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HAL Id: hal-00632718

https://hal.science/hal-00632718

Submitted on 15 Oct 2011

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Ab initio DFT – the seamless connection between WFT and DFT

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Orbital-dependent exchange-correlation functionals and potentials play an increasingly important role in Density Functional Theory (DFT). Methods which use explicit orbital-dependent functionals can be viewed as a natural extension to the standard Kohn-Sham (KS) procedure in DFT, that traditionally have used functionals with explicit density-dependence but only implicit orbital-dependence. *Ab initio* DFT, invented at the Quantum Theory Project, is the method which could define rigorous orbital-dependent exchange-correlation functionals and potentials in the context of KS DFT theory. The local and multiplicative exchange-correlation potentials are derived from a general theoretical framework based on the density condition in KS theory and from coupled-cluster theory and many-body perturbation theory. *Ab initio* DFT guarantees to converge to the right answer in the correlation and basis set limit, just as does *ab initio* Wave Function Theory (WFT) and solves in a rigorous way most of the short-comings of standard density-dependent KS DFT. It is also the route toward understanding the relationships between traditional *ab initio* WFT and DFT.

The Optimized Effective Potential "journey" on the borderline of WFT and DFT was inspired and possible only because of the Quantum Theory Project where we stay as a postdocs in the 1999-2001. It seems to us then we were in the right place and the right time, and certainly with the right people. The QTP scientific melting pot and Sanibel's meetings gave us an excellent possibility to work together, learn and hopefully solve many important scientific problems.

Keywords: optimized effective potential method, electron correlation, density functional theory, *ab initio* DFT

1.   Introduction

The most powerful and popular contemporary many-electron theory methods used for calculating the electronic structure of atoms, molecules, and solids, originate from two main categories of quantum mechanical theories: the traditional *ab initio* theories directly grounded on the concept of the wave function (Wave Function Theories – WFT) and the density functional theory (DFT) essentially based on the concept that the electron density is fundamental. WFT provides methods in which we are able to control and predict the accuracy of the results. There is a the

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well known hierarchy of converging, size extensive methods MBPT(2) < CCD <

CCSD < CCSD(T) < CCSDT < ... < FCC. = FCI establishes the standards in

ab initio WFT methods. MBPT(2) means second order many-body perturbation

theory, CC - coupled cluster methods with S- single, D-double, T-triple excitations.

Taking into account n-fold excitations for n electrons defines the Full CC method

which is equal to the FCI (CI -configuration interaction) method and is the best

possible solution for the given basis set used in the calculations. Unfortunately as

the inclusion of electron correlation effects is systematically improved the WFT

methods become extremely expensive for larger systems, so, we still are limited

to the systems with only few dozen of atoms. The computationally much cheaper

DFT methods are the most widely used electronic structure methods and are rou-

tinely used for calculating ground state and dynamical properties of many-electron

systems. Currently DFT seems to be the only practical method which can perform

calculations on systems of hundreds and thousands of electrons. The huge reduc-

tion of the computational cost is due to the single-particle effective Hamiltonian in

the Kohn-Sham [1, 2](KS) implementation of DFT, compared to the two-particle

Hamiltonian in most WFT methods. In this method all unknown information is

contained in the exchange-correlation (xc) functional E_{xc}, which must be approx-

imated in any practical implementation. Unfortunately DFT establishes the exis-

tence of E_{xc} but does not provide the energy functional or even a prescription how

to approximate it. Existing standard density-dependent approximations to the xc

functionals, e.g. local-density LDA [2], generalized gradient approximations GGA

[3–5], or hybrid functionals [6], despite their great popularity and success, suffer

for many fundamental problems like lack of strict cancellation of self-interaction

energies between Coulomb and exchange energies, incorrect asymptotic behaviour

of the KS xc-potentials [7], missing the derivative discontinuity of the energy, quali-

tatively incorrect correlation potentials [8], and lack of the possibility of systematic

improvement of existing functionals. KS-DFT cannot describe van der Waals inter-

actions, there are problems with computation of response properties of molecular

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systems (polarization, excitation, etc.) , also activation barrier heights for a variety of chemical reactions are predicted incorrectly [9].

On one side we have excellent but unfortunately very expensive methods (WFT) which cannot routinely be applied to very large systems. On the other side KS DFT methods can be, but we have little confidence in the reliability of the results. The main problems are not fundamental rather "technical" problems - approximations of the xc functionals and potentials in KS DFT. Since the beginning of KS DFT an enormous amount of effort has been invested in the search for realistic representations of the unknown exchange and correlation functionals (see e.g. the discussion in Ref. [10]), adding new rungs to the Jacob's Ladder [11], and adding more and more empirical adjustable parameters in new xc functionals. The new xc functionals usually only correct existing ones and only partially solve some of their problems but do not really improve the reliability of the DFT methods.

So, the important questions are: can we make DFT methods as predictive as e.g. coupled cluster theory? Can we find a method capable of rigorously defining an xc functional and potential in the context of KS theory? And how can we effectively use our experience in WFT to help DFT to be more reliable?

