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Approximation of Exchange-Correlation Potentials for Orbital-Dependent Functionals

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Graduate Program in Chemistry

A thesis submitted in partial fulfillment of the requirements for the degree in Master of Science

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(Thesis format: Integrated Article)

by

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Abstract

Density-functional theory (DFT) is the most widely used method of modern computational chemistry. All practical implementations of DFT rely on approximations to the unknown exchange-correlation functional. These approximations may be devised in terms of energy functionals or effective potentials. In this thesis, several approximations of the latter type are presented.

Given a set of canonical Kohn–Sham orbitals, orbital energies, and an external potential for a many-electron system, one can invert the Kohn–Sham equations in a single step to obtain the corresponding exchange-correlation potential, $v_{\mathrm{XC}}(\mathbf{r})$. We show that for orbitals and orbital energies that are solutions of the Kohn–Sham equations with a multiplicative $v_{\mathrm{XC}}(\mathbf{r})$ this procedure recovers $v_{\mathrm{XC}}(\mathbf{r})$ (in the basis set limit), but for eigenfunctions of an orbital-specific one-electron operator it produces an orbital-averaged potential. In particular, substitution of Hartree–Fock orbitals and eigenvalues into the Kohn–Sham inversion formula is a fast way to compute the Slater potential. In the same way we obtain, for the first time, orbital-averaged exchange and correlation potentials for hybrid and kinetic-energy-density-dependent functionals. We also show how the Kohn–Sham inversion approach can be used to compute functional derivatives of explicit density functionals and to approximate functional derivatives of orbital-dependent functionals.

Motivated by the absence of an efficient practical method for computing the exact-exchange optimized effective potential (OEP) we devised the Kohn–Sham exchange-correlation potential corresponding to a Hartree–Fock electron density. This potential is almost indistinguishable from the OEP and, when used as an approximation to the OEP, is vastly better than all existing models. Using our method one can obtain unambiguous, nearly exact OEPs for any finite one-electron basis set at the same low cost as the Krieger–Li–Iafrate and Becke–Johnson potentials. For all practical purposes, this solves the long-standing problem of black-box construction of OEPs in exact-exchange calculations.

Keywords: quantum chemistry, density-functional theory, model exchange-correlation potentials, orbital-averaged potentials, optimized effective potential, functional derivatives

Co-Authorship Statement

Chapter 2 is based on the paper "Efficient construction of exchange and correlation potentials by inverting the Kohn–Sham equations" by A. A. Kananenka, S. V. Kohut, A. P. Gaiduk, I. G. Ryabinkin and V. N. Staroverov [*J. Chem. Phys.* **139**, 074112 (2013)]. Alexei Kananenka performed the derivations, implemented the method and carried out all the calculations. The manuscript was prepared by Dr. Ryabinkin and Dr. Staroverov. Chapter 3 is based on the paper "Accurate and efficient approximation to the optimized effective potential for exchange" by I. G. Ryabinkin, A. A. Kananenka and V. N. Staroverov [*Phys. Rev. Lett.* **111**, 013001 (2013)]. Alexei Kananenka performed the derivations, implemented the method and carried out all the calculations. The manuscript was prepared by Dr. Ryabinkin and Dr. Staroverov.

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List of Abbreviations

BJ	—	Becke–Johnson
C	—	correlation
CEDA	—	common energy denominator approximation
DFT	—	density functional theory
EXX	—	exact exchange
GGA	—	generalized gradient approximation
HF	—	Hartree–Fock
HFXC	—	Hartree–Fock exchange-correlation potential
H	—	Hartree
HOMO	—	highest occupied molecular orbital
KLI	—	Krieger–Li–Iafrate
LDA	—	local density approximation
LHF	—	localized Hartree–Fock
LYP	—	Lee–Yang–Parr
OEP	—	optimized effective potential
PBE0	—	Perdew–Burke–Ernzerhof hybrid
PBE	—	Perdew–Burke–Ernzerhof
SCF	—	self-consistent field
S	—	Slater
TPSS	—	Tao–Perdew–Staroverov–Scuseria
UGBS	—	universal Gaussian basis set
VWN	—	Vosko–Wilk–Nusair
XC	—	exchange-correlation
X	—	exchange

List of Symbols

E_{h}	—	atomic unit of energy (1 hartree = 2625.50 kJ mol^{-1}= 27.2114 eV)
a_0	—	atomic unit of length (1 bohr = 0.529177 Å)
N	—	number of electrons
Z	—	nuclear charge
$\mathbf{r}$	—	position vector
ρ	—	electron density
$\gamma(\mathbf{r}, \mathbf{r'})$	—	density matrix
$F[\rho]$	—	general density functional
e	—	general energy density
E	—	total energy
E_{XC}	—	exchange-correlation energy
E_{X}	—	exchange energy
E_{C}	—	correlation energy
v_{ext}	—	external potential
v_{eff}	—	Kohn–Sham potential
v_{H}	—	Hartree (electrostatic) potential
v_{XC}	—	exchange-correlation potential
$v_{\mathrm{X}}^{\mathrm{S}}$	—	Slater exchange potential
v_{X}	—	exchange potential
ϕ_i	—	Kohn–Sham orbitals
ϵ_i	—	Kohn–Sham eigenvalues

Chapter 1

Introduction

1.1 Kohn–Sham density-functional theory

Density-functional theory (DFT) is a powerful approach to electronic-structure calculations because it offers a high ratio between accuracy and computational cost. This makes DFT a very attractive tool for computing properties of systems with thousands of electrons. DFT is used by many researchers in areas as diverse as drug design, metallurgy, nanotechnology, and other fields.

DFT provides a formally exact solution to the nonrelativistic electronic many-body problem. The static Schrödinger equation for a system of N interacting nonrelativistic electrons is [1]

$$\hat{H}\Psi(\mathbf{x}_1, ..., \mathbf{x}_N) = E\Psi(\mathbf{x}_1, ..., \mathbf{x}_N). \tag{1.1}$$

Here, the antisymmetric N-electron wave function $\Psi(\mathbf{x}_1, ..., \mathbf{x}_N)$ is an eigenstate of the Hamiltonian $\hat{H}$ with the energy eigenvalue E, and $\mathbf{x}_i \equiv (\mathbf{r}_i, \sigma_i)$ are the position and spin of the ith electron.

