally, similar approaches have been examined by Liu and Parr [22], however, they only focused on atoms and correlation, here we also examine molecules, as well as we consider Eqs.5-6 as the main and correction terms together. Most importantly [22], Parr introduced a genius form of expansion in  $\rho$ , which is correct in density scaling. The related ideas of the contracted Schrodinger equation by Nakatsuji [46] and March's density differential equation [47] should also be taken into account. These latter two papers, which are more than thirty years old, have established an idea to reduce the dimensionality of the electronic Schrodinger equation, but up until today, the main task is to work out a tractable algorithm that overcomes the difficulty stemming from its non-linear nature.

The N-representability (meaning that anti-symmetric wave function exists which generates this  $\rho$  via  $\rho(\mathbf{r}_1) = \int \Psi^* \Psi d\mathbf{s}_1 d\mathbf{x}_2 \dots d\mathbf{x}_N$ , most importantly for ground state) is simple [48-49] in one-electron DFT, where in fact there is no N-representability problem, however, one must approximate the exact energy functional (F or D). In this N-representability problem, we cite Garrod and Percus for the pair density (first attempt, [50]), Davidson (explicit demonstraton, [51]), Pistol (lattice model solution, [52]), and Ayers (real-space solution [53]), as well as there is a review by Davidson [54]. According to our particular problem here, the best references for the N-representability of the one-electron distribution function (the normal electron density) are refs.[55-56]. The advantage of the refs.[17, 48-49] is that they demonstrate that even without the (quite simple) constraints on the electron density, one can minimize the energy, provided that the functionals are defined appropriately. Below, a model is introduced wherein the HF-SCF or KS orbitals will be completely eliminated from the DFT formulation and the density can be solved directly from these DFT functionals. It has been a commonly desired task [17] and this work targets that task. More precisely, the only real disadvantage of KS orbitals in DFT is their  $3N$  dimensional nature in spatial space, otherwise, by using KS orbitals one regains a one-electron picture from a many electron DFT problem where electron correlation is included. The form and energies of KS orbitals are the basis of many qualitative rationalizations of DFT results.

Here we perform the first ever variational calculation with a moment functional (to our knowledge) and have several interesting, provocative, and even controversial ideas on how the method might be applied. There has been a lot of work on orbital-free DFT, those methods are effective, but not very accurate, see details on this in refs.[57-60]. Finally, Eqs.4-6 are not restricted to the vicinity of stationary points on the potential energy surface, and do not suffer with the open or closed shell programming complexities that are present in HF-SCF or KS methods.

### 3. Lagrangian for Scaling Correct Power Series Energy Functional to Estimate Ground State Electronic Energy, its solution, analysis and discussion

Now, we are at the main part of our work. Using the ‘‘Lagrange’s method of undetermined multiplier’’ for the 2<sup>nd</sup> HK theorem, we must minimize the functional  $L^* = E_{\text{electr}}[\rho_0] - \lambda(\int \rho_0(\mathbf{r}_1) d\mathbf{r}_1 - N)$  with respect to ground state one-electron density,  $\rho_0$ , where we emphasize the ground state

with subscript zero. The  $\lambda$  is the Lagrange multiplier, providing that the density is normalized to  $N$  electrons as constrain. Using Eqs.1-6 it takes the form

$$L^* = \sum_{j=1,\dots,n} A_j [\int \rho_0^{[1+2/(3j)]} d\mathbf{r}_1]^j + \sum_{j=1,\dots,n} B_j [\int \rho_0^{[1+1/(3j)]} d\mathbf{r}_1]^j + \int v(\mathbf{r}_1) \rho_0(\mathbf{r}_1) d\mathbf{r}_1 - \lambda (\int \rho_0(\mathbf{r}_1) d\mathbf{r}_1 - N) \quad (\text{Eq.10})$$

In HF-SCF there are also constrains for all pairs of molecular orbitals (MO) to get them orthonormal, here we have only one constraint: the  $N$ -normalization. (To be more precise, we also need to force the density to be nonnegative, e.g., by writing it as the square of some other function, see a particular choice in Eq.18 below.) Therefore, we set the first variation in  $L^*$  equal to zero

$$0 = \delta L^* = \int \{ \sum_{j=1,\dots,n} (1+2/(3j)) j A_j [\int \rho_0^{[1+2/(3j)]} d\mathbf{r}_1]^{j-1} \rho_0^{2/(3j)} + \sum_{j=1,\dots,n} (1+1/(3j)) j B_j [\int \rho_0^{[1+1/(3j)]} d\mathbf{r}_1]^{j-1} \rho_0^{1/(3j)} + v(\mathbf{r}_1) - \lambda \} \delta \rho_0(\mathbf{r}_1) d\mathbf{r}_1 \quad (\text{Eq.11})$$

where we have integrals to evaluate inside the integrand. Since  $\delta \rho_0$  is arbitrary, it follows that the quantity in the curly brackets must be zero. It yields

$$\sum_{j=1,\dots,n} \{ (1+2/(3j)) j A_j [\int \rho_0^{[1+2/(3j)]} d\mathbf{r}_1]^{j-1} \rho_0^{2/(3j)} + (1+1/(3j)) j B_j [\int \rho_0^{[1+1/(3j)]} d\mathbf{r}_1]^{j-1} \rho_0^{1/(3j)} \} + v(\mathbf{r}_1) = \lambda \quad (\text{Eq.12})$$

which is a 3 spatial dimension integral equation. Eq.12 is a substitute for the  $4N$  spin-orbit dimension partial differential electronic Schrodinger equation, and the ground state electronic energy is just  $E_{\text{electr},0}(\{\mathbf{R}_A, Z_A\})/N \equiv \lambda$ . The  $\lambda$  is called the chemical potential. (More precisely, the electronic chemical potential is the partial derivative  $\partial E_{\text{electr},0}/\partial N$ , which is more sensible if  $N$  is large.) The larger the  $n$ , the more accurate Eq.12 is, and hopefully it converges fast. (We mention that there are other ways to choose terms to the exact answer in the moment expansion [23].) Recall that in the HF-SCF formalism the single Slater determinant is a very good but not a very precise form of approximation, the drawback of HF-SCF, that is, it needs correction (correlation calculation) to reach chemical accuracy even for energy differences. In Eqs.11-12 the series expansion of  $\Psi_0$  via  $\rho_0$  ala Parr can be taken as arbitrarily accurate with increasing  $n$ .

### 3.1 Semi-analytical solutions for truncated scaling correct power series functionals or Lagrangian

#### 3.1.1 First order truncation

It is useful to consider the truncations for Eq.12. If  $n=1$ , then

$$(5/3)A_1 \rho_0^{2/3} + (4/3)B_1 \rho_0^{1/3} + v(\mathbf{r}_1) \approx \lambda \equiv E_{\text{electr},0} / N \quad (\text{Eq.13})$$

This equation, which is a crude approximation for the solution of Eq.3 or the SE for ground state, has been considered in detail in ref.[15]. Although it does have some flaws (see below), it maintains some positive properties, e.g. it approximates absolute ground state electronic energy values quite well for atoms with  $\{Z_A < 11 \text{ and } 2 < N < Z_A + 2\}$  and molecules built of these atoms. For atoms, it predicts [15] ionization potential better in some cases than e.g. the HF-SCF/6-31G\*. For atoms, and irrespective of the nuclear frame of equilibrium geometry molecules, it provides [15] a very close value to the virial theorem value: 2. It should also be noticed that such comparisons (HF and definitely a too small basis set) are not relevant, because actual calculations in practice try to use larger and larger basis sets. However, many researchers agree that functionals should be equally suitable for smaller basis sets too. Generally, one should use a relatively small basis to start with and put more emphasis on the empirical parameterization. It is an appealing idea to assume that the parameterization performed within a small basis expansion set can absorb some deficiencies of the basis limitations itself (see p.108 in ref.[3]). The latter has also been confirmed as a side result in a new correlation calculation method published in ref. [61]. Actually, at this point in this section we show a basis set free algorithm, but in later truncations for more accurate results below, basis set will be necessary.