One of the possible solutions to aforementioned problems is by exploiting orbital-dependent functionals and potentials in KS DFT. This step, from explicitly density-dependent xc functionals, to orbital-dependent ones can be viewed in some sense as analogous to the transition from the Thomas-Fermi equation to the KS equations. Therefore the KS DFT with orbital-dependent xc functionals can be called a third generation of DFT [12]. By using orbitals to define the xc orbital-dependent functionals we have much more flexibility in the construction of the functional. It presents the possibility for using, almost directly, orbital-dependent expressions for the xc energy functionals from well known and established WFT methods. This is particularly visible e.g. in the case of the exchange energy functional E_x, which is naturally formulated in terms of orbitals, and has the form of the usual

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Hartree-Fock (HF) exchange energy functional

$$E_x^{\text{OEP}}[\{\phi_p\}] = -\frac{1}{2}\sum_{i,j}^{N}(ij|ji), \tag{1}$$

where two-electron integrals are defined as:

$$(pq|rs) = \int \phi_p^*(\mathbf{r})\phi_q(\mathbf{r})\frac{1}{|\mathbf{r}-\mathbf{r}'|}\phi_r^*(\mathbf{r}')\phi_s(\mathbf{r}')d\mathbf{r}d\mathbf{r}'. \tag{2}$$

and $\phi_p(\mathbf{r})$ are the KS orbitals, which are the self-consistent solutions of the standard KS equation. Here and in the following we use the convention that i,j,k,l label occupied orbitals, a,b,c,d label virtual orbitals, and p,q,r,s label either. With this choice for the exchange functional there is no self interaction error in KS DFT, and we have precisely defined the dominant part of the xc energy functional. Unfortunately the corresponding KS exchange potential, which is by definition the functional derivative of E_x with respect to the electron density, cannot be obtained directly as in the case of density-dependent functionals. Nonetheless the orbital-dependent exchange-only (x-only) approximation combined with the KS principles most naturally leads to the optimized effective potential (OEP) method of Talman and Shadwick [13] following the original suggestion of Sharp and Horton [14]. In the KS DFT context, OEP is a rigorous exchange-only method in DFT akin to the HF method in *ab initio* WFT and it has been implemented using various modern algorithms for the ground state [15–22], and even for excited states [23].

Extensions of the x-only OEP to the correlation problem are not straightforward and have been the subject of substantial interest since the development of the x-only OEP method [18, 24–27]. The first fully self-consistent inclusion of correlation effects in the DFT OEP procedure used the second-order many-body perturbation theory (MBPT(2)) energy functional (OEP2-KS method [28]), where numerical results on a few atoms supported the methodology. Numerical results for a set of atoms and molecules, was presented by us in 2002 [28]. The proposed correlation potential has the correct overall shape as compared to quantum Monte-Carlo re-

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sults, especially for He-isoelectronic series, and is much better than the potentials obtained from the standard DFT calculations, which are frequently qualitatively wrong. However, we have also observed that, for larger systems, the depth of the correlation potentials may be significantly overestimated and correlation energies too negative. We have also found much slower convergence, or even divergence, of the iterative solutions of the self-consistent KS-OEP equation for the orbitals and potential [29] of the Be atom, where the quasi-degeneracy of the $(1s)^2$ $(2s)^2$ and $(1s)^2$ $(2p)^2$ configurations is present [30]. This baffling behaviour of the OEP2-KS method caused much confusion. Misunderstandings and failures to describe and solve this problem (see Refs. [31–33]), ending with the very pessimistic, but incorrect conclusion [31] " This failure basically excludes PT based orbital functionals for practical applications in DFT". Since then we have found [29] that the cause of this aforementioned problem of OEP2-KS is due to the choice of the zeroth-order Hamiltonian H_0, which, in this method, is the sum of eigenvalues of the KS equation, and which is not optimal although it is also made in Görling–Levy perturbation theory (GLPT)[25, 34], and it appears to be a natural choice from the KS DFT point of view. A solution of this and other problems has been proposed by us [29] and consists of making a different choice of the unperturbed Hamiltonian to define the second-order OEP correlation functionals and potentials. Also in that paper [29], we have rederived the correlated OEP equation from a more general perspective, starting with the density condition [35] in conjunction with the CC energy functional. Defined this way the OEP exchange-only functional and OEP2-KS, OEP2-sc, OEP-ccpt2 [36] etc., correlation functionals constitute *ab initio DFT* a hierarchy of systematic approximations [37–41] converging to the exact solution of the Schrödinger equation in the correlation and basis set limit, just as does *ab initio* WFT. Independently other interesting algorithms which include correlation effects in the OEP method were proposed [42–46] which extend the applicability, and theoretical foundations of orbital-dependent functionals and potentials in DFT.

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This article is dedicated to a survey of the work done at QTP mainly on correlated

OEP focusing on challenges, problems and applications. In the following we present

a short theory of correlated OEP, a few important results and conclusions.