The total Hamiltonian of the N-electron system within the fixed-nucleus approx-

imation is given by (atomic units are used throughout the thesis)

$$\hat{H} = -\frac{1}{2} \sum_{i=1}^{N} \nabla_i^2 + \sum_{i=1}^{N} v_{\text{ext}}(\mathbf{r}_i) + \sum_{i<k}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_k|}, \qquad (1.2)$$

where $v_{\text{ext}}(\mathbf{r})$ is the external potential, and $1/(|\mathbf{r}_i - \mathbf{r}_k|)$ represents the electron-electron interaction. Note that, for a system with fixed nuclei, the Hamiltonian need not include the term describing the nuclear repulsion energy because this term is just a constant shift of the total energy.

Even today, solving the full many-body Schrödinger Eq. (1.1) remains a formidable numerical problem except for special cases such as one- and two-electron systems as well as few-electron systems with high symmetry and reduced dimensionality. The many-body wave function is a function of $3N$ variables, and it contains much more information than one would ever need to know about an N-electron system. Actually, we are interested in properties of the system such as the total energy, dipole moment, infrared and Raman frequencies, and polarizability. In fact, these properties are just real-valued numbers. Sometimes we also need properties that are functions of one or a few variables, for example, the single-particle probability density or the two-electron reduced density matrix. Calculating the full many-body wave function to obtain these properties seems like an unnecessarily complicated approach, especially when N is large. This is exactly the case where DFT can be best employed.

By using DFT one can in principle obtain all properties of a many-body system exactly, without having to solve the many-body Schrödinger equation. The origin of DFT dates back to 1964, when Hohenberg and Kohn published [2] a basic existence proof that later became known as the Hohenberg–Kohn theorem. This theorem states that the external potential $v_{\text{ext}}(\mathbf{r})$ is determined (up to a constant) by an electron density $\rho(\mathbf{r})$. This theorem is of special importance in atomic and molecular systems because in these systems the external potential is completely determined by

the number of electrons and the types and positions of the nuclei

$$v_{\text{ext}}(\mathbf{r}) = -\sum_{A}^{\text{nuclei}} \frac{Z_A}{|\mathbf{r} - \mathbf{R}_A|}, \tag{1.3}$$

where Z_A is the charge of the nucleus at position R_A. Within the Kohn–Sham framework of DFT, the ground-state electron density can be found by minimizing the total energy expression [2, 3]

$$E_{\text{tot}} = \int v_{\text{ext}}(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} + F[\rho], \tag{1.4}$$

with respect to the density. The functional $F[\rho]$ is *universal* in the sense that it is the same for any N-electron system, regardless of the external potential. Although the Hohenberg–Kohn theorem guarantees the existence of the functional Eq. (1.4), the form of this functional is unknown and must be approximated.

It was the key insight of Hohenberg and Kohn to assume that for any real (interacting) system with the ground-state density $\rho(\mathbf{r})$ there always exists a noninteracting system with the same ground-state density $\rho(\mathbf{r})$. This allows one to transform many-body Schrödinger equation (1.1) into a set of N one-electron Schrödinger equations of the form

$$\left[-\frac{1}{2}\nabla^2 + v_{\text{eff}}(\mathbf{r}) \right] \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r}), \tag{1.5}$$

where $v_{\text{eff}}(\mathbf{r})$ is an effective Kohn–Sham potential, $\phi_i(\mathbf{r})$ are Kohn–Sham orbitals, and ϵ_i are Kohn–Sham eigenvalues. The sum of the squared occupied Kohn–Sham orbitals gives the ground-state density of the real interacting system

$$\rho(\mathbf{r}) = \sum_{i=1}^{N} |\phi_i(\mathbf{r})|^2. \tag{1.6}$$

In Kohn–Sham DFT the total ground-state energy is given by the following ex-

pression [4]

$$E_{\text{tot}} = -\frac{1}{2} \sum_{i=1}^{N} \langle \phi_i | \nabla^2 | \phi_i \rangle + \int v_{\text{ext}}(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \int \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + E_{\text{XC}}[\rho], \quad (1.7)$$

where E_{XC} is the exchange-correlation energy functional defined by

$$E_{\text{XC}}[\rho] \equiv F[\rho] + \frac{1}{2} \sum_{i}^{N} \langle \phi_i | \nabla^2 | \phi_i \rangle - \frac{1}{2} \int \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'. \quad (1.8)$$

Equation (1.8) expresses the total energy of the real interacting system as a sum of kinetic energy for a noninteracting system (first term, usually denoted by T_s), the attraction between the electrons and the nuclei via $v_{\text{ext}}(\mathbf{r})$ (second term), electron-electron Coulomb repulsion energy (third term), and the exchange-correlation energy E_{XC} which incorporates all nonclassical contributions: Pauli exchange, electron correlation and the difference between the kinetic energy of real interacting system and the noninteracting model system. Now, instead of approximating the universal functional $F[\rho]$ we need to approximate only a small part of it—the exchange-correlation energy.

It is remarkable that the Kohn–Sham method can be applied to both interacting and noninteracting systems. Variation of Eq. (1.4) with respect to ρ gives the expression for the effective Kohn–Sham potential [4]

$$v_{\text{eff}}(\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{\text{XC}}(\mathbf{r}), \quad (1.9)$$

where

$$v_{\text{XC}}(\mathbf{r}) = \frac{\delta E_{\text{XC}}[\rho]}{\delta \rho(\mathbf{r})} \quad (1.10)$$

is an exchange-correlation potential. Equations (1.9) and (1.10) are known as Kohn–Sham equations.

The Hohenberg–Kohn theorem allows for exact mapping between interacting and noninteracting systems. This greatly simplifies the complicated many-body problem

into a set of self-consistent one-electron equations with all complexity hidden in v_{XC}. But the impact of Hohenberg–Kohn theorem on quantum physics is much more fundamental. It represents a new paradigm of the electronic many-body problem: the wave function Ψ (a function of $3N$ variables) is replaced by the ground-state density $\rho(\mathbf{r})$ (a function of three variables) as the basic quantity to be calculated. However, in order to use the Kohn–Sham method in practical calculations one needs an approximate form either for the exchange-correlation energy or for the exchange-correlation potential.