The algorithm to solve Eq.3 for this truncation is as follows. With the substitution  $z \equiv \rho_0^{1/3}$ , Eq.13 is a second order algebraic equation, and can be solved for  $z(\mathbf{r}_1, \lambda_{\text{approx}})$ , providing the  $\rho_{0,\text{approx}} \equiv z^3(\mathbf{r}_1, \lambda_{\text{approx}})$ . (We draw attention to the fact that  $v(\mathbf{r}_1)$  does not appear in the kinetic and electron-electron Hamiltonian or DFT operator explicitly: however,  $\rho$  includes it implicitly as  $\rho = \rho(v(\mathbf{r}_1))$ , a known functional relationship, see ref.[2] – it is satisfied via the approximate Eq.13.) For Eq.13, it is important and convincing to mention some early work of March's [47] who derived the  $\rho_0(x_1) = \text{const} \cdot (\lambda - v(x_1))^{1/2}$  for independent fermions in one dimension (which is exact in those very simple conditions as well as  $\lambda$  being the chemical potential). The energy functional in Eq.10 in this case ( $n=1$ ) is

$$E_{\text{electr}}[\rho_0] \approx E_{\text{electr},0,\text{approx}} \equiv \int (A_1 \rho_0^{5/3} + B_1 \rho_0^{4/3} + v(\mathbf{r}_1) \rho_0) d\mathbf{r}_1 \quad (\text{Eq.14})$$

and  $\rho_{0,\text{approx}}(\mathbf{r}_1) \equiv C z^3(\mathbf{r}_1, \lambda_{\text{approx}})$  is supposed to be substituted for  $\rho_0$  in the integrand, where  $C$  fixes  $N = C \int z^3(\mathbf{r}_1, \lambda_{\text{approx}}) d\mathbf{r}_1$  to be satisfied in every step. Integral in Eq.14 depends on  $\lambda$  such as exhibiting one well defined minimum, and the numerical solution for  $\partial E_{\text{electr}}[\rho_0] / \partial \lambda = 0$  yields the approximation for ground state electronic energy (recall the 2<sup>nd</sup> HK theorem). This completes the procedure indicated in the title of this section. All the integral evaluations must be numerical. Its two parameters,  $c_{10}$  and  $c_{20}$  via Eqs.7-8, were fitted [15] to ground state electronic energies of CI atomic ions. The limit and integral behavior of model  $\rho_0$  from Eq.13 is as follows. For a peak at  $\mathbf{R}_A$ , the integral  $\int Z_A^{3/2} R_{A1}^{-3/2} d\mathbf{r}_1 = Z_A^{3/2} \int |\mathbf{r}_1|^{-3/2} d\mathbf{r}_1 = 4\pi Z_A^{3/2} \int u^2 u^{-3/2} du = (8\pi/3)(Z_A r_{\text{max}})^{3/2}$  over a sphere with radius  $r_{\text{max}}$  around  $\mathbf{R}_A$ , i.e. finite, although the integrand value is infinite at  $\mathbf{R}_A$ . Similarly holds for other algebraic powers of model  $\rho_0$  appearing for integration in Eq.14. However, because the “ring off” at around a radial  $r_{\text{max}}$  value via the discriminant in Eq.13 (that is a 2<sup>nd</sup> order algebraic equation for  $\rho_0^{1/3}$ ), the integral in Eq.14 is finite in the algorithm. Computer investigations have shown that this internal  $r_{\text{max}}$  value in the calculation is about 3-4 times the van der Waals' radius of atoms in a molecule. Although the energy integral is finite in Eq.14, one drawback of model  $\rho_0$  in Eq.13 is that  $\lim_{\mathbf{r}_1 \rightarrow \mathbf{R}_A} [\rho_{0,\text{approx}}] = \infty$ , instead of an expected finite value as has just been mentioned. Recall e.g. the analytic atomic 1s solution for H-like atoms.

The flaws of truncation at  $n=1$  can be summarized as follows: 1. The normalization constant,  $C$ , is not 1 (it was introduced after the solution of a second order equation), but about 0.46, however, it has at least a very small dependency on  $(Z_A, N)$  of atoms and nuclear frame  $(\{\mathbf{R}_A, Z_A\}, N = \sum Z_A)$  of (at least neutral or close to neutral) molecules. 2. The  $\rho_{0,\text{approx}}$  depends on certain power of  $v(\mathbf{r}_1)$  yielding infinite values at any nuclei  $\mathbf{R}_A$ , and as it is characteristic in certain DFT approximations, it can not show the shell structure for atoms, it is only a decaying function. 3. The value of  $\lambda_{\text{approx}}$  at minimum ( $\lambda_{\text{approx},\text{min}}$ ) multiplied by  $N$ , and the integral  $(E_{\text{electr},0,\text{approx}})$  at this  $\lambda_{\text{approx},\text{min}}$  has to be the same, i.e. they have to be self-consistent, however, instead [15],  $E_{\text{electr},0,\text{approx}} / (N \lambda_{\text{approx},\text{min}}) \approx 3$ , showing a marginally stronger dependency on the nuclear frame than  $C$  above. 4. The check for virial theorem for atoms and equilibrium molecules gives values between 1.95-2.05, which is a bit off the expected theoretical value 2.00. 5. If atoms with atomic charge  $Z > 10$  are involved in the molecular system, the calculated electronic energy value is absolutely invalid, it means that powers belonging to  $n=1$  are not enough. 6. It can not account for chemical bond, for example calculating energy of atomization yields that known stable molecules are not stable via Eq.14; it is in accord with the known weakness of TF functional if it stands alone for kinetic energy – again, the truncation at  $n=1$  is too early.

We also note, that the energy functional in Eq.14 is a known, well-established expression [2] as first approximation. The  $\rho_{0,\text{approx}}$  from Eq.13 provides an educated guess for trial one-electron density that was new in ref.[15], and new here is that how it relates to the Lagrangian. Another



way to originate Eq.13 is by integrating SE yields  $\int(\Psi^*H\Psi-E\Psi^*\Psi)d\mathbf{x}_1\dots d\mathbf{x}_N = 0$ , and if – trivially – one substitutes a true solution  $\Psi$  (more specifically the ground state  $\Psi_0$ ) into the left hand side, the integral is zero because the integrand itself is a zero function. Actually, it has a more rigorous internal relationship because an integral can be zero too if the integrand is not a zero function. This integral form of SE also leads to the true DFT functional with the device of reducing the variables of integration mentioned in Eq.1. Now, start with the approximate Eq.14 as established in the literature and rearrange it as  $\int(\mathbf{N}A_1\rho_0^{5/3} + \mathbf{N}v(\mathbf{r}_1)\rho_0 + \mathbf{N}B_1\rho_0^{4/3} - \rho_0E_{\text{electr},0,\text{approx}})d\mathbf{r}_1 \approx 0$  with back-substitution (or extension) of  $\mathbf{N}=\int\rho_0d\mathbf{r}_1$ . All terms in the integrand are supposed to follow the individual energy terms (kinetic, etc.). In this way one can suppose, that the integrand in this case is also an approximate zero function, and we have recovered a similar equation to Eq.13 for expressing  $\rho_{0,\text{approx}}$ , if one divides with  $\rho_0$  and  $\mathbf{N}$ . The  $\lambda \equiv E_{\text{electr},0}/\mathbf{N}$  correspondence can be recognized. (Notice that fitting parameters,  $c_{10}$  in  $A_1$  and  $c_{20}$  in  $B_1$ , can absorb 5/3 and 4/3 respectively in Eq.13 as was done in ref.[15].) This derivation is a bit more complex than it looks at first take, some more details can be found in ref.[14]: For example, there can be additive terms in the integrand which individually yield zero integral value, although they are not zero functions, see equation 32 in ref.[14]. Consequently, these terms do not show up in  $F$  but shapes the  $\rho_0$  in an equation like Eq.13 for Eq.14. Generally speaking, it is just another relationship between the exact DFT functional  $F$  and the exact DFT integro-differential operator  $D$  mentioned above. Eq.13 suffers from the crude truncation ( $n=1$ ) after a rigorous and exact derivation yielding Eq.12, but Eqs.13-14 at least show explicitly how the DFT functional and its approximate solution behave as functions.

### 3.1.2 Second order truncation

Truncation of Eq.12 at  $n=2$  yields

$$(5/3)A_1\rho_0^{2/3} + (8/3)A_2[\int\rho_0^{4/3}d\mathbf{r}_1]\rho_0^{1/3} + (4/3)B_1\rho_0^{1/3} + (7/3)B_2[\int\rho_0^{7/6}d\mathbf{r}_1]\rho_0^{1/6} + v(\mathbf{r}_1) \approx \lambda \quad (\text{Eq.15})$$

With substitution  $u \equiv \rho_0^{1/6}$ , one yields the integral-equation for  $u(\mathbf{r}_1)$  as

$$(5/3)A_1u^4 + (8/3)A_2[\int u^8d\mathbf{r}_1]u^2 + (4/3)B_1u^2 + (7/3)B_2[\int u^7d\mathbf{r}_1]u + v(\mathbf{r}_1) \approx \lambda \quad (\text{Eq.16})$$