2.   Orbital-dependent functionals in KS DFT, Optimized Effective Potential Method and *ab initio* DFT - theory and numerical results

2.1.   *Theory and implementation*

In the KS implementation of DFT, the computed electron density, $\rho(\mathbf{r}) = \sum_{i=1}^{N} |\phi_i(\mathbf{r})|^2$, is formed from the occupied KS orbitals $\phi_i(\mathbf{r})$ which are the self-consistent solutions of the KS equation [2]:

$$\left\{ -\frac{1}{2}\nabla^2 + v_s[\rho](\mathbf{r}) \right\} \phi_p(\mathbf{r}) = \varepsilon_p \phi_p(\mathbf{r}), \tag{3}$$

with the local effective KS potential

$$v_s[\rho](\mathbf{r}) = v(\mathbf{r}) + \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + V_{xc}[\rho](\mathbf{r}), \tag{4}$$

where

$$V_{xc}[\rho](\mathbf{r}) = \frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r})} \tag{5}$$

is the local xc potential formally defined as the functional derivative of the xc energy

with respect to the electron density $\rho(\mathbf{r})$. In the case of orbital-dependent xc func-

tionals in KS DFT $E_{xc}[\{\phi_p\}]$ the common route to the obtain orbital–dependent

form of xc OEP potentials is by using the chain rule for functional derivatives and

first order perturbation theory [18, 19, 28, 35]. But this seems not to be a very

effective route to obtain explicit expressions for xc potentials, especially in the

case when correlation is included and causes problems with extending correlation

to higher orders effects.

In the following we will utilize the ideas of Bartlett *et al.* [29], where the den-

sity condition together with the CC methodology is employed to derive orbital-

dependent multiplicative exchange-correlation potentials in KS OEP, and define

correlated OEP methods in an effective way. Thus, for the sake of completeness, we only briefly recall the basic ideas and notation employed, skipping the detailed diagrammatic and algebraic derivation [29, 36, 37, 39] and focusing on the main steps and basics ideas of *ab initio* DFT.

By construction, the KS density is an exact density. This means that any corrections to the converged KS density introduced by changes in $\phi_i(\mathbf{r})$ have to vanish [29, 35, 42];

$$\rho(\mathbf{r}) = \rho^{KS}(\mathbf{r}) + \delta\rho^{KS}(\mathbf{r}), \tag{6}$$

and

$$\delta\rho^{KS}(\mathbf{r}) = 0. \tag{7}$$

We use this condition to define a local exchange-correlation potential, instead of following the alternative derivative definition of the exchange-correlation potential $\widehat{V}_{xc}$ Eq.(5). The density correction $\delta\rho^{KS}(\mathbf{r})$ can be written using density matrix correction $\Delta\gamma_{qp}$ from the CC theory [47]

$$\delta\rho^{KS}(\mathbf{r}) = \sum_{p,q} \varphi_q(\mathbf{r})\Delta\gamma_{qp}\varphi_p^*(\mathbf{r}), \tag{8}$$

where

$$\Delta\gamma_{qp} = \langle 0|e^{T^\dagger}\{p^\dagger q\}e^T|0\rangle/\langle 0|e^{T^\dagger}e^T|0\rangle = \langle 0|[e^{T^\dagger}\{p^\dagger q\}e^T]_C|0\rangle, \tag{9}$$

and T is the cluster operator [47–49].

We separate the total Hamiltonian

$$H = \sum_i \widehat{h}(i) + \sum_{i<j} 1/r_{ij} \tag{10}$$

into the zeroth-order H_0 and a perturbation V

$$H = H_0 + V, \tag{11}$$

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where

$$H_0 = \sum_i [\widehat{h}(i) + \widehat{u}(i)], \tag{12}$$

$$V = \sum_{i<j} 1/r_{ij} - \sum_i \widehat{u}(i), \tag{13}$$

and $\widehat{u} = \widehat{J} + \widehat{V}_{xc}$ is the one-particle potential which we determine in our approach. In the above, $\widehat{h}(i)$ is the sum of the kinetic energy operator and the external potential and $\widehat{J}$ is the Coulomb potential. Then we can expand the density corrections, Eq.(8), from CC theory in orders of the perturbation V.

The density condition requirement at first order, $\delta\rho^{(1)}(\mathbf{r}) = 0$, leads to the x-only OEP (OEPx) equation which defines local exchange potential $\widehat{V}_x$ [13, 29] by

$$\sum_{a,i} \varphi_a(\mathbf{r}_1)\varphi_i^*(\mathbf{r}_1)[\langle a|\widehat{K} + \widehat{V}_x|i\rangle/(\epsilon_i - \epsilon_a)] = 0, \tag{14}$$

and $\widehat{K}$ is the non-local Hartree-Fock (HF) exchange potential. This OEP exchange potential $\widehat{V}_x^{\mathrm{OEP}}$ corresponds to the x-only OEP functional E_x^{OEP}, which has the form of usual HF exchange energy functional Eq.(1) in terms of KS orbitals . In matrix form, as shown elsewhere[29, 50] the x-only OEP equation which would define V_X for a particular iteration can be written,

$$\mathbf{X}\mathbf{V}_X^{(1)} = \mathbf{Y}^{(1)} \tag{15}$$

where $\mathbf{X}$ is the matrix (auxiliary basis) representation of the density response function [19, 28]

To include correlation effects in *ab initio* DFT and introduce the correlation potential, we have to go to higher orders in perturbation theory. At the next – second-order, the density condition requires that the second-order correction to the KS density must vanish: $\delta\rho^{(2)}(\mathbf{r}) = 0$. This directly results in the orbital-dependent OEP equations for the second-order correlation potential - the detailed derivation and the explicit form of the correlated OEP equations can be found elsewhere.