1.1.1 Explicit density functionals

Approximations to the exchange-correlation energy that depend on the density and its derivatives are called explicit density functionals. In 1964, Hohenberg and Kohn proposed a very simple approximate form of the exchange-correlation energy functional known as the local density approximation (LDA). This approximation can be derived if one assumes that exchange-correlation energy density e_{XC} is the same as for a homogeneous electron gas,

$$E_{\mathrm{XC}}^{\mathrm{LDA}}[\rho] = \int e_{\mathrm{XC}}(\rho(\mathbf{r}))d\mathbf{r}, \qquad (1.11)$$

where the exchange-correlation energy e_{XC} is a function of $\rho(\mathbf{r})$ only. The LDA approximation is a simple explicit function of electron density that lends itself to immediate practical implementation. However, it is known that real electron densities are not uniform. Within atoms and molecules densities can change rapidly. Therefore, one should not expect LDA to give realistic results for such systems. In spite of that it has been found that LDA gives qualitatively correct results in comparison with experiment. Quantitative results computed using LDA turn out to be far from experimental ones. The list of LDA failures includes high errors in atomization energies

and underestimation of bond lengths in molecules, etc.

By adding a nonlocal contribution one can overcome some of the limitations of LDA. Such functionals are called generalized gradient approximations (GGA) [5–8],

$$E_{\text{XC}}^{\text{GGA}}[\rho] = \int e_{\text{XC}}(\rho(\mathbf{r}), \nabla\rho(\mathbf{r}))d\mathbf{r}. \tag{1.12}$$

GGAs take into account deviation from the homogeneity by considering the gradient of electron density. GGAs give three times smaller errors in atomization energies than LDA. In spite of this GGAs also have limitations. For example, they do not predict stability of small anions [9–12].

1.1.2   Orbital-dependent functionals

Density-dependent approximations have served to computational chemists for many years by providing good qualitative and sometimes good quantitative results. They allow easy access to the exchange-correlation potential via functional differentiation Eq. (1.10). However, they are not perfect, so that further development is needed to improve their accuracy. The next step in designing approximations to the exchange-correlation energy (or at least to the exchange-only energy) is to consider Kohn–Sham orbitals and possibly Kohn–Sham eigenvalues as building blocks. It is beneficial for the following reasons.

First, use of orbitals in DFT is actually as old as Kohn–Sham DFT itself. For example, the kinetic energy of a noninteracting system is given in terms of orbitals (see the first term in Eq. (1.4)). Second, adding orbitals to the functional allows more flexibility. Instead of dealing with only density and its gradient one can make use of the whole set of Kohn–Sham orbitals, thus increasing the number of independent variables. Third, orbital-dependent functionals are able to overcome the limitations of LDA and GGAs [13]. For instance, density-functional calculations with orbital-dependent

functionals predict the stability of anions. Last, but not least, the exchange energy—a fundamental quantity of many-body physics is formulated in terms of orbitals,

$$E_X^{\text{exact}} = -\frac{1}{4} \int d\mathbf{r} \int \frac{|\gamma(\mathbf{r}, \mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}', \qquad (1.13)$$

where $\gamma(\mathbf{r}, \mathbf{r}') = \sum_{i=1}^{N} \phi_i(\mathbf{r})\phi_i^*(\mathbf{r}')$ is the spinless reduced density matrix.

From this point of view it should be clear that the idea of using orbital-dependent density functionals is very tempting. However, attempts to use such functionals face serious difficulties associated with deriving corresponding effective Kohn–Sham potentials.

1.1.3   Kohn–Sham method versus Hartree–Fock method

The Kohn–Sham density functional scheme that treats exchange energy exactly as an orbital-dependent functional of Eq. (1.13) is called exchange-only DFT. It is conceptually close to the Hartree–Fock method. In fact, both methods employ the same total energy functional

$$E_{\text{tot}} = -\frac{1}{2} \sum_{i=1}^{N} \langle \phi_i | \nabla^2 | \phi_i \rangle + \int v_{\text{ext}}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + \frac{1}{2} \int \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' + E_X^{\text{exact}}. \quad (1.14)$$

but the density matrix $\gamma(\mathbf{r}, \mathbf{r}')$ in E_X^{exact} is different. The Kohn–Sham density matrix is built from the Kohn–Sham orbitals. The Hartree–Fock density matrix is constructed from Hartree–Fock orbitals, eigenfunctions of the Fock operator [14, 15]

$$\hat{F} = -\frac{1}{2}\nabla^2 + v_{\text{ext}} + v_H + \hat{K}, \qquad (1.15)$$

where v_{H} is the electrostatic potential and $\hat{K}$ is the nonlocal Hartree–Fock exchange potential defined by the following expression

$$\hat{K}\phi_i(\mathbf{r}) = \frac{\delta E_{\mathrm{X}}^{\mathrm{exact}}}{\delta \phi_i^*(\mathbf{r})}. \tag{1.16}$$

Since Hartree–Fock and Kohn–Sham orbitals are different the Hartree–Fock exchange energy is also different from the Kohn–Sham exact-exchange energy. An important difference between the Hartree–Fock and Kohn–Sham schemes is hidden in the exchange operator. The Hartree–Fock exchange operator $\hat{K}$ is *nonlocal* (non-multiplicative) in the sense that the result of operating with it on an orbital depends on the values of all occupied orbitals everywhere in the coordinate space. The Kohn–Sham potential should be *local* (multiplicative). Therefore the Kohn–Sham exchange (exchange-correlation) potential must also be multiplicative.

In Hartree–Fock theory, the nonlocal exchange potential is known. The exchange potential in DFT is unknown. It could have been derived from Eq. (1.13) with Kohn–Sham orbitals if it was a simple functional of an electron density. However, $E_{\mathrm{X}}^{\mathrm{exact}}$ does not depend on electron density explicitly. The Hohenberg–Kohn theorem implies that the Kohn–Sham orbitals $\phi_i(\mathbf{r})$ are functionals of the electron density. Thus we have an implicit dependence of orbital-dependent functionals on electron density. Because of this implicit dependence one cannot evaluate the functional derivative of an orbital-dependent functional with respect to electron density. An alternative route is to derive such potential as the optimized effective potential.

1.2 Optimized effective potential

The problem of finding a functional derivative of orbital-dependent functional with respect to electron density is even older than Kohn–Sham DFT itself. In 1953, Sharp and Horton [16] derived an integral equation for a *local* potential that minimizes the

Hartree–Fock total energy expression. They treated this potential as an approximation to the Hartree–Fock exchange operator and named it the optimized effective potential (OEP).

Due to the mathematical complexity of the equation proposed by Sharp and Horton (OEP equation) the first solution of this equation appeared only twenty-four years later. In 1976, Talman and Shadwick [17] solved the OEP equation numerically for spherical atoms. Soon after Perdew and coworkers [18] realized that OEP is the exact-exchange potential of Kohn–Sham theory, i.e. the effective potential corresponding to exact-exchange energy (Eq. (1.13)). Today, the term OEP is generally used to denote the exchange-correlation potential of any orbital-dependent functional.