The procedure should be similar to truncation at  $n=1$ , however, it is much more difficult to solve this equation for  $u \equiv \rho_0^{1/6}$  than Eq.13 for  $z \equiv \rho_0^{1/3}$ . But obviously, Eq.16 is more flexible than Eq.13, i.e. it provides a more realistic  $u^6 \equiv \rho_{0,\text{approx}}(\mathbf{r}_1, \lambda)$  in accord with the fact that the series in Eqs.5-6 converge rapidly [22]. Furthermore, because it is not an algebraic equation like Eq.13, but a relation between functions and their integrals (or functions and their derivatives), the cusp condition for  $\rho_{0,\text{approx}}$  is better satisfied, e.g. it yields finite value at any nuclei,  $\mathbf{R}_A$ . It can be simplified crudely as  $\int u^8d\mathbf{r}_1 \equiv \int \rho_0^{8/6}d\mathbf{r}_1 \approx \int u^7d\mathbf{r}_1 \equiv \int \rho_0^{7/6}d\mathbf{r}_1 \approx (\int \rho_0d\mathbf{r}_1) = \mathbf{N}$  or  $\mathbf{N}^{8/6}$  or  $7/6$ , or more realistically as  $G(x=4/3)$  and  $G(x=7/6)$ , respectively, according to Eq.9. With the later, Eq.16 degrades to

$$(5/3)A_1u^4 + [(8/3)G(x=4/3)A_2 + (4/3)B_1]u^2 + (7/3)G(x=7/6)B_2u + v(\mathbf{r}_1) \approx \lambda, \quad (\text{Eq.17})$$

which is a 4<sup>th</sup> order algebraic equation in  $u$ , a more powerful equation than Eq.13, which was 2<sup>nd</sup> order in  $z$ . It can be solved analytically because the general analytic solution exists up to a 4<sup>th</sup> order algebraic equation: however, like  $z$  from Eq.13,  $u$  via Eq.17 contains certain positive powers of  $v(\mathbf{r}_1)$ , crudely represented as  $\rho_{0,\text{approx}} \sim v(\mathbf{r}_1)^c$ , which suffers again from the unrealistic cusp  $\lim_{\mathbf{r}_1 \rightarrow \mathbf{R}_A} [\rho_{0,\text{approx}}] = \infty$ . On the other hand, the analytic solution of a 4<sup>th</sup> order algebraic equation is via the 3<sup>rd</sup> order algebraic equation, and Eq.17 does not have the problem of negative discriminant (artificial error) for some far away positions from the nuclear frame as Eq.13 has. The better properties of Eq.17 to predict electronic energy will be reported in a later work. Notice the fine

detail that the truncation  $n=1$  of Eq.12 it only yields an algebraic equation (second order, Eq.13) suffering from e.g. the wrong cusp description beside the not adequate accuracy, while truncation  $n=2$  (or higher) of Eq.12 yields integral (or differential) equation (Eq.15) which is more flexible to describe properties, e.g. cusps, it is also more accurate.

### 3.1.3 Larger than second order truncation

Equations 13 and 17 reveal that Eqs.10-12 need numerical integration and the power series in it should go up to at least  $n=4$  in the truncation to accurately describe shell structure, ground state electronic energy ( $E_{\text{electr},0}$ ) and ground state one-electron density ( $\rho_0(\mathbf{r}_1)$ ), as a function of nuclear frame ( $\{\mathbf{R}_A, Z_A\}$ ) and number of electrons ( $N$ ). Numerically solving Eq.15 has similar, at least, not fewer programming complexities than the more accurate Eq.12, so, one should evaluate the latter for more accuracy wherein the  $n$  is a tuning variable for accuracy. Eqs.13 and 17 can show approximately how the true algebraic form of  $\rho_0(\mathbf{r}_1)$  may analytically behave, what is less visible by the numerical solution of Eq.12.  $E_{\text{electr},0}(\{\mathbf{R}_A, Z_A\}, N)$  via Eq.12 is supposed to be accurate not only in the vicinity of stationary points but in the van der Waals regions as well, and for open and closed shell molecular systems since spin pairing effect does not come up in this method in contrast to HF-SCF and post HF-SCF methods. Analytical integration may possibly be used for Gaussian type atomic orbital (GTO) basis set, see chapter 5 below. If numerical integration is chosen, the Slater type atomic orbital (STO) basis set can also be used, a more realistic choice, since it provides faster convergence. The parameters  $c_{10}, a_2, a_3, a_4, \dots$  and  $c_{20}, c_{200}, b_2, b_3, b_4, \dots$  entered in Eqs.7-8 must be fitted to e.g. CI atomic and atomic ion ground state energies, which are supposed to be transferable [15] for molecular systems at any place on the potential energy surface for ground state. Of course, accurately known molecular  $E_{\text{electr},0}$  values can also be used for fitting procedure, e.g. stationary point G2 values, however these are not totally accurate in contrast to atomic  $E_{\text{electr},0}$  values from CI calculations or measurements, of which accuracy is far below the chemical accuracy. Eq.13 ( $n=1$ ) needed fit [15] for  $A_1$  and  $B_1$  or equivalently for  $c_{10}$  and  $c_{20}$ , Eq.15 ( $n=2$ ) needs fit for  $A_1, A_2, B_1$  and  $B_2$  or equivalently for  $c_{10}, a_2, c_{20}$  and  $b_2$  as well as  $c_{200}$  is unity or additional fitting parameter for Eqs.13 and 15. If truncation is at  $n > 2$ , see chapter 3.2 below, the  $c_{10}, a_2, \dots, a_n, c_{20}, c_{200}, b_2, \dots, b_n$  parameters need to be fitted. It will be detailed in a later paper, the theoretical foundation is described in chapters below.

We also mention that, it is pretty well known that e.g. the ionization potential can be well approximated using the moment expansion. However, if one considers a long series of atoms, with very different electron numbers, the density-moment expansion stops working as well [31]. In the literature there are opinions that, first, it is difficult to expand the Coulomb energy in terms of moments. For example, in the study of Tran, there are impressive results but the results are far from the sub-milli-Hartree accuracy that is needed in practical computations of the Coulomb energy [32], and that work only treats the absolute simplest case – atoms. Second, and more importantly, the moment expansion (at least the linear moment expansion [23]) does not necessarily converge. Not every functional can be exactly expressed as a simple power series of the moments, even trying to reproduce a simple functional (like the Weizsäcker kinetic energy, or the Coulomb energy). One must keep these in mind when we suggest alternative functional in Eq.25 below. However, the promising results in ref.[15] on atoms and molecules indicate the opportunities in this direction.

## 3.2 Numerical solution for scaling correct power series functional at larger truncations

### 3.2.1 LCAO approximation of one-electron density to start the minimization

As was just analyzed, Eq.10 must be solved numerically for the minimum (extremum) because Eq.16 and the higher n-truncated cases of Eq.12 cannot be solved analytically. For this purpose, we have to proceed further with Eq.11. The density can be expanded as a linear combination of atomic orbitals (LCAO) where the basis,  $\{b_k(\mathbf{r}_1)\}_{k=1\dots L}$ , is consisted of e.g. L Cartesian,  $x^a y^b z^c \exp(-\alpha r_{A1}^i)$  STO ( $i=1$ ) or GTO ( $i=2$ ) basis functions (or contracted basis functions), a wisely chosen bunch, grouped and centered on each nuclei (as in HF-SCF or KS methods for MO's). A good choice for this form is

$$\rho_0(\mathbf{r}_1) \approx (\sum_{k=1\dots L} d_k b_k(\mathbf{r}_1))^2 \quad (\text{Eq.18})$$

,a function which is positive everywhere, as required by the 2<sup>nd</sup> HK. If L is large enough and the basis set is wisely chosen, the true  $\rho_0$  will be approximated correctly. One must at least consider the concept of “minimal basis” [1]. Recall the form of HF-SCF or KS one-electron density [1] with  $N/2$  ( $>1$ , e.g. closed shell) ortonormal molecular orbitals,  $\rho_0(\mathbf{r}_1) \approx 2\sum_{i=1\dots N/2} [\sum_{k=1\dots L_1} c_{ik} b_k(\mathbf{r}_1)]^2 \geq 0$ , wherein the  $\{c_{ik}\}$  set, also called LCAO coefficients, contains  $L_1(N/2)$  elements, and the square brackets contain the  $i^{\text{th}}$  MO, called  $f_i(\mathbf{r}_1)$ , see also Eq.23 below. Though there are only  $L_1$  square terms in it,  $(2\sum_i c_{ik}^2) b_k^2$ , running via index k and the  $2\sum_i c_{ik}^2$  corresponds to  $d_k^2$ , but more cross terms,  $b_k b_j$ , if  $L=L_1$ , in comparison to Eq.18. (For example, if  $N=4$  and  $L=L_1=2$ , it yields  $\rho_0 \approx d_1^2 b_1^2 + d_2^2 b_2^2 + 2d_1 d_2 b_1 b_2$  by Eq.18, i.e. the weight of cross term (inter-nuclear electron density,  $b_1 b_2$ ) is fixed by square term coefficients  $d_1$  and  $d_2$ . On the other hand, the HF-SCF density (just mentioned or Eq.23 below) provides  $2(c_{11}^2 + c_{21}^2) b_1^2 + 2(c_{12}^2 + c_{22}^2) b_2^2 + 4(c_{11} c_{12} + c_{21} c_{22}) b_1 b_2$ , i.e. there are four coefficients to weight the three terms, i.e. the inter-nuclear electron density can be tuned more independently from the weight of cusps ( $b_1^2$  and  $b_2^2$ ). Notice, that in this simple example Eq.18 requires 2 parameters ( $d_1, d_2$ ) to fit vs. 4 parameters ( $c_{11}, c_{12}, c_{21}, c_{22}$ ) via Eq.23; to improve the flexibility of the former we must allow for the fact  $L > L_1$ . Notice also, that Eq.23 builds the parts of electron density (cusps  $b_1^2$  and  $b_2^2$  and bond  $b_1 b_2$ ) via 4 parameters, although 3 would be enough as in  $C_1 b_1^2 + C_2 b_2^2 + C_3 b_1 b_2$  for the DFT central variable on this basis set  $\{b_1, b_2\}$  level.) In this way one should accept  $L > L_1$ , but first, one should use STO and numerical integration instead of GTO with analytical integration employed by HF-SCF or KS. This allows the basis set to have fewer elements, i.e. with a lower value L. Secondly, using the HF-SCF or KS methods  $N/2$  or  $(N+1)/2$  pieces of MO's must be approximated, while here there is only one quantity, the  $\rho_0$ . Finally, if L is large enough, Eq.18 is a good approximation. There is another way to choose the form than Eq.18:  $\rho_0(\mathbf{r}_1) \approx \sum_{k=1\dots L} \sum_{j=k\dots L} (c_{kj} b_k(\mathbf{r}_1) b_j(\mathbf{r}_1))$  with symmetric  $c_{kj} = c_{jk}$  property, containing  $L(L+1)/2$  terms, i.e. more cross terms. However, one must ensure that it provides everywhere positive one-electron density which is more difficult than in the case of Eq.18. In Eq.18, the right hand side is obviously  $\geq 0$ , only the L needs to be increased for more accuracy. (For example,  $[\sum_{k=1\dots L} \sum_{j=k\dots L} (c_{kj} b_k(\mathbf{r}_1) b_j(\mathbf{r}_1))]^2$  is a way to ensure positive function values or the form in Eq.23 itself, but in respect to programming it has more difficult indexing than Eq.18. Like the approximate Slater form of the wavefunction in HF-SCF, this model serves to approximate one-electron density in DFT, and along with the choice of basis set, both are crucial points for effective calculation.)