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[29, 37, 39] In a compact matrix form the relevant OEP equations become

$$\mathbf{X}\mathbf{V}_{XC}^{(1+2)} = \mathbf{Y}^{(1)} + \mathbf{Y}^{(2)} \tag{16}$$

where $\mathbf{Y}^{(2)}$ arises from the correlation functional, MBPT2, and we understand $\mathbf{V}_{XC}^{(1+2)}$ to mean the combined potential through second order, which would then be used in an iterative, self-consistent scheme.

As was indicated elsewhere [29, 36, 40], the partitioning of the total Hamiltonian plays a prime role in determining the performance of the second-order correlated OEP functional. The zeroth-order Hamiltonian can be chosen in different ways. The natural choice of H_0 in OEP DFT would seem to be a simple sum of KS one-particle Hamiltonians, $H_0^{KS} = \sum_i [h(i) + v_s(i)] = \sum_p \varepsilon_p^{KS} \{p^\dagger p\}$. This is the choice made by Görling–Levy [18], by Jiang and Engel [32], by Mori-Sanchez, *et al.* [31], and by Rohr, *et al.* [33] and also by us: Grabowski *et al.* [28] in our first attempt to solve the OEP correlation problem (OEP2-KS method). However, as indicated above, this choice is a very poor one, which causes many problems in OEP2-KS calculations, and is *not* the one used to define *ab initio* DFT. [29, 36, 37, 41, 46]

By removing the large diagonal contribution $\langle p|\widehat{K} + \widehat{V}_{xc}|p\rangle$ from the perturbation and include it in the new H_0.

$$H = \underbrace{\sum_p [\varepsilon_p^{KS} - \langle p|\widehat{K} + \widehat{V}_{xc}|p\rangle]\{p^\dagger p\}}_{H_0 = \sum_p f_{pp}\{p^\dagger p\}} - \sum_{p \neq q} \langle p|\widehat{K} + \widehat{V}_{xc}|q\rangle\{p^\dagger q\} + \frac{1}{4}\sum_{p,q,r,s} \langle pq||rs\rangle\{p^\dagger q^\dagger sr\} + \langle 0|H|0\rangle, \tag{17}$$

and following the idea of generalized many body perturbation theory (GMBPT) [47], to reinstate orbital invariance of the MBPT(2) energy for rotations which mix occupied or virtual orbitals among themselves, we immediately define a more optimal partitioning of the Hamiltonian [29], the semi-canonical one. In this case the semi-canonical rotation of the orbitals additionally eliminates off-diagonal f_{ij}

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and f_{ab} terms from the perturbation

$$V = \sum_{ai} f_{ai}\{a^\dagger i + i^\dagger a\} + W, \tag{18}$$

where f_{pq} are the usual Fock matrix elements defined in terms of KS OEP spinor-bitals

$$f_{pq} = \varepsilon_p^{KS}\delta_{pq} - \langle p|\widehat{K} + \widehat{V}_{xc}|q\rangle. \tag{19}$$

Then H_0 becomes

$$H_0 = \sum_p f_{pp}\{p^\dagger p\} + \sum_{i\neq j} f_{ij}\{i^\dagger j\} + \sum_{a\neq b} f_{ab}\{a^\dagger b\}. \tag{20}$$

Defined in this way, the OEP2-sc method, has been found to be the most effective and stable second-order *ab initio* DFT method [29, 37, 40, 41], in which all of the aforementioned problems of OEP2-KS were solved. A further generalization of *ab initio* DFT including higher then second-order terms was made by a change of H_0 in the OEP2-sc case to a form that has selected double excitation contributions along with single excitations [36, 51]. The two-particle terms are those that correspond to operators that do not change the particle number of the diagrams that constitute the OEP functional (CCPT2). The new H_0 which defines OEP-ccpt2 method can be written as

$$H_0^{CCPT} = \sum_p f_{pp}\{p^\dagger p\} + \frac{1}{4}\sum_{a,b,c,d}\langle ab||cd\rangle\{a^\dagger b^\dagger dc\} + \frac{1}{4}\sum_{i,j,k,l}\langle ij||kl\rangle\{i^\dagger j^\dagger lk\} \tag{21}$$

$$+ \sum_{a,b,i,j}\langle aj||bi\rangle\{a^\dagger j^\dagger ib\} + \langle\Phi_{KS}|H|\Phi_{KS}\rangle \tag{22}$$

The OEP equations Eq. (16) for V_{xc} functional differs only in the form of $\mathbf{Y}^{(2)}$ which arises from the correlation functional, and certainly depends on the choice of H_0 in our derivation.

We have to stress here that it is not necessary to solve the CC equations in our implementation of *ab initio* DFT. In our methodology, we use the CC theory

to properly define orbital-dependent exchange and correlation potentials in the context of KS DFT. All correlated OEP equations (OEP2-KS, OEP2-sc and OEP-ccpt2) for the potentials are solved fully self-consistently together with KS-DFT equations until final (usually 10^{-9}) convergence is achieved.

Our implementations of *ab initio* DFT are based on the linear combination of atomic orbital (LCAO) OEP method [19, 20], which permits OEP calculations of atoms and molecules on an equal footing to the conventional molecular orbital or DFT calculations, i.e., with conventional Gaussian-type basis sets, but without any further approximations. The finite basis set implementation of OEP involves a projection method [19, 50] for solving the required integral equation, and by construction all potentials are expanded in terms of auxiliary Gaussian functions. With these LCAO OEP methods, it is possible to extract local exchange and correlation potentials and other properties from the OEP calculations of atoms and molecules. The local exchange-correlation potentials generated from the OEP method, can be plotted and may be used in developing accurate exchange and correlation potentials and functionals which can be systematically improved. [21, 28, 29, 36].