There are several different ways to derive the OEP equation and therefore different representations of essentially the same equation [19]. The following OEP equation is obtained by applying the chain rule for functional derivatives to $v_{\mathrm{XC}}(\mathbf{r}) = \delta E_{\mathrm{XC}}[\{\phi_i\}]/\delta\rho(\mathbf{r})$ twice ("c.c." denotes complex conjugate),

$$\sum_{i=1}^{N} \phi_i^*(\mathbf{r}') \left[v_{\mathrm{XC}}(\mathbf{r}') - \hat{u}_{\mathrm{XC}}(\mathbf{r}')\right] G_{\mathrm{KS},i}(\mathbf{r}',\mathbf{r})\phi_i(\mathbf{r})d\mathbf{r}' + \mathrm{c.c.} = 0, \qquad (1.17)$$

where $G_{\mathrm{KS},i}(\mathbf{r},\mathbf{r}')$ denotes the Kohn–Sham Green's function

$$G_{\mathrm{KS},i}(\mathbf{r}',\mathbf{r}) = \sum_{j=1,j\neq i}^{\infty} \frac{\phi_j(\mathbf{r}')\phi_j^*(\mathbf{r})}{\epsilon_i - \epsilon_j}, \qquad (1.18)$$

and $\hat{u}_{\mathrm{XC}}$ is an operator defined by

$$\hat{u}_{\mathrm{XC}}\phi_i(\mathbf{r}) = \frac{\delta E_{\mathrm{XC}}[\{\phi_i\}]}{\delta\phi_i^*(\mathbf{r})}. \qquad (1.19)$$

Equation (1.17) is an integral equation. It involves the full set of occupied and unoccupied Kohn–Sham orbitals and orbital energies, and has to be solved self-consistently along with the Kohn–Sham equations. This results in a set of com-

plicated integro-differential equations. Solving these equations is a highly nontrivial task. However, there are several ways to cope with this problem. OEP equations can be solved directly or different approximations as well as model potentials may be employed.

1.2.1 Direct solution of the OEP equation

A straightforward approach to finding the OEP is to solve the OEP equation directly. The Kohn–Sham potential is expanded in a basis set and then the total energy is minimized with respect to the expansion coefficients. One such approach was developed by Wu and Yang [20]. In their method, $v_{\text{eff}}(\mathbf{r})$ is obtained from the following equation:

$$v_{\text{eff}}(\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + v_0(\mathbf{r}) + \sum_{n=1}^{M} b_n g_n(\mathbf{r}), \qquad (1.20)$$

where v_0 is a fixed (Fermi–Amaldi) potential [21–23] constructed from the converged Hartree–Fock electron density,

$$v_0(\mathbf{r}) = -\frac{1}{N} v_{\text{H}}(\mathbf{r}), \qquad (1.21)$$

$\{g_n(\mathbf{r})\}$ is a set of auxiliary primitive Gaussian-like functions, and b_n are expansion coefficients.

At convergence, the exchange part of the OEP is given by

$$v_{\text{X}}(\mathbf{r}) = \sum_{n=1}^{M} b_n g_n(\mathbf{r}) + v_0(\mathbf{r}) - v_{\text{H}}(\mathbf{r}). \qquad (1.22)$$

Due to the ill-posed nature of the OEP problem in finite basis sets [24] the Wu–Yang method cannot be reliably implemented in actual calculations of many systems. For practical reasons, several approximations to OEP as well as model exchange potentials were derived.

1.2.2 Approximations to the OEP

The first successful approximation to the OEP was proposed in the early 1990s by Krieger, Li, and Iafrate [25]. They introduced an approximate solution to the OEP equation for the exchange-correlation potential which is today referred to as the KLI approximation

$$v_X^{KLI}(\mathbf{r}) = v_X^S(\mathbf{r}) + \frac{1}{\rho(\mathbf{r})} \sum_i |\phi_i(\mathbf{r})|^2 \langle \phi_i | v_X - \hat{K} | \phi_i \rangle, \tag{1.23}$$

where

$$v_X^S(\mathbf{r}) = -\frac{1}{2\rho(\mathbf{r})} \int \frac{|\gamma(\mathbf{r}, \mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r}' \tag{1.24}$$

is the Slater potential. The Krieger–Li–Iafrate (KLI) potential is considerably simpler than the full OEP and it yields total energies and Kohn–Sham eigenvalues that are in close agreement with the full OEP values in many cases.

The Slater potential is a common ingredient of several others approximations to the OEP. If one assumes that the Hartree–Fock and exchange-only Kohn–Sham determinants are identical one obtains the so-called localized Hartree–Fock (LHF) approximation to the exchange potential [26]

$$v_X^{LHF}(\mathbf{r}) = v_X^S(\mathbf{r}) + \frac{1}{\rho(\mathbf{r})} \sum_{i,j} \phi_i(\mathbf{r})\phi_j(\mathbf{r}) \langle \phi_i | v_X - \hat{K} | \phi_j \rangle. \tag{1.25}$$

Note that the LHF potential is more general than KLI potential because later can be obtained from LHF potential by neglecting off-diagonal elements of the Kohn–Sham Hamiltonian matrix.

The same approximation has been proposed independently by Gritsenko and Baerends in a different way under the name of "common energy denominator approximation" (CEDA) [27, 28].

The effective local potential method (ELP) [29, 30] is another equivalent of

the LHF approximation. The ELP potential minimizes the variance of operator $\sum_{i=1}^{occ} \left(v_\text{X} - \hat{K} \right)$ evaluated with the Hartree–Fock determinant converged in a given one-electron basis set, where $\hat{K}$ is the Hartree–Fock exchange operator [31].