### 3.2.2 Numerical recipe for direct minimization

Inserting Eq.18 into Eq.10, and taking the derivative with respect to  $d_k$  and  $\lambda$ , Eq.11 reformulates as

$$0 = \partial L^* / \partial d_i = \sum_{j=1, \dots, n} (1+2/(3j)) j A_j \left[ \int \rho_0^{[1+2/(3j)]} d\mathbf{r}_1 \right]^{j-1} \int \rho_0^{2/(3j)} \rho_{0i} d\mathbf{r}_1 + \sum_{j=1, \dots, n} (1+1/(3j)) j B_j \left[ \int \rho_0^{[1+1/(3j)]} d\mathbf{r}_1 \right]^{j-1} \int \rho_0^{1/(3j)} \rho_{0i} d\mathbf{r}_1 + \int (v(\mathbf{r}_1) - \lambda) \rho_{0i} d\mathbf{r}_1 \quad (\text{Eq.19})$$

$$0 = \partial L^* / \partial \lambda = N - \int \rho_0(\mathbf{r}_1) d\mathbf{r}_1 \quad (\text{Eq.20})$$

for  $i=1 \dots L$ . Using Eq.18, the partial derivatives are simply

$\rho_{0i} \equiv \partial \rho_0(\mathbf{r}_1) / \partial d_i = 2 b_i(\mathbf{r}_1) (\sum_{k=1 \dots L} d_k b_k(\mathbf{r}_1))$ , and  $\rho_{0im} \equiv \partial^2 \rho_0(\mathbf{r}_1) / \partial d_i \partial d_m = 2 b_i(\mathbf{r}_1) b_m(\mathbf{r}_1)$  (Eq.21) i.e. the second and third indices refer to the partial derivatives. As mentioned [22], a truncation at  $n=4$  in Eq.10 is adequate. The system in Eqs.19-21 is non-linear, so e.g. the “steepest descent (gradient)” method can be employed. This method needs the second derivatives or Jacobian  $\partial^2 L^* / (\partial d_i \partial d_m)$  for all  $i, m=1, \dots, L+1$ , where  $d_{L+1} \equiv \lambda$ . The Jacobian matrix is  $((L+1) \times (L+1))$  dimensional, with element at row  $i$  and column  $m$  as  $W_{im} \equiv \partial^2 L^* / (\partial d_i \partial d_m)$  a straightforward  $2^{\text{nd}}$  derivative.

Eqs.10 and 18 yield the powers for the recently defined LCAO parameters in Eq.18,  $d_k$ . In  $L^*$ , the  $d_k$  parameters obtain the integer and non-integer power values between 1 and maximum  $2(1+2/(3n))n = 2(n+2/3) = 9.333$  for  $n=4$ ; roughly and generally  $2n+1$ . It means, that the  $L^*$ , that we have to optimize via Eqs.19-20, is an  $L+1$  dimensional polynomial with parameter vector  $\{d_k\}_{k=1 \dots L+1}$  with roughly the degree of about  $2n+1$  if truncation at  $j=n$  is taken – and hopefully, the truncation  $n=4$  will provide a flexible enough function to calculate ground state electronic energy and one-electron density for molecular systems. The coefficients to  $d_k$  come from integrating certain powers of linear combinations of the basis functions  $b_k(\mathbf{r}_1)$ , see note on the non-integer powers as well as GTO and STO basis sets in this respect below. Also, see Eq.19 for the algebraic position of  $v(\mathbf{r}_1)$ , where the  $\int b_k(\mathbf{r}_1) b_i(\mathbf{r}_1) r_{A1}^{-1} d\mathbf{r}_1$  kind of integral comes up, but the  $\int b_k(\mathbf{r}_1) b_i(\mathbf{r}_2) r_{12}^{-1} d\mathbf{r}_1 d\mathbf{r}_2$  kind (also characteristic in HF-SCF or KS method) does not.

### 3.3 On some expected behaviors of the Lagrangian

Note must be made on the asymptotic (far from the nuclei) behavior of the density: From the general theory [3], as well as it was discussed above, the  $\rho_0(\mathbf{r}_1)$  must 1. be a non-negative function of only the three spatial variables, 2. vanish at infinity ( $\rho_0(\mathbf{r}_1 \rightarrow \infty) = 0$ ), and 3. integrate to the total number of electrons (Eq.2). The first property is ensured with the right hand side of Eq.18, the second is ensured with e.g. a nuclear centered GTO or STO basis set, and the third is ensured with Eq.10 via  $\lambda$ . However, a finer relationship [3] is its asymptotic exponential decay for large distances from all nuclei, that is  $\rho_0(\mathbf{r}_1) \sim \exp[-2 \sqrt{2I} |\mathbf{r}_1|]$ , where  $I$  is the exact first ionization energy of the system. This latter can be easily ensured with e.g. an STO basis set, and the LCAO coefficients are supposed to yield the constant value,  $2 \sqrt{2I}$  as well as the large enough value of  $n$  in Eqs.5-6 is important in this respect.

For the question, how do these series mathematically converge, the answer can come from refs.[15, 22]. Evidences have been shown [15] that the main parts of different energies come from  $j=1$  in Eqs.5-6 or 10, and the convergence is very fast [22] thereafter: a truncation at  $n=4$  or 5 may enough for chemical accuracy.

With respect to the spin states or spin polarization (measured through the spin-polarization parameter as  $\xi \equiv (\rho_{0,\alpha} - \rho_{0,\beta}) / \rho_0$  with  $\rho_0 = \rho_{0,\alpha} + \rho_{0,\beta}$  [3, 62]), Eq.10, solved e.g. via Eqs.19-20, describes the one having the lowest, i.e. the ground state energy, inherent in the Lagrangian method and  $2^{\text{nd}}$  HK theorem. This means that, the choice, what HF, post HF, and KS methods have in this respect, e.g. to enforce singlet vs. triplet spin state calculation, for example  $1s^2 2s^2 2p_x^2$  (excited state) vs.  $1s^2 2s^2 2p_x^1 2p_y^1$  (ground state in agreement with Hund’s rule) carbon atom, is not available here; Eq.10 always provides the ground state only. But on the other hand, basic problem present in HF, post HF, and KS methods with increasing bonds lengths or atom-atom distance inside a molecule toward transforming non-stable molecule or system with van der Waals distances, that is, for example stable  $H_2$  molecule (Spin =  $1/2 - 1/2 = 0$ , approximate wave function =

$(\alpha_1\beta_2 - \alpha_2\beta_1)f(\mathbf{r}_1)f(\mathbf{r}_2))$  vs. well but not infinitively separated two H atoms (e.g. Spin =  $\frac{1}{2} + \frac{1}{2} = 1$ , recall RHF, UHF modes etc.), is not a problem in Eq.10, it is supposed to handle any change in inter-nuclear distances in the system under consideration continuously. At this point we call the attention that although Eqs.3-6 are valid for ground and excited states too, but Eq.10, or its solution via e.g. Eqs.19-20, is on the calculation track for ground state only, (recall that the HK theorems apply to ground states).