Some computational difficulties in the LCAO OEP method have been found in routine calculations with exchange-only calculations [21, 50], and with correlation included [36, 39], were the manifestation of the well-known instability associated with the numerical solutions of Fredholm integral equation of the first kind. To obtain numerical solutions of reasonable accuracy for this class of equations, an appropriate choice of basis functions is crucial. Common numerical problems which appear are the slow convergence of the projected exchange-correlation potential with respect to the size of the expansion basis set for the orbitals. The basis set incompleteness has a much more important effect on the finite basis set OEP implementation than on other SCF procedures i.e., HF method. Certainly by making a judicious choice of the orbital basis set, we can obtain reasonably accurate exchange and correlation potentials for atoms and molecules. Unfortunately, large uncontracted basis sets must be employed for orbitals, and additionally we must

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make an adequate basis set choice to include correlation effects in correlated OEP

calculations.

2.2. *Numerical results*

We have implemented various OEP methods defined above in the ACES II package

[52] developed in Bartlett's group in QTP. Many testing calculations have been

performed using all variants of OEP methods showing their properties, successes

and failings (see the Refs. [28, 29, 36, 37, 40, 41] and also the Conclusions).

Here we present another example, the comparison of fundamental DFT quantities

- electron density and KS correlation potentials obtained in different WFT an DFT

methods. This analysis helps us to get more insight into the links between the

coverage of dynamic electron correlation effects defined in *ab initio* WFT, standard

DFT and *ab initio* DFT.

We have performed similar kind of analysis before [53–55], and here we present

only few selected results obtained for the Neon atom. The Neon atom in its ground

state is a perfect subject for this kind of analysis, because it has an almost ideal

closed-shell structure and its correlation effects are classified as almost entirely

dynamic. This allows us to avoid confusions at time of analysis with the presence

of the non-dynamical correlation effects, which is often used as an explanation of

failings of some methods. All calculations were performed with the uncontracted

ROOS-ATZP basis set.[56] In order to make such a comparison of describing corre-

lation effects by a different classes of various methods we have made the calculations

using the main representative members of *ab initio* WFT methods: MP2, CCSD

and CCSD(T), standard DFT methods SVWN5[57, 58] from LDA class off func-

tionals, and gradient corrected BLYP [6], and *ab initio* DFT methods OEP2-KS,

OEP2-sc and OEP-ccpt2.

In Fig.1. we compare the KS correlation potentials of the Neon atom calculated

by standard density-dependent DFT methods, *ab initio* DFT ones and from MP2,

CCSD and CCSD(T) *ab initio* WFT methods with the exact correlation KS poten-

tial [8]. To calculate the xc potentials form the MP2, CCSD and CCSD(T) densities,

we employ the direct optimization technique of Wu and Yang [44]. Details of this

procedure adopted to calculate xc KS potentials can be found elsewhere. [55] The

resulting xc potential can be written

$$v_{\mathrm{xc}}([\rho^{\mathrm{A}}]; \mathbf{r}) = \sum_t b_t g_t(\mathbf{r}) + v_0([\rho^{\mathrm{A}}]; \mathbf{r}) - J([\rho^{\mathrm{A}}]; \mathbf{r}) \tag{23}$$

where $J = \int \frac{\rho^{\mathrm{A}}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{r}'$ is the Coulomb potential, $v_0(\mathbf{r})$ is the Fermi-Amaldi poten-

tial [59] used to ensure the correct $-1/r$ asymptotic behaviour of the resulting

xc potential. The first term is an expansion in an auxiliary basis set of Gaussian

functions $g(\mathbf{r})$ and the coefficients $\{b_t\}$ are the only unknown parameters and are

determined in our procedure [44, 55]. In the following we perform calculations of

v_{xc} for a variety of *ab initio* WFT densities ρ^{A}, where A = HF, MP2, CCSD or

CCSD(T). In order to determine an approximate correlation potential, we calcu-

late it by simply taking difference of the xc potential calculated in MP2, CCSD or

CCSD(T) and x-only potential obtained in the same procedure from HF density,

e.g. for the MP2 we have

$$v_{\mathrm{c}}([\rho^{\mathrm{MP2}}]; \mathbf{r}) = v_{\mathrm{xc}}([\rho^{\mathrm{MP2}}]; \mathbf{r}) - v_{\mathrm{xc}}([\rho^{\mathrm{HF}}]; \mathbf{r}) \tag{24}$$

Calculated this way correlation potentials are plotted together with the exact one

and other KS potentials. As we can see in the Fig.1., the *ab initio* WFT potentials

are very close to the exact one and can be used as a reference correlation potentials

in a comparison with DFT results. The standard density-dependent correlation

potentials VWN and LYP are qualitatively incorrect, they have the wrong shape,

magnitude and even the opposite sign to the exact results almost everywhere in

the space. This fact is well known [8, 28], but for some reason ignored by the

DFT community. On the other side, the orbital-dependent correlation potentials

calculated from *initio* DFT methods are very close to the exact results. Only the

OEP2-KS correlation potential, as we indicated before, significantly overestimates

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the exact correlation potential, which is the result of the wrong choice of the H_0

in the definition of perturbation problem. But as we have shown elsewhere [29, 36,

37, 40] it can be fixed by proper splitting of the total Hamiltonian. The improved

OEP2-sc and OEP-ccpt2 are very close not only to the exact correlation potential,

but they are also close to their *ab initio* WFT counterparts - correlation potentials

calculated from MP2 and CCSD densities respectively. This shows the systematic

improvement of the *ab initio* DFT methods mentioned above, which is reflected

not only by e.g. the correlation and total energies but also by the KS correlation

potentials, which are the very subtle correlation effect in the total xc potential.