1.2.3 Model potentials as approximations to OEP
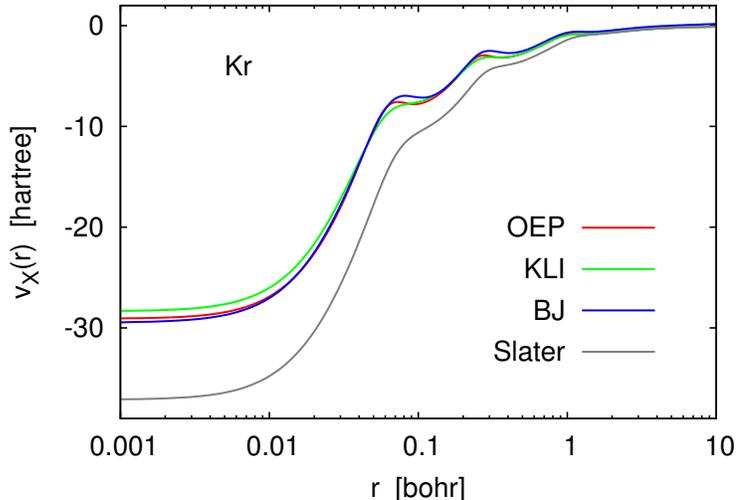
Figure 1.1: BJ, KLI and OEP potentials for Kr atom.

Along with direct approximations to the OEP equations there exist several model potentials for exchange. Among those perhaps the most popular was proposed by Becke and Johnson [32]:

$$v_\text{X}^\text{BJ}(\mathbf{r}) = v_\text{X}^\text{S}(\mathbf{r}) + \frac{k_\text{BJ}}{2\pi}, \tag{1.26}$$

where

$$k_\text{BJ} = \left(\frac{10}{3} \frac{\tau}{\rho} \right)^{1/2}, \tag{1.27}$$

and $\tau = \frac{1}{2} \sum_{i=1}^{N} |\nabla \phi_i|^2$ — kinetic energy density. This potential gives accurate exact-exchange energies via Eq. (1.13). Inclusion of τ-dependent term makes Becke–Johnson potential closer to the OEP but due to the correction term, $k_\text{BJ}/2\pi$, this potential has a wrong asymptotic behavior.

1.3 Objectives of the research

Despite numerous attempts to solve the OEP problem, there still exists no routine procedure for generating orbital-dependent exchange and exchange-correlation potentials. The main goal of this study is to develop new approximations to the OEP and compare them with existing models. In Chapter 2 we plan to study the Kohn–Sham potentials that follow from a simple idea of inverting the Kohn–Sham equations Eq. (1.9). We consider two cases. First, we use orbitals and orbital energies that are solutions of Kohn–Sham equations with a local Kohn–Sham potential. Second, we employ orbitals and orbital energies that do not correspond to any local potential. This procedure opens a route to efficient and simple calculation of orbital-averaged exchange and correlation potentials. In Chapter 2 we also propose a method for computing the functional derivatives of orbital-dependent functionals. In Chapter 3 we propose the solution of a long-standing problem of generating OEP in a black-box manner. We focus our attention on kinetic-energy-density dependence of the exchange potential. We devise a self-consistent procedure with a local exchange potential that gives Hartree–Fock electron density and investigate how close this approximation is to the OEP.

Bibliography

[1] C. A. Ullrich, *Time-Dependent Density Functional Theory. Concepts and Applications*, Oxford University Press, New York (2012).

[2] P. Hohenberg and W. Kohn, "Inhomogeneous electron gas", *Phys. Rev.* **136**, B864 (1964).

[3] M. Levy, "Electron densities in search of hamiltonians", *Phys. Rev. A* **26**, 1200 (1982).

[4] S. Kümmel and L. Kronik, "Orbital-dependent density functionals: Theory and applications", *Rev. Mod. Phys.* **80**, 3 (2008).

[5] J. P. Perdew, K. Burke, and M. Ernzerhof, "Generalized gradient approximation made simple", *Phys. Rev. Lett.* **77**, 3865 (1996).

[6] A. D. Becke, "Density-functional exchange-energy approximation with correct asymptotic behavior", *Phys. Rev. A* **38**, 3098 (1988).

[7] J. P. Perdew, "Accurate density functional for the energy: Real-space cutoff of the gradient expansion for the exchange hole", *Phys. Rev. Lett.* **55**, 1665 (1985).

[8] C. Lee, W. Yang, and R. G. Parr, "Development of the Colle–Salvetti correlation-energy formula into a functional of the electron density", *Phys. Rev. B* **37**, 785 (1988).

[9] H. B. Shore, J. H. Rose, and E. Zaremba, "Failure of the local exchange approximation in the evaluation of the H^- ground state", *Phys. Rev. B* **15**, 2858 (1977).

[10] L. A. Cole and J. P. Perdew, "Calculated electron affinities of the elements", *Phys. Rev. A* **25**, 1265 (1982).

[11] N. Rösch and S. B. Trickey, "Concerning the applicability of density functional methods to atomic and molecular negative ions", *J. Chem. Phys.* **106**, 8940 (1997).

[12] K. Schwarz, "Instability of stable negative ions in the $X\alpha$ method or other local density functional schemes", *Chem. Phys. Lett.* **57**, 605 (1978).

[13] J. P. Perdew and A. Zunger, "Self-interaction correction to density-functional approximations for many-electron systems", *Phys. Rev. B* **23**, 5048 (1981).

[14] A. Szabo and N. S. Ostlund, *Modern Quantum Chemistry. Introduction to Advanced Electronic Structure Theory*, McGraw-Hill, Inc., 1st ed. (1989).

[15] F. Jensen, *Introduction to Computational Chemistry*, John Wiley & Sons, New York (1999).

[16] R. T. Sharp and G. K. Horton, "A variational approach to the unipotential many-electron problem", *Phys. Rev.* **90**, 317 (1953).

[17] J. D. Talman and W. F. Shadwick, "Optimized effective atomic central potential", *Phys. Rev. A* **14**, 36 (1976).

[18] V. Sahni, J. Gruenebaum, and J. P. Perdew, "Study of the density-gradient expansion for the exchange energy", *Phys. Rev. B* **26**, 4371 (1982).

[19] E. Engel and R. M. Dreizler, *Density Functional Theory: An Advanced Course*, Springer, Berlin, Berlin (2011).

[20] Q. Wu and W. Yang, "A direct optimization method for calculating density functionals and exchange–correlation potentials from electron densities", *J. Chem. Phys.* **118**, 2498 (2003).

[21] E. Fermi and E. Amaldi, "Le orbite ∞ s degli elementi", *Mem. della Reale Accad. d'Itale* **6**, 117 (1934).

[22] R. G. Parr and S. K. Ghosh, "Toward understanding the exchange-correlation energy and total-energy density functionals", *Phys. Rev. A* **51**, 3564 (1995).

[23] P. W. Ayers, R. C. Morrison, and R. G. Parr, "Fermi–Amaldi model for exchange-correlation: atomic excitation energies from orbital energy differences", *Mol. Phys.* **103**, 2061 (2005).