Dobson [63-64] have shown, among others, that van der Waals complexes can be accurately accounted by  $\rho_0(\mathbf{r}_1)\rho_0(\mathbf{r}_2)h(\mathbf{r}_1,\mathbf{r}_2)$  kernels, which use only the density and not its derivatives – notice that this kernel description is formally the definition of the Coulomb hole. Approximations leading to Eq.10 also use only  $\rho_0$ , but with using local functionals, capable to account for correlation effects [22].

#### 4. Two serious tests have already been made for the scaling correct power series energy functionals

The calculation and proof test on atoms and molecules in ref.[15] for  $n=1$  in Eqs.5-6 leading to Eq.13, which is  $(5/3)NA_1\rho_0^{5/3} + (4/3)NB_1\rho_0^{4/3} + Nv(\mathbf{r}_1)\rho_0 \approx \rho_0 E_{\text{electr},0}$  via a small reformulation to get comparable expression to the one reported in ref.[15], has yielded that 1:  $(5/3)NA_1 = 1.4433781907 N c_F$ ; notice that  $A_1 \equiv c_{10}c_F$  (Eq.7) so  $(5/3)c_{10} = 1.4433781907$ , (to avoid confusion, the entire product  $(5/3)c_{10}$  here was called  $c_{10}$  in ref. [15], i.e.  $(5/3)c_{10}^{\text{here}} = c_{10}^{\text{ref.}[15]}$ ), 2:  $(4/3)NB_1 = 0.8374131087 N 2^{-1/3}(N-1)^{(2/3)}$ , notice that  $B_1 \equiv c_{20}(2^{-1/3}(N-1)^{(2/3)})$  (Eq.8 with  $c_{200}=1$ ) so  $(4/3)c_{20} = 0.8374131087$ , (to avoid confusion, the entire product  $(4/3)c_{20}$  here was called  $c_{20}$  in ref. [15], i.e.  $(4/3)c_{20}^{\text{here}} = c_{20}^{\text{ref.}[15]}$ ). Calculation on ionisation potentials of atoms is demonstrated on Figure.1. Important, in ref.[15] a direct calculation for  $\rho_0$  and  $E_{\text{electr},0}$  was done with a non-HF-SCF one-electron density, where the latter is the second order algebraic solution for  $\rho_0$  via Eq.13. The weakness of this fit from ref.[15] is that  $n$  was truncated early, namely at  $n=1$ , as detailed in section 3.1 above.

Another calculation and proof test on atoms was made in ref.[22] for  $n=3$  in Eqs.5-6: however, they used HF-SCF one-electron density, and accurate  $E_{\text{electr},0}$  to fit the parameters of Eqs.5-6, i.e. not a direct calculation for  $\rho_0$  and  $E_{\text{electr},0}$ , but a fit after an *ab initio* calculation. Another difference is that instead of Eq.6, they used the form  $J[\rho_0] + \sum_{j=1,\dots,n} C_{xj} [\rho_0^{[1+1/(3j)]} d\mathbf{r}_1]^j$ , where  $J[\rho_0] = C_J [\rho_0^{6/5} d\mathbf{r}_1]^{5/3}$ . In this way the classical Coulomb repulsion energy  $J[\rho_0]$  was modeled with a DFT form (i.e. with a functional of  $\rho_0$ ) and the scaling correct series (Eq.6) was used to estimate the related part of correlation energy. (Recall the Dirac form mentioned above for comparison.) In this way  $T$  and  $J$  were high values, while  $C_{xj}$ 's served for only a correction. The fitted constants they have obtained are  $A_1 = 3.26422$ ,  $A_2 = -0.02631$ ,  $A_3 = 0.00498$ ,  $C_J = 1.0829$ ,  $C_{x1} = -0.85238$ ,  $C_{x2} = 0.004911$ ,  $C_{x3} = -0.000074$ . Although this fit in ref.[22] was suggested for correlation calculation after a HF-SCF routine, and its credence was demonstrated, its artifact in the view of this work is that it was not a direct calculation for  $\rho_0$  for the fit. Furthermore, we draw attention to the fact that the form,  $V_{ee} = C_J [\rho_0^{6/5} d\mathbf{r}_1]^{5/3} + \sum_{j=1,\dots,n} C_{xj} [\rho_0^{[1+1/(3j)]} d\mathbf{r}_1]^j$ , used instead of Eq.6 is another proper power series, and Eq.10 can be changed accordingly (that is: the sum for  $B_j$  has to be replaced by this sum for  $C_J$  and  $C_{xj}$ ).

We should also mention the classical example known for decades [2-3] and indicated above, with respect to this parameter value and fitting: Slater's approximation of HF exchange energy  $\int \varepsilon_x(\rho(\mathbf{r}_1))\rho(\mathbf{r}_1)d\mathbf{r}_1 \approx C_x \int \rho(\mathbf{r}_1)^{4/3} d\mathbf{r}_1$ , where  $C_x = -(9/8)(3/\pi)^{1/3}\alpha$  and is called the  $X\alpha$  method. It depends solely on the local values of the electron density, and  $\alpha$  is an adjustable, semi-empirical

parameter. It has enjoyed a significant amount of popularity among physicists, but has never made much impact on chemistry. This 4/3-power law of electron density was obtained from two completely different approaches [3]: Slater (based on the potential of a uniformly charged sphere from standard electrostatics with radius corresponding to the Fermi hole), Bloch in 1929, and Dirac (as named above and as it is cited among chemists) in 1930 - using the concept of uniform electron gas, a fictitious model system of constant electron density. Typical values obey  $0.666 < \alpha < 1$  and depend on molecular frame ( $N, \{\mathbf{R}_A, Z_A\}$ ) slightly i.e.  $\alpha$  stays in this interval: however, taking only an average value from this interval can destroy the chemical accuracy (1 kcal/mol) even for differences of ground state electronic energy in the outcome of the calculation for different systems. Exact mathematical form for this small functional dependence or fluctuation is unknown, but a well-established fact is that a major part of it is described by this 4/3-power formula. The rest can be described by higher power terms via Eq.6. Similarly, as mentioned above, in their model Thomas and Fermi [2-3] have arrived at the  $T_{TF} = c_F \int \rho^{5/3} d\mathbf{r}_1$ , very simple expression for the kinetic energy based on the uniform electron gas also.

As it has been demonstrated in refs.[15 and 22] fit to existing ground state (e.g. CI) atomic, atomic ions and (e.g. G2 or G3) molecular energies are feasible for parameters in Eqs.5-6. The best next step is a parameter fit for Eqs.5-6 with direct calculation for  $\rho_0$  and  $E_{\text{electr},0}$  and  $n>3$  as described above in section 3 and based on Eq.10 – it is our plan and will be reported in a later work.

We must mention some other parametrizations and tests: Burke and coworkers have recently developed semi-classical approaches, for example for the kinetic energy of one-dimensional model finite systems the leading corrections to local approximations as a functional of the potential have been derived [65]. Furthermore, condition on the Kohn–Sham kinetic energy and modern parametrization of the Thomas–Fermi density was elaborated by them [66], being the recovery of the correct expansion yields a condition on the Kohn–Sham kinetic energy that is important for the accuracy of approximate kinetic energy functionals for atoms, molecules, and solids – see also the discussion in section 5 in this relation.

## 5. Relation to HF-SCF and Kohn-Sham formalism, and replacing all the time consuming gaussian based two and four center integrals

### 5.1 Comparing the energy functionals

Classically, to solve the SE for ground state electronic energy,  $E_{\text{electr},0}$ , and normalized, anti-symmetric  $\Psi_0$  with the help of the variation principle, one must minimize the energy functional  $E[\Psi_{0,\text{trial}}] = \langle \Psi_{0,\text{trial}} | H | \Psi_{0,\text{trial}} \rangle$ , where  $H$  is the electronic Hamiltonian (used also at the beginning for Eq.1) with the known bra-ket notation [1-2]. The HF approximation [1-2] uses a single Slater determinant for  $\Psi_{0,\text{trial}}$ , denoted by  $S_{\text{trial}}$ , obtaining

$$E_{\text{HF}}[S_{\text{trial}}] = \sum_{i=1,\dots,N} \int \psi_i^*(\mathbf{x}_1) [(-1/2)\nabla_1^2 + v(\mathbf{r}_1)] \psi_i(\mathbf{x}_1) d\mathbf{x}_1 + (1/2) \sum_{i,j=1,\dots,N} (J_{ij} - K_{ij}) \quad (\text{Eq.22})$$

where the Coulomb integral is  $J_{ij} = \iint \psi_i(\mathbf{x}_1) \psi_i^*(\mathbf{x}_1) [r_{12}^{-1}] \psi_j(\mathbf{x}_2) \psi_j^*(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2$ , and the exchange integral is  $K_{ij} = \iint \psi_i^*(\mathbf{x}_1) \psi_j(\mathbf{x}_1) [r_{12}^{-1}] \psi_i(\mathbf{x}_2) \psi_j^*(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2$ . In Eq.22, the  $\psi_i$  are the orto-normalized MO's approximated with LCAO using a GTO basis to be able to solve the integrals analytically, they also have pair-wise the same spatial part to build up  $S_{\text{trial}}$ . The latter means that there is a common spatial function,  $f$ , such as  $\psi_1(\mathbf{x}_1) = \alpha_1 f(\mathbf{x}_1)$  and  $\psi_2(\mathbf{x}_2) = \beta_2 f(\mathbf{x}_2)$  for  $i=1,2$ ,  $g$  for  $i=3,4$ , and so on, where  $f, g, \dots$  are orto-normalized also. A systematic notation for them is  $\{f_1, f_2, \dots, f_{(N/2)}\}$  or  $\{f_{(N+1)/2}\}$  for even and odd  $N$  respectively. In this way the ground state one-electron density (via  $\rho_0 \equiv \int \Psi_0^* \Psi_0 ds_1 d\mathbf{x}_2 \dots d\mathbf{x}_N \approx \int S_{\text{opt}}^* S_{\text{opt}} ds_1 d\mathbf{x}_2 \dots d\mathbf{x}_N$ ) is

$$\rho_{0,\text{Slater},\text{trial}} = 2 \sum_{i=1,\dots,N/2} f_i^2 \quad \text{or} \quad 2 \sum_{i=1,\dots,(N-1)/2} f_i^2 + f_{(N+1)/2}^2. \quad (\text{Eq.23})$$