In the following we include in our analysis of the behaviour of the correlated OEP

methods also the electron density. The studies of the impact of electron correlation

effects on the electron density are based on an analysis of graphical representations

of difference radial-density distributions [53, 54] calculated between radial densities

$D(r)$ obtained from correlated method $D^{XC}(r)$ and x-only method $D^X(r)$,

$$\delta^{XC/X}(r) = D^{XC}(r) - D^X(r), \tag{25}$$

where the radial charge densities are defined as

$$D^A(r) = 4\pi r^2 \rho^A(r), \tag{26}$$

and $\rho^A(r)$ denotes the electron density at the distance r from the nucleus calcu-

lated by means of the method A. In the Fig. 2 we present a comparison of the plots

which represent the response of the density on a correlation effects. We plot curves

representing *ab initio* WFT difference radial density distributions: $\delta^{MP2/HF}(r)$

$\delta^{CCSD/HF}(r)$ and $\delta^{CCSD(T)/HF}(r)$, together with the curves which represent im-

pact on the density $\delta^{XC/X}(r)$ of the correlation functionals C (C=VWN5,LYP,

OEP2-KS, OEP2-sc, OEP-ccpt2) on the exchange functionals X (X=S, B88, and

OEPX), all generated for the Ne atom. The curves $\delta^{MP2/HF}(r)$, $\delta^{CCSD/HF}(r)$ and

$\delta^{CCSD(T)/HF}(r)$ represent *ab initio* WFT correlation effects on the density, and

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are our reference response density distribution curves. Going to the standard DFT results, we plot the response curves for $\delta^{SVWN5/S}(r)$, $\delta^{LYP/B88}(r)$, representing the impact of inclusion of the correlation functionals on the density distributions obtained at the X-only level. One can see in this figure that the plot obtained for the VWN5 and the LYP correlation functionals, do not show similarity with the $\delta^{MP2/HF}(r)$ and $\delta^{CCSD/HF}(r)$ ones. This disagreement may be explained by the fact that the LYP and VWN5 correlation functionals do not represent any considerable dynamic correlation effects.[53] A completely different situation takes place for the curves corresponding to the OEP2-KS, OEP2-sc and OEP2-ccpt2 functionals. One can see in this figure that the plots obtained for the orbital–dependent OEP correlation functional very well, except OEP2-KS, resemble the MP2 and CCSD distributions. The OEP2-KS correlation response density curve significantly overestimates the reference WFT results, but still have qualitative good shape. It confirms the previous findings on the energy and correlation potential level and additionally supports the previous conclusions about problems with OEP2-KS method.[29, 36] Using of the OEP2-sc and OEP-ccpt2 methods significantly improves the results. OEP2-sc and OEP-ccpt2 curves are very close to the *ab initio* WFT reference ones. The shape and magnitude are almost the same, and additionally, like in correlation potential case (see. Fig. 1.), the OEP2-sc curve is closer to the MP2 one, and curve generated from OEP-ccpt2 method approaches the CCSD result. This is very systematic behaviour of the correlated OEP results, visible on the density level, which confirms findings and conclusions from the energy– and correlation KS potential– analysis. Improvement of the correlation KS-OEP functional, not only improves correlation energies, KS-potentials and other properties, but is also reflected in a systematic way on the electron density.

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3. Conclusions

The use of systematically improvable, orbital-dependent approximations to the exact energy in DFT allows us to circumvent virtually all of the aforementioned shortcomings of the density-dependent functionals in KS DFT. There is no problem with the self interaction error, correlation potentials calculated in *ab initio* DFT provide the correct shape compared to those from reference quantum Monte Carlo calculations [28, 29, 36]. Exchange-only and exchange-correlation potentials are reasonable, and have the correct long-range behavior [21, 28]. As a consequence, other calculated quantities are also reasonable, e.g. total and correlation energies calculated in correlated OEP methods are almost of CC accuracy [29, 36]. Moreover *ab initio* DFT provides good ionization potentials and excitations energies [23, 37, 38]. We also have shown that the OEP2 method is capable of consistently recovering dispersion effects in weakly bounded dimers [41], which extends the applicability of *ab initio* DFT to areas which were inaccessible by standard DFT methods.