[24] V. N. Staroverov, G. E. Scuseria, and E. R. Davidson, "Optimized effective potentials yielding Hartree–Fock energies and densities", *J. Chem. Phys.* **124**, 141103 (2006).

[25] J. B. Krieger, Y. Li, and G. J. Iafrate, "Construction and application of an accurate local spin-polarized Kohn–Sham potential with integer discontinuity: Exchange-only theory", *Phys. Rev. A* **45**, 101 (1992).

[26] F. Della Sala and A. Görling, "Efficient localized Hartree–Fock methods as effective exact-exchange Kohn–Sham methods for molecules", *J. Chem. Phys.* **115**, 5718 (2001).

[27] O. V. Gritsenko and E. J. Baerends, "Orbital structure of the Kohn–Sham exchange potential and exchange kernel and the field-counteracting potential for molecules in an electric field", *Phys. Rev. A* **64**, 042506 (2001).

[28] M. Grüning, O. V. Gritsenko, and E. J. Baerends, "Exchange potential from the common energy denominator approximation for the Kohn–Sham Green's func-

tion: Application to (hyper)polarizabilities of molecular chains", *J. Chem. Phys.* **116**, 6435 (2002).

[29] A. F. Izmaylov, V. N. Staroverov, G. E. Scuseria, E. R. Davidson, G. Stoltz, and E. Cancès, "The effective local potential method: Implementation for molecules and relation to approximate optimized effective potential techniques", *J. Chem. Phys.* **126**, 084107 (2007).

[30] V. N. Staroverov, G. E. Scuseria, and E. R. Davidson, "Effective local potentials for orbital-dependent density functionals", *J. Chem. Phys.* **125**, 081104 (2006).

[31] A. P. Gaiduk and V. N. Staroverov, "Virial exchange energies from model exact-exchange potentials", *J. Chem. Phys.* **128**, 204101 (2008).

[32] A. D. Becke and E. R. Johnson, "A simple effective potential for exchange", *J. Chem. Phys.* **124**, 221101 (2006).

Chapter 2

Efficient construction of orbital-averaged exchange and correlation potentials by inverting the Kohn–Sham equations

2.1 Introduction

The success of Kohn–Sham density-functional theory [1–3] is rooted in a highly efficient approximate treatment of electron correlation. Instead of solving the many-electron Schrödinger equation, the Kohn–Sham scheme requires solving a one-electron equation,

$$\left[-\frac{1}{2}\nabla^2 + v_{\text{eff}}(\mathbf{r}) \right] \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r}), \tag{2.1}$$

where $v_{\text{eff}}(\mathbf{r})$ is an effective potential, such that the electron density of an N-electron system is given by

$$\rho(\mathbf{r}) = \sum_{i=1}^{N} |\phi_i(\mathbf{r})|^2. \tag{2.2}$$

(By ϕ_i we mean the spatial part of the ith spin-orbital.) The potential $v_{\text{eff}}(\mathbf{r})$ is normally constructed as the sum

$$v_{\text{eff}}(\mathbf{r}) = v(\mathbf{r}) + v_{\text{H}}(\mathbf{r}) + v_{\text{XC}}(\mathbf{r}), \tag{2.3}$$

where $v(\mathbf{r})$ is the external potential (e.g., the potential of the nuclei), $v_{\text{H}}(\mathbf{r})$ is the Hartree (electrostatic) potential of $\rho(\mathbf{r})$, and $v_{\text{XC}}(\mathbf{r})$ is the exchange-correlation potential. The terms $v(\mathbf{r})$ and $v_{\text{H}}(\mathbf{r})$ are known exactly, but $v_{\text{XC}}(\mathbf{r})$ must be approximated. Direct approximations to $v_{\text{XC}}(\mathbf{r})$ in terms of ρ or ϕ_i and possibly ϵ_i $(i = 1, 2, \ldots, N)$ are known as *model* Kohn–Sham potentials [4–6].

Suppose we have a set of occupied canonical Kohn–Sham orbitals and their eigenvalues. Can we recover from this information the corresponding $v_{\text{eff}}(\mathbf{r})$ and hence $v_{\text{XC}}(\mathbf{r})$? From Eq. (2.1) we have the expression

$$v_{\text{eff}}(\mathbf{r}) = \frac{1}{2} \frac{\nabla^2 \phi_i(\mathbf{r})}{\phi_i(\mathbf{r})} + \epsilon_i, \tag{2.4}$$

which is formally valid for each real ϕ_i, but in practice can be used only for the nodeless lowest-eigenvalue orbital. Equation (2.4) has been employed for studying the exact Kohn–Sham potentials in spin-compensated two-electron systems such as the He atom and the H_2 molecule [7–11]. In finite-basis-set calculations, however, Eq. (2.4) leads to severe numerical difficulties [11–13].

Another way to extract $v_{\text{eff}}(\mathbf{r})$ from $\{\phi_i\}$ and $\{\epsilon_i\}$ is to multiply Eq. (2.1) by ϕ_i^*, sum over i from 1 to N, and divide through by ρ. The result may be written as [1]

$$v_{\text{eff}}(\mathbf{r}) = \frac{1}{\rho(\mathbf{r})} \sum_{i=1}^{N} \left[\frac{1}{2} \phi_i^*(\mathbf{r}) \nabla^2 \phi_i(\mathbf{r}) + \epsilon_i |\phi_i(\mathbf{r})|^2 \right]. \tag{2.5}$$

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[1] The right-hand sides of Eqs. (2.5) and (2.7) are real despite the presence of generally complex-valued individual terms. This is because the eigenfunctions ϕ_i of a static Kohn–Sham Hamiltonian are either real or occur in degenerate pairs which are complex conjugates of one another, so the products $\phi_i^* \nabla^2 \phi_i$ are also either real or occur in pairs of complex conjugates.

Observe that the potential of Eq. (2.5) may be regarded as a weighted average of N orbital-specific potentials of Eq. (2.4) with the normalized weights $|\phi_i(\mathbf{r})|^2/\rho(\mathbf{r})$. This observation will play a key role in situations where the potential defined by Eq. (2.4) is orbital-specific (i.e., different for different orbitals).

Equation (2.5), called here the Kohn–Sham inversion formula, is the basis of a popular numerical algorithm [14, 15] for determining the exchange-correlation potential from a given electron density. It has been also used for computing the functional derivative of the kinetic energy functional [16, 17]. In this work, we show that the Kohn–Sham inversion formula may be also used to construct orbital-averaged exchange-correlation potentials for orbital-dependent functionals. In particular, we point out an efficient method for constructing the Slater exchange potential. Finally, we show how Kohn–Sham inversion can be used to obtain functional derivatives of explicit density functionals without tedious calculations and to develop approximations to functional derivatives of orbital-dependent functionals.