Above we have used the notation  $\rho_{0,\text{HF-SCF}}$  for this, meaning the optimized one - electron density, but now we want to emphasize the Slater determinant formalism included during the optimization. The main cases [1] abbreviated as RHF, ROHF and UHF, etc. will not be detailed further now. Eq.22 is decomposed to the so called HF or Fock differential equations and with standard computer routines the minimization problem can be treated to find the LCAO parameters for all HF molecular orbitals  $f_i$ . Because a single Slater determinant is only an approximation for the  $\Psi_0$ ,  $E_{\text{electr},0} < E_{\text{HF}}[S_{\text{opt}}]$  (see, variation principle), and the difference comes from the basis set error and correlation energy mentioned above. The latter, called  $E_{\text{corr}}$ , is calculated after [1-2] the HF-SCF routine.

The KS theory [2-3], based on DFT, corrects this error during (i.e. not after) the algorithm using the single determinant form via the functional

$$E_{\text{KS}}[\rho_{0,\text{Slater},\text{trial}}] = -\sum_{i=1,\dots,N/2} \int f_i^*(\mathbf{r}_1) \nabla_1^2 f_i(\mathbf{r}_1) d\mathbf{r}_1 + \int v(\mathbf{r}_1) \rho_{0,\text{Slater},\text{trial}}(\mathbf{r}_1) d\mathbf{r}_1 + (1/2) \int \rho_{0,\text{Slater},\text{trial}}(\mathbf{r}_1) \rho_{0,\text{Slater},\text{trial}}(\mathbf{r}_2) r_{12}^{-1} d\mathbf{r}_1 d\mathbf{r}_2 + E_{\text{xc}}(\rho_{0,\text{Slater},\text{trial}}) \quad (\text{Eq.24})$$

for the even N in the sum and the corresponding one for the odd N. Comparing Eq.22 and 24, the terms with nablas are basically the same (before and after integration over spins), actually it is a main idea in KS formalism. The latter means that the functional in Eq.24 does not only contain one-electron density, as it should in DFT (e.g. in Eq.10), but it also contains one-electron orbitals - overcoming the difficulties of not knowing the peculiar form of kinetic energy functional. The terms with the external (mostly nuclear frame) potential,  $v$ , in Eq.24 is also basically the same as the single determinant based approximation in Eq.22. However, the terms with  $r_{12}^{-1}$  have basically different forms in Eq.22 vs. 24 even though they yield similar values in comparison to the magnitude of  $E_{\text{electr},0}$ . The term  $E_{\text{xc}}$  (exchange-correlation) [1-3] in Eq.24 is an extra device in comparison to Eq.22, and according to DFT it can correct the error that Eq.22 makes. Actually, the main idea in KS formalism comes into effect during the SCF routine, and for this reason the HF orbitals from Eq.22 and KS orbitals from Eq.24 are not the same: however, they are close to each other. Similarly, the final correlation energy and basis set error, the  $E_{\text{corr}}$  and  $E_{\text{xc}}$  values are also close to each other at least on the same basis set level, and about 1-2 % of  $E_{\text{electr},0}$ . Eq.24 is decomposed to the so called KS differential equations, and with standard computer routines the minimization problem can be solved to find the LCAO parameters for all KS molecular orbitals  $f_i$ . Here we do not address the problem of the single Slater determinant RHF vs. UHF behavior in the vicinity of stationary points vs. dissociating or van der Waals region etc. that Eq.22 has, but Eq.24 can treat better.

A great technical advantage of KS formalism was that all the previously existing HF-SCF routines in the history of computation chemistry could be modified easily to handle any or both of Eq.22 or Eq.24. Knowing a very good form approximating the exact  $E_{\text{xc}}$  in Eq.24, the  $E_{\text{electr},0} \approx E_{\text{KS}}[\text{optimized } \rho_{0,\text{Slater}}]$  would hold very accurately. Without details, the acceptable approximate forms of  $E_{\text{xc}}$  in Eq.24 embody the following properties focusing on the subject of this work: 1, it provides algebraic variation properties, but not necessarily variation with respect to  $E_{\text{electr},0}$ , 2, it is designed (e.g. in its parameter fit for approximate  $E_{\text{xc}}$ ) to Slater determinant or Eq.23, although  $\rho_{0,\text{trial}}$  can possess other algebraic forms, see e.g. the solution of Eq.13 [15] and Eq.17 or Eq.18, 3, there are some simple but important mathematical properties [3] that  $E_{\text{xc}}$  or parts of it should provide, for example, the two-electron density is factorized as  $d_2(\mathbf{x}_1, \mathbf{x}_2) = \rho(\mathbf{x}_1)\rho(\mathbf{x}_2)(1+f(\mathbf{x}_1, \mathbf{x}_2))$ , where  $f$  is called the correlation factor, and of course it strongly relates to the correlation energy, and theoretically  $\int \rho(\mathbf{x}_2)f(\mathbf{x}_1, \mathbf{x}_2)d\mathbf{x}_2 = -1$ , a property that an approximation must have - at least approximately, etc.. For property 1, recall DFT concerning the variation of the true functional  $E_{\text{electr},0} \leq E[\rho_{0,\text{trial}}] = T[\rho_{0,\text{trial}}] + V_{\text{ee}}[\rho_{0,\text{trial}}] + V_{\text{ne}}[\rho_{0,\text{trial}}]$  with true  $T$ ,  $V_{\text{ne}}$  and  $V_{\text{ee}}$  functionals and the

minimum at the true N-normalized  $\rho_0$ , as opposed to the fact that  $E_{xc}$  in Eq.24 is only an approximate functional in practice. For property 2, recall that a theoretically correct  $E_{xc}$  for true  $\rho_0$  re-corrects the error made by the previous terms in Eq.24, but  $\rho_0$  is approximated with a Slater form, so its correction has to be provided also. Furthermore, the basis set error is always present in practice. As we have emphasized,  $E_{xc}$  in Eq.24 is not exactly known, only approximate forms are available and tested. We do not summarize the vast literature about it, but we do mention that no overall approximate form is yet known which provides the chemically accurate calculations: geometry optimums, energy differences, vibronic frequencies, dipol moments, van der Waals forces, etc. for any system. Instead, each existing and accepted functional is good for certain groups of chemical systems and problems only, but fails for some others. For this reason, different functionals are used in different systems or problems, that is not adequate scientifically. We have also mentioned above that the suggested and accepted approximate forms for  $E_{xc}$  in the literature include derivatives (gradients) of the one-electron densities (or spin densities), in contrast, here we deal with scaling correct power series including the main ( $j=1$ ) and correction terms ( $j>1$ ) in Eqs.5-6.

Based on the previous parts of this work, an alternative functional to the ones in Eqs.22 and 24 used in HF-SCF and KS routines, respectively, is

$$E_{SCMF-1}[\rho_{0,Slater,trial}] = -\sum_{i=1,\dots,N/2} [f_i^*(\mathbf{r}_1) \nabla_1^2 f_i(\mathbf{r}_1) \mathbf{d}\mathbf{r}_1 + \int v(\mathbf{r}_1) \rho_{0,Slater,trial}(\mathbf{r}_1) \mathbf{d}\mathbf{r}_1 + \sum_{j=1,\dots,n} \{ C_j [\int \rho_{0,Slater,trial}^{[1+2/(3j)]} \mathbf{d}\mathbf{r}_1]^j + B_j [\int \rho_{0,Slater,trial}^{[1+1/(3j)]} \mathbf{d}\mathbf{r}_1]^j \}] \quad (\text{Eq.25})$$

for the even N in the sum and the corresponding for odd N, as well as SCMF stands for “scaling correct moment functional”. In Eq.25 the terms with  $C_j$  originate from Eq.5 knowing that (unlike Eq.5) it does not approximate the entire kinetic energy, T, but only the correction to the first sum with nabla (now it is used as in the original idea from Parr et al. [22]). For this reason, the values of  $C_j$  are different from  $A_j$  in Eq.5, but presumably  $C_1, C_2, C_3, \dots$  are similar to  $A_2, A_3, A_4, \dots$  respectively, in magnitude. (Compare it algebraically to the aforementioned Dirac exchange term - an algebraic form that can be a correction term as well as a main term, depending how one uses it.) The terms with  $B_j$  in Eq.25 account for the entire electron-electron repulsion energy from Eq.6, and being a scaling correct power series, it is supposed to account accurately if n is large enough and the accurate  $\rho_0$  is used, and no correction like  $E_{xc}$  (exchange correlation, Fermi and Coulomb hole, etc.) is needed. The only adjustment needed in the values of C and B coefficients with respect to Eqs.5-6 is that in Eq.25 the Slater type one-electron density in Eq.23 is used, not the real one as in Eqs.5-6 – although with a larger basis set, the difference may be negligible. According to practice [22], n should go up to 4 or 5 to reach chemical accuracy.