   The different correlated OEP methods could be easily derived thanks to the *ab initio* DFT formalism of Bartlett *et al.*[29] based on the density condition and the CC functional. Our general approach also has important technical features: It eliminates the necessity of directly taking the cumbersome functional derivatives to arrive at the working equations to be implemented, giving us greater flexibility in defining new correlation potentials, even at infinite order. Indeed, it had been considered impossible to improve the approximations to exchange and/or correlation functionals in a systematic fashion until the concept and practical realisation of *ab initio* DFT was put forward capitalizing on the systematic orbital-dependent approximations to the exact energy in *ab initio* wave function theory (WFT). So, we are able to define a hierarchy of DFT methods (with orbital-dependent functionals) OEPx < OEP2-KS < ... < OEP2-sc < OEP-ccpt2 < ... which converge to the right answer in the infinite and complete basis set limit as the correlation level is increased. This systematic improvement of the *ab initio* DFT methods is

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reflected not only in total and correlation energies, ionization potentials, and excitation energies, but also in fundamental DFT quantities like electron density or correlation potentials.[53, 55]

The derivation of *ab initio* DFT from CC theory and the KS density condition along with the numerical results, directly compared with their WFT counterparts (MP2 – OEP2-sc, CCSD – OEP-ccpt2) shows very systematic behaviour and clearly indicates the interconnections between these two independent types of theories DFT and WFT.

But certainly, "nothing is for free". We have to mention some negative aspects of using orbital-dependent functionals in DFT. First of all, xc functionals and potentials are orbital–dependent, so in the KS procedure we have to solve additional OEP equations, which are numerically demanding and in the LCAO-OEP implementation large uncontracted basis sets must be used in calculations to provide high quality of the solutions. Additionally our equations for correlated OEP are complicated (even if the *ab initio* DFT procedure helps significantly in their derivation) and numerically more demanding the standard density-dependent DFT - they scale as $N_{it}n_{occ}^2 n_{virt}^3$ (at the OEP2 level). Also, the extension of our procedure to TD-DFT is possible but is extremely complicated especially at the correlated level [60].

But the price seems to be acceptable, because right now, even in DFT calculations, we are able to control and predict the accuracy level of the results, like in *ab initio* WFT, which makes DFT method much more reliable than before and brings a hope to the DFT world that there is a way to do DFT correctly, not only theoretically but also in practice.