2.2 Kohn–Sham inversion

Let us rewrite Eq. (2.5) more compactly as

$$v_{\text{eff}}(\mathbf{r}) = \frac{-\tau_L(\mathbf{r}) + \sum_{i=1}^{N} \epsilon_i |\phi_i(\mathbf{r})|^2}{\rho(\mathbf{r})}, \tag{2.6}$$

where

$$\tau_L(\mathbf{r}) = -\frac{1}{2} \sum_{i=1}^{N} \phi_i^*(\mathbf{r}) \nabla^2 \phi_i(\mathbf{r}) \tag{2.7}$$

is the Laplacian form of the kinetic energy density. From Eqs. (2.3) and (2.6),

$$v_{\text{XC}}(\mathbf{r}) = \frac{-\tau_L + \sum_{i=1}^{N} \epsilon_i |\phi_i(\mathbf{r})|^2}{\rho(\mathbf{r})} - v(\mathbf{r}) - v_{\text{H}}(\mathbf{r}). \tag{2.8}$$

For a given set of occupied canonical orbitals $\{\phi_i\}$, orbital energies $\{\epsilon_i\}$, and an external potential $v(\mathbf{r})$, Eq. (2.8) specifies an exchange-correlation potential. The meaning of this potential depends on whether $\{\phi_i\}$ and $\{\epsilon_i\}$ are solutions of a one-electron Schrödinger equation with an effective multiplicative $v_{\mathrm{XC}}(\mathbf{r})$ or with an orbital-specific potential. Let us consider these two possibilities in detail.

2.2.1 Inversion for multiplicative effective potentials

Local density functionals such as the local density approximation (LDA) and generalized gradient approximations (GGAs) such as the Perdew–Burke–Ernzerhof [18] (PBE) functional give rise to multiplicative exchange-correlation potentials defined by

$$v_{\mathrm{XC}}(\mathbf{r}) = \frac{\delta E_{\mathrm{XC}}[\rho]}{\delta \rho(\mathbf{r})}. \tag{2.9}$$

For orbitals and orbital energies that are solutions of the Kohn–Sham equations with potentials of this type, Eq. (2.8) is clearly an identity, but only in the basis set limit [10, 11, 19]. If the Kohn–Sham equations are solved in a finite basis set and the basis-set expansions for the orbitals are substituted into Eq. (2.8), the resulting potential may strongly deviate from the original $v_{\mathrm{XC}}(\mathbf{r})$. In particular, when the Kohn–Sham orbitals are expanded in a Gaussian basis set, the recovered potential exhibits large spurious oscillations (especially near the nucleus) and diverges at large r [10, 11, 19].

To illustrate this point, we have solved the Kohn–Sham equations for the krypton atom within the exchange-only LDA (LDA-X) scheme using the universal Gaussian basis set [20] (UGBS) of the composition $(30s, 20p, 14d)$. Then we used the self-consistent orbital and orbital energies to construct the LDA-X potential in two different ways: directly by definition,

$$v_{\mathrm{X}}^{\mathrm{LDA}}(\mathbf{r}) = -\frac{k_F(\mathbf{r})}{\pi}, \tag{2.10}$$
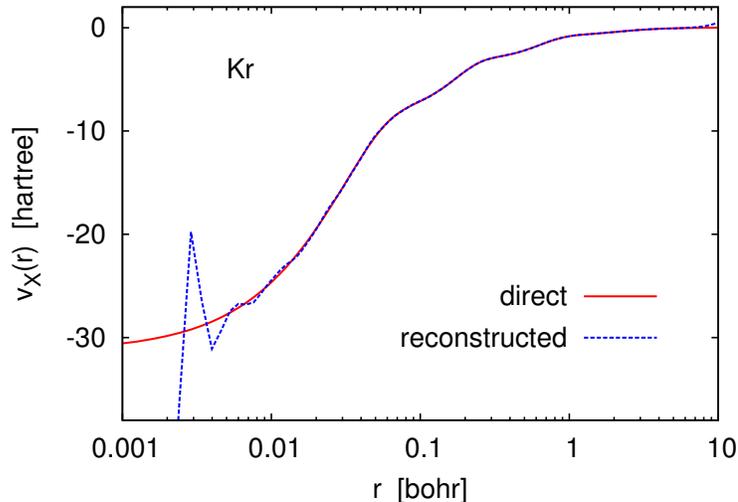
Figure 2.1: Exchange potentials constructed from the self-consistent LDA-X/UGBS orbitals and orbital energies in two different ways: by definition (original) and by the Kohn–Sham inversion formula (reconstructed).

where $k_F = (3\pi^2\rho)^{1/3}$, and by Eq. (2.8). Figure 2.1 shows that the two potentials coincide almost everywhere except at very small and very large r. Such artifacts are inevitable, and are even more dramatic in calculations with small and medium-size Gaussian basis sets, where the reconstructed potential may be distorted beyond recognition [10, 11, 19].

Fortunately, spurious oscillations and divergences of Kohn–Sham potentials obtained in finite basis sets by Eq. (2.8) can be almost completely eliminated using the method proposed by us recently in Ref. [21]. This method is based on the observation that the difference

$$\Delta v_{\rm osc}(\mathbf{r}) = v_{\rm reconstructed}(\mathbf{r}) - v_{\rm original}(\mathbf{r}), \tag{2.11}$$

called the "oscillation profile", is determined almost exclusively by the basis set in which $v_{\rm reconstructed}$ is obtained, not the nature of the potential. For example, the oscillation profile of an LDA-X potential is almost exactly the same as that of any other exchange or exchange-correlation potential for the same system, provided that both potentials are reconstructed using the same basis set. This means that the oscillation

profile obtained for one potential (A) may be subtracted from a raw reconstructed potential of another approximation (B) to obtain a smoothened potential B as

$$v^{\mathrm{B}}_{\mathrm{smooth}}(\mathbf{r}) = v^{\mathrm{B}}_{\mathrm{reconstructed}}(\mathbf{r}) - \Delta v^{\mathrm{A}}_{\mathrm{osc}}(\mathbf{r}). \tag{2.12}$$

The easiest way to generate $\Delta v_{\mathrm{osc}}(\mathbf{r})$ for a given basis set is by using a self-consistent LDA-X potential, which is the choice we adopt here. We will make use of this smoothening method in all subsequent examples.