In the Fock equations associated to HF-SCF or KS method the two-electron operators ( $r_{ij}^{-1}$ ) are reduced to one-electron operators via some standard non-local integration technique. In this way, algebraically a Slater determinant is a 100% accurate form on the way to finding the antisymmetric solution for the system of Fock equations [3]. With  $E_{xc}$  in Eq.24 the Fock equations own the “perturbation” toward a solution to hit the value of the ground state electronic energy of its stem equation - the electronic Schrodinger equation, more accurately. In Eq.25 there are only one-electron terms and operators, so for the associated Fock equations, a Slaterian form for the solution is also adequate in the beginning too. The role of  $E_{xc}$  in Eq.24 corresponds to the role of terms with coefficients B for  $j>1$  or 2 in Eq.25, and terms with coefficients C provide even more improvement (namely in the form of kinetic operators used). An accepted drawback of  $E_{xc}$  in Eq.24 in the literature, is that it cannot be improved systematically, while the scaling correct power series in Eq.25 provides systematic improvement by the increasing n. Moreover, in the next



chapter we analyze that the integration needed in Eq.25 puts us on the road to improve upon Eq.22-24; the key point is that there is no term with  $r_{ij}^{-1}$ .

In the literature there are opinions that it is difficult to expand the Coulomb energy in terms of moments, although the above mentioned  $C_j[\int \rho_0^{6/5} d\mathbf{r}_1]^{5/3}$  main term does the job good [22] with three correctional terms, and even the  $B_1 \int \rho_0^{4/3} d\mathbf{r}_1$  main term in Eq.6 performs remarkable [15] without correctional terms. We mention that some researchers strictly say that, expanding the Coulomb term in moments is ridiculous. It may work for atoms, or for molecules near equilibrium. But it can never work for a system like the stretched HF dimer because the  $1/r$  electrostatic repulsion between electrons on the fragments is missed. Of course, this is a practical point (not a mathematical point): it just suggests that (mathematically) the moment expansion converges very (perhaps infinitely) slowly. By this reason, instead of Eqs.6 or 10, the alternative form (compare what KS uses,  $V_{ee} \approx (1/2) \int \rho_0(\mathbf{r}_1) \rho_0(\mathbf{r}_2) r_{12}^{-1} d\mathbf{r}_1 d\mathbf{r}_2 + \int \epsilon_{xc} \rho_0 d\mathbf{r}_1$ , the origin of the huge literature on exchange-correlation energy) is

$$V_{ee}[\rho(\mathbf{r}_1)] = (1/2) \int \rho_0(\mathbf{r}_1) \rho_0(\mathbf{r}_2) r_{12}^{-1} d\mathbf{r}_1 d\mathbf{r}_2 + \sum_{j=1, \dots, n} B_j [\int \rho_0^{[1+1/(3j)]} d\mathbf{r}_1]^j \quad (\text{Eq.26})$$

In this way, the classical Coulomb term is the major one, and the entire set of coefficients  $B$  falls into correction terms - compare to Eq.6 where  $B_1$  was connected to the major term and  $B_2, B_3, \dots$  were the correctional ones. It can be used to develop Eq.25, more, another alternate energy functional to Eqs.22, 24 and 25, and to the parts in Eq.10 without  $\lambda$  is

$$E_{\text{SCMF-2}}[\rho_0] = \sum_{j=1, \dots, n} A_j [\int \rho_0^{[1+2/(3j)]} d\mathbf{r}_1]^j + \int v(\mathbf{r}_1) \rho_0(\mathbf{r}_1) d\mathbf{r}_1 + (1/2) \int \rho_0(\mathbf{r}_1) \rho_0(\mathbf{r}_2) r_{12}^{-1} d\mathbf{r}_1 d\mathbf{r}_2 + \sum_{j=1, \dots, n} B_j [\int \rho_0^{[1+1/(3j)]} d\mathbf{r}_1]^j \quad (\text{Eq.27})$$

with e.g. the use of Eq.18. The expressions in Eqs.10 and 19 can be changed accordingly. The additional term entering to Eq.19, by the replacement of Eq.6 with Eq.26, is  $\int \rho_0(\mathbf{r}_2) (\partial \rho_0(\mathbf{r}_1) / \partial d_i) r_{12}^{-1} d\mathbf{r}_2 d\mathbf{r}_1$ . Notice that Eq.27 contains only  $\rho_0$  at this point and Slaterian form is not a restriction. The only major restriction coming up by this classical Coulombic term is that GTO basis must be used for all terms (no way to use STO) in the corresponding expression to Eq.19, as well as numerical integration cannot be used for this term (containing  $r_{12}^{-1}$ ) but analytical one; but of course the other terms can be evaluated only numerically. However, the known, relatively good long-range behavior of this major non-local functional in Eq.26 (firs term) is well established in a light contrast to the local functional in Eq.6. There is no nabla terms in Eq.27, so this form algebraically is rather belong to the ones in section 3.2 with respect to solution algorithm and DFT, like Eq.10, and unlike Eqs.22, 24-25.

## 5.2 In relation to numerical integration and programming

It is quite obvious that existing HF-SCF routines solving Eq.22 can easily be modified to solve Eq.25, as it was possible for the KS formalism in Eq.24. The advantage of Eq.25 is that expensive analytical integration for terms containing  $r_{12}^{-1}$  are not necessary as opposed to Eqs.22 and 24, the most time consuming procedure, despite the fact that subroutines for these analytical integrals, i.e.  $r_{12}^{-1}$  in the integrand multiplied with GTO's, are highly developed today in practice. On the other hand, the necessary tools of numerical integration for the nonlinear  $E_{xc}$  (Eq.24) are already built in existing codes using KS formalism. The terms with  $C$  and  $B$  coefficients in Eq.25 can also be calculated numerically and accurately without larger additional programming input. Numerical integration is the first choice for the terms with  $B_j$  and  $C_j$  in Eq.25, because of its not-integer powers. Furthermore, since the numerical integration used in these tasks is very accurate, the first two terms in Eq.25 - kinetic and nuclear-electron attraction, can also be shifted to the numerical integration subroutine, making the program structure simpler. Recall, that in the case of GTO basis set these two terms are traditionally evaluated analytically. In this way, even the faster, more

powerful STO basis set can be used. (Notice that for integrals with  $r_{ij}^{-1}$  in the integrand, the 6 dimensional  $\int \dots d\mathbf{r}_1 d\mathbf{r}_2$  must be evaluated after all algebraic reductions, not so, for the simpler 3 dimensional  $\int \dots d\mathbf{r}_1$ , e.g. for the kinetic and nuclear-electron terms. For analytic integration one had to switch from STO to GTO basis set in the HF-SCF method, but with the KS method, the additional non-linear  $E_{xc}$  term has entered the arena, and it cannot be integrated analytically, even though it only needs the  $\int \dots d\mathbf{r}_1$  and the use of the GTO basis set cannot counterbalance the non-linearity. As a consequence, numerical integration is necessary for this part: however, with computational chemistry problems, fast numerical integration is not available for  $\int \dots d\mathbf{r}_1 d\mathbf{r}_2$ , not so, in the case of  $\int \dots d\mathbf{r}_1$ , but Eq.25 is free of  $r_{ij}^{-1}$ .) It must be emphasized that “numerical integration for all integrals” has an important effect on computation time, i.e. the computation time in this case is proportional to the number of nuclei (M) in contrast to  $N^c$  characteristic in HF-SCF or KS routines ( $c = 2$  to  $4$ ), where N is the number of electrons. Recall that  $M \ll N$  in practically important systems, also recall the study in ref.[15]. The use of STO or GTO basis with numerical integration for all terms in Eq.25 and the fit for C and B parameters will be reported in later work.

We must mention that many powerful multicenter integration schemes, based on density fitting (close to proposal above), have been developed since, see e.g. review chapters 7.3–7.6 in ref.[3] and references therein, as well as Ahlrichs et al. [67-68] and Parrinello et al. [69].