18   *Taylor & Francis and I.T. Consultant*

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4   # Figure captions
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6   Figure 1. Comparison of correlation potentials of the Neon atom obtained from
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8   the OEP2-KS, OEP2-sc, OEP-ccpt2 with the correlation potentials obtained from
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10   MP2, CCSD and CCSD(T), and from standard DFT: VWN5 and LYP and the
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12   exact correlation potential Ref. ([8]).
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17   Figure 2. Comparison of difference radial density distributions, $\delta^{MP2/HF}(r)$
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19    $\delta^{CCSD/HF}(r)$ and $\delta^{CCSD(T)/HF}(r)$ with the impact on the density $\delta^{XC/X}(r)$ of
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21   the correlation functionals C (C=VWN5, LYP, OEP2-KS, OEP2-sc, OEP-ccpt2)
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23   on the exchange functionals X (X=S, B88, and OEPX) generated for the Ne atom.
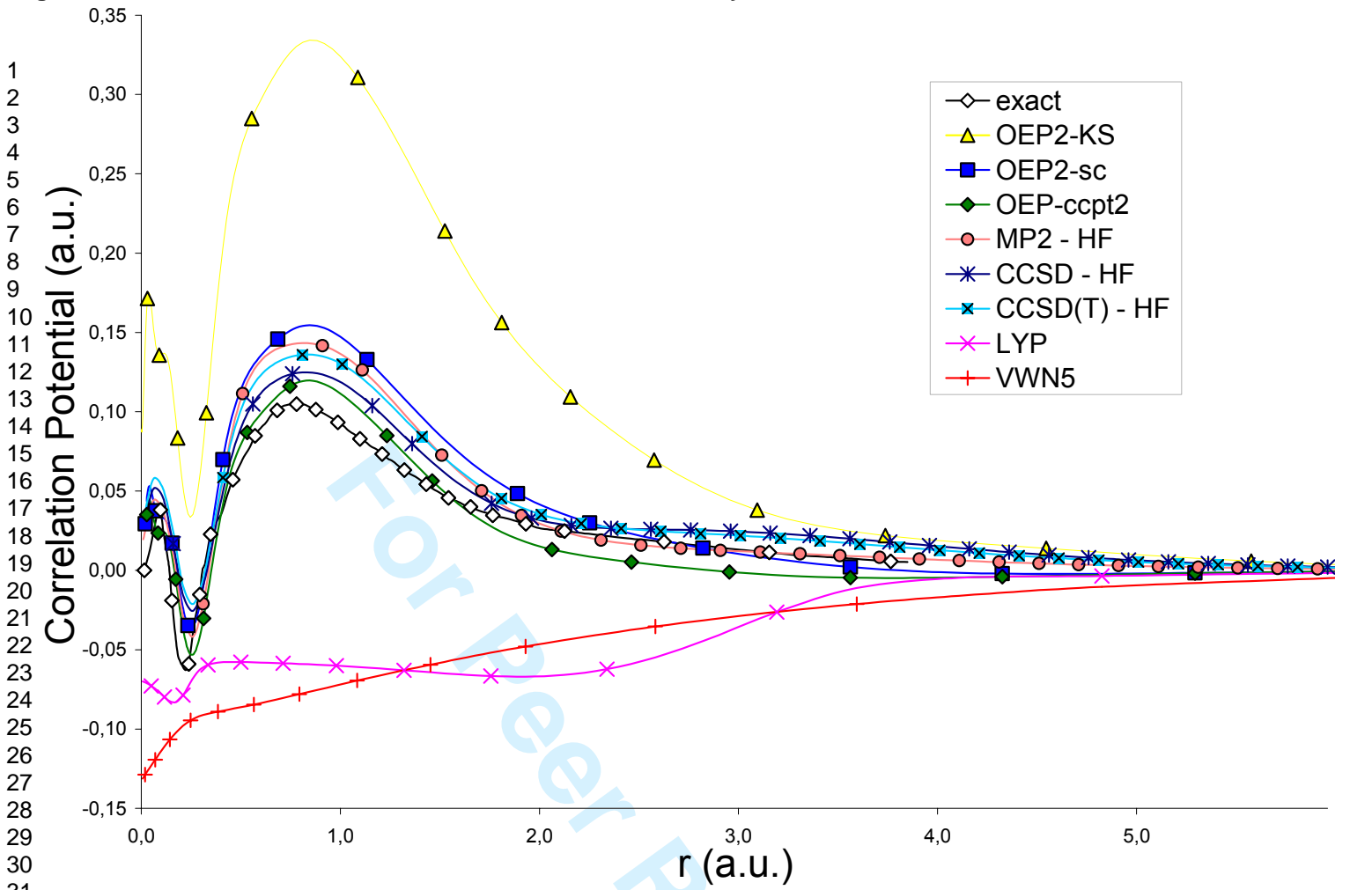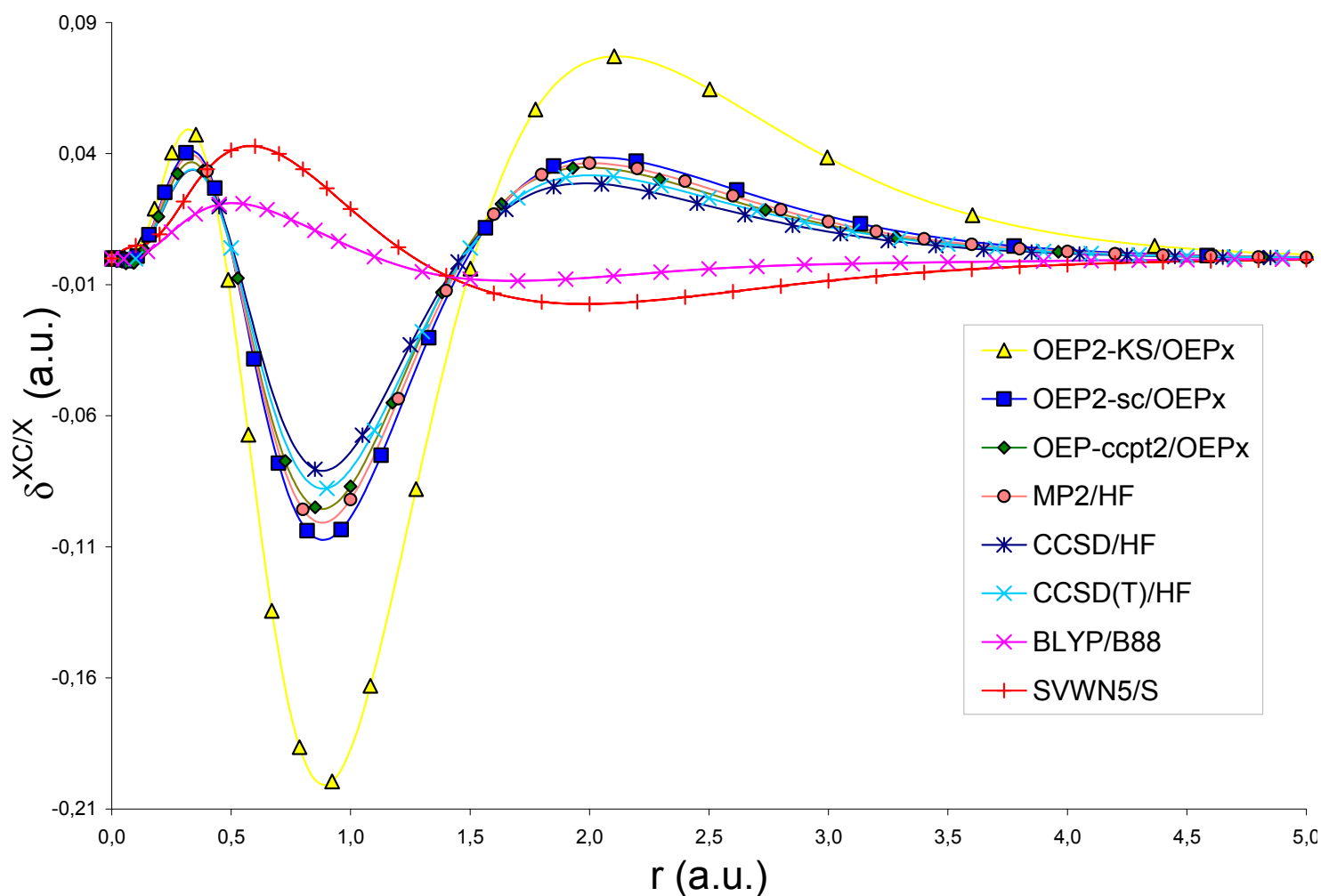24
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Figure 1. Grabowski, Lotrich, Hirata

Figure 2. Grabowski, Lotrich, Hirata