Other than oscillations and divergences observed in finite-basis-set calculations, there is nothing remarkable about inverting Kohn–Sham equations with multiplicative potentials. Therefore, we will now move on to the more interesting case of orbital-specific potentials.

2.2.2   Inversion for orbital-specific potentials

Many modern density-functional approximations for the exchange-correlation energy depend on $\rho(\mathbf{r})$ implicitly through the Kohn–Sham orbitals [22–24]. Examples of such orbital-dependent functionals include the exact-exchange functional, functionals with a fraction of exact exchange such as the PBE hybrid [25, 26] (PBE0), and meta-GGAs that depend on the kinetic energy density such as the Tao–Perdew–Staroverov–Scuseria [27] (TPSS) approximation. When implicit functionals are employed, it is customary to adopt the orbital-dependent Kohn–Sham formalism [28–32] in which Eq. (2.1) is replaced with a one-electron Schrödinger equation

$$\left[-\frac{1}{2}\nabla^2 + v(\mathbf{r}) + v_{\mathrm{H}}(\mathbf{r}) + \hat{u}_{\mathrm{XC}} \right] \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r}), \tag{2.13}$$

where $\hat{u}_{\mathrm{XC}}$ is a one-electron operator defined by

$$\hat{u}_{\mathrm{XC}}\phi_i(\mathbf{r}) = \frac{\delta E_{\mathrm{XC}}[\{\phi_i\}]}{\delta \phi_i^*(\mathbf{r})}. \tag{2.14}$$

This operator may be either integral (as in the case of exact-exchange) or differential (e.g., for kinetic-energy-density-dependent functionals) [30, 33], but in either case it is such that $(\hat{u}_{XC}\phi_i)/\phi_i \neq (\hat{u}_{XC}\phi_j)/\phi_j$ for all orbital pairs except $\phi_i = \phi_j$. Thus, if we substitute the solutions of Eq. (2.13) into the Kohn–Sham inversion formula, we generally do not expect to obtain the functional derivative $\delta E_{XC}/\delta\rho$ even in the basis set limit.

To find out the meaning of the Kohn–Sham inversion formula for solutions of Eq. (2.13), we again multiply Eq. (2.13) by ϕ_i^*, sum over i from 1 to N, divide both sides by ρ, and write the result as

$$\bar{v}_{XC}(\mathbf{r}) = \frac{-\tau_L + \sum_{i=1}^{N} \epsilon_i |\phi_i(\mathbf{r})|^2}{\rho(\mathbf{r})} - v(\mathbf{r}) - v_H(\mathbf{r}). \qquad (2.15)$$

where

$$\bar{v}_{XC}(\mathbf{r}) \equiv \frac{1}{\rho(\mathbf{r})} \sum_{i=1}^{N} \phi_i^*(\mathbf{r}) \hat{u}_{XC}\phi_i(\mathbf{r}). \qquad (2.16)$$

By analogy with Eq. (2.8) we interpret $\bar{v}_{XC}(\mathbf{r})$ as an effective exchange-correlation *potential*. For explicit density functionals, $\bar{v}_{XC}$ reduces to the functional derivative $\delta E_{XC}/\delta\rho$, but for orbital-dependent functionals Eq. (2.16) defines a model potential that is distinct from $\delta E_{XC}/\delta\rho$. Orbital-averaged potentials of this type were discussed by Arbuznikov and coworkers [29–32].

The practical significance of Eq. (2.15) is that it can be used to construct orbital-averaged potentials $\bar{v}_{XC}$ simply by combining the standard ingredients τ_L, ϵ_i, ϕ_i, and v_H rather than by computing the quantities $\hat{u}_{XC}\phi_i$. As far as we are aware, this application of the Kohn–Sham inversion formula is proposed here for the first time.

Consider an important example: the exact-exchange functional. The orbital-dependent extension of the Kohn–Sham scheme for the exact-exchange functional

is equivalent to the Hartree–Fock method. The Hartree–Fock equations are

$$\left[-\frac{1}{2}\nabla^2 + v(\mathbf{r}) + v_{\text{H}}(\mathbf{r}) + \hat{K} \right] \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r}), \tag{2.17}$$

in which $\hat{K}$ is an integral operator defined by

$$\hat{K}\phi_i(\mathbf{r}) = \frac{\delta E_{\text{X}}^{\text{HF}}}{\delta \phi_i^*(\mathbf{r})} = -\frac{1}{2}\int \frac{\gamma(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}\phi_i(\mathbf{r}')\,d\mathbf{r}', \tag{2.18}$$

where

$$E_{\text{X}}^{\text{HF}} = -\frac{1}{4}\int d\mathbf{r} \int \frac{|\gamma(\mathbf{r}, \mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|}\,d\mathbf{r}' \tag{2.19}$$

is the Hartree–Fock exchange energy functional and

$$\gamma(\mathbf{r}, \mathbf{r}') = \sum_{j=1}^{N} \phi_j(\mathbf{r})\phi_j^*(\mathbf{r}') \tag{2.20}$$

is the one-electron reduced density matrix.

The orbital-averaged exchange potential corresponding to E_{X}^{HF} is known as the Slater potential [34],

$$v_{\text{X}}^{\text{S}}(\mathbf{r}) = \frac{1}{\rho(\mathbf{r})}\sum_{i=1}^{N} \phi_i^* \hat{K}\phi_i = -\frac{1}{2\rho(\mathbf{r})}\int \frac{|\gamma(\mathbf{r}, \mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|}\,d\mathbf{r}', \tag{2.21}$$

which is the statistical average of orbital-specific potentials $[\hat{K}\phi_i(\mathbf{r})]/\phi_i(\mathbf{r})$ weighted by $|\phi_i(\mathbf{r})|^2/\rho(\mathbf{r})$.

Direct construction of the Slater potential by Eq. (3.5) is computationally expensive because it involves integration over $\mathbf{r}'$ for each $\mathbf{r}$. Given a set of Hartree–Fock orbitals and eigenvalues, a much faster way to obtain v_{X}^{S} is by using the Kohn–Sham inversion formula,

$$v_{\text{X}}^{\text{S}}(\mathbf{r}) = \frac{-\tau_L + \sum_{i=1}^{N} \epsilon_i |\phi_i(\mathbf{r})|^2}{\rho(\mathbf{r})} - v(\mathbf