### 5.3 In relation to analytical integration

If one wants to stay with analytical integration, avoiding the numerical, our note on it is as follows for terms with C and B coefficients in Eq.25, or A and B coefficients in Eqs.10 or 27: The fractional (i.e. not integer) power,  $\rho_{\square 0, \text{Slater, trial}}^c$  in Eq.25 with Eq.23 or  $\rho_0^c$  in Eqs.10 or 27 with Eq.18 takes the values  $c = 5/3, 8/6, \dots$  and  $4/3, 7/6, \dots$  up to a truncation, where the  $c$ 's are between 1 ( $j$  or  $n \rightarrow \infty$ ) and  $5/3 = 1.6667$  ( $j=1$ ). The  $\rho_0^c$  can be expanded with the help of e.g. a truncated Taylor series containing integer powers instead of  $c$ 's: in this way, the use of GTO basis, allows analytical integration. It is important to note that the Taylor series must be expanded with a region of values of  $\rho_0$ , and not with a particular value of it. Here we briefly mention the way to analytical integration. Using the least square device  $\int [\rho_0^c - (\sum_{i=1 \dots k} a_i \rho_0^i)]^2 d\rho_0 = \text{minimum}$ , where the integration is from 0 to R, the  $a_i$  coefficients can be obtained, as well as  $k=4-6$  is enough according to our preliminary tests. The one-electron density is always positive, so the interval for integration starts from zero (far away from the molecule or at the nodes, if any, inside the molecular frame), while the maximum value (R) is what a one-electron density can pick up. The latter is at the nuclei with maximum  $Z_A$  in the nuclear frame. (In the view of “atoms in molecule” and “core electrons” concepts, recall that in H-like atoms the radial part of 1s wavefunction is  $R_{10} = 2Z_A^{3/2} \exp(-Z_A r_1)$ , so the maximal value (R) is  $\max(\rho_0) \sim R_{10}^2 \sim Z_A^3$  – i.e. magnitudes larger than the values at bonds or inter-atomic regions.) The arising difficulty is, that generally  $\rho_0$  has high sharp spherical-like peaks at the nuclei and much smoother curves and lower values on a graph, for example in the case of an equilibrium molecular system. As a consequence, weighted least square is more suitable. The above form is an adequate choice, since the value of  $c$  is not far from the integer powers (i) present, as well as that, it has a similar monotony to the integer powers in the expression. In this way  $\rho_{\square 0, \text{Slater, trial}}^c$  is replaced with  $\sum_{i=1 \dots k} a_i \rho_{\square 0, \text{Slater, trial}}^i$  in Eq.25 and similarly in Eqs.10 and 27, and with integer powers analytical integration is possible, since the product of GTO type functions (via the sum in  $\rho_{\square 0, \text{Slater, trial}}$ ) is also GTO type: however, an arising problem may cancel this opportunity, e.g. in the case of, let us say, 100 or 1000 or more GTO basis functions in a basis set, the 4-6<sup>th</sup> power of their sum (see Eqs.18 or 23) generate an enormous number of terms to sum up. In contrast, the numerical integration needs to sum up these 100 or

1000 terms only and taking the  $c^{\text{th}}$  power of that value thereafter. Finally, we must state that numerical integration is the only choice when Eqs.5-6 are involved in the functional, however, the faster STO basis set can be used.

We must mention one other way for integration: Numerical integration on a finite grid (see e.g. refs.[14-15] or chapter 7.4 in ref.[3]) may have a disadvantages, mostly due to the ‘numerical noise’ inherent in this approach. To get rid of these problems it is possible to have grid-free implementations to compute terms like the ones in Eqs.5-6 or  $E_{xc}$  in Eq.24. A well-known fact from linear algebra is that a function of a matrix which is expressed in an orthonormal basis can be evaluated by first diagonalizing the matrix, then applying the function on the diagonal elements and finally transforming the matrix back to its original basis. An illustration of this simple procedure for the functional  $\rho_0^{4/3}$  can be found in chapter 7.5 in ref.[3], see also the related references therein.

## 6. Summary

The contribution of addressing moment functionals in a true variational method is very interesting, important and useful, and it should have been done long ago - at least the author thinks that beside the many related research referenced, this has not been done yet in a complete discussion, and this work has targeted to do that. After summarising the scaling correct power series or moment functionals for the different energy terms in the electronic Schrodinger equation, the Lagrangian method was applied first in the literature (to the author’s knowledge) for variational solution of the ground state with restricting the N-normalization of the one-electron density. Possible semi-analytical solutions were discussed for some early truncations, as well as feasible numerical recipe was described for any high level later truncation. Reporting some promising preliminary calculations and results, the method was compared with the Hartree-Fock-SCF and Kohn-Sham methods on theoretical ground along with the discussion of opportunities for analytical vs. numerical integration – the inclusion or substitution of the crucial classical Coulombic term was also discussed.

## Appendix

In Eq.9 the first, weaker approximation is  $[\int \rho^{[1+a/(3j)]} d\mathbf{r}_1]^j \approx [\int \rho d\mathbf{r}_1]^j = N^j$ , which is fine for a large  $j$ , but for the smallest index  $j=1$ , the largest power  $\int \rho^{5/3} d\mathbf{r}_1 \approx N$  is not accurate enough. The idea is reasonable for large  $j$ , because  $1 \leq 1+a/(3j) \leq 5/3 = 1.6667$  and  $\lim_{j \rightarrow \infty} (1+a/(3j)) = 1$  for both  $a=1$  and  $2$  with rigorous monotonicity. However, the number of electrons in a system is generally high, recall e.g. that  $N=10$  for  $\text{CH}_4$ , so an additional fact to this very weak approximation is that although the power in the integrand decrease with  $j$ , but the integral is on power  $j$  – counterbalancing the decreasing  $a/(3j)$ . Being  $\rho \geq 0$ , a better approximation is  $\int \rho^{[1+a/(3j)]} d\mathbf{r}_1 \approx [\int \rho d\mathbf{r}_1]^{[1+a/(3j)]} = N^x$ . An even more accurate approximation is as follow. The  $\exp(-2Zr_1)$  is an atomic 1s orbital, and let us approximate the decay of  $\rho$  with it (at 2-3 van der Waals distances from the molecule), as well as we can use  $Z = \sum Z_A = N$  for a molecule owing peaks at nuclei. Take the known integral equality  $\int (Z^3/\pi)^x \exp(-2Zx r_1) d\mathbf{r}_1 = (Z^3/\pi)^{x-1}/x^3$  with the extension  $\int N^x (Z^3/\pi)^x \exp(-2Zx r_1) d\mathbf{r}_1 = N^x (Z^3/\pi)^{x-1}/x^3 = N^x (N^3/\pi)^{x-1}/x^3$  for  $x=1+a/(3j)$ . For example, for  $N=20$  and considering a 1s density for 20 electrons  $\rho(\mathbf{r}_1) = N(Z^3/\pi) \exp(-2Zr_1) = N(N^3/\pi) \exp(-2Nr_1) = (1.6/\pi) 10^5 \exp(-40r)$  the  $\int \rho d\mathbf{r}_1 = N = 20$  and  $\int \rho^{4/3} d\mathbf{r}_1 \approx 313$  in contrast to  $N=20$  or  $N^{4/3} = 20^{4/3} = 54.29$ . An  $N^x (N^3/\pi)^{x-1}/x^3$  with  $x=1+a/(3j)$  is more accurate than  $N$  or  $N^x$  for  $\int \rho^{[1+a/(3j)]} d\mathbf{r}_1$ .

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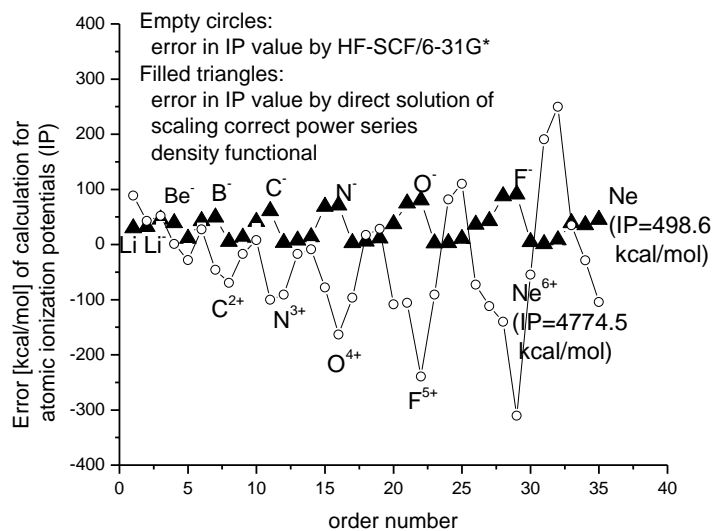


Figure 1.: Error of calculation for atomic ionization potentials (IP for  $A \rightarrow A^+$ ) by HF-SCF/6-31G\*, and Eq.10 ( $n=1$ , basis set free calculation) with optimized parameters from ref.[15], ordered with increasing atomic number,  $Z$ , and number of electrons,  $N$ ; (the huge IP values for  $Ne^{6+}$  and Ne are marked for comparison).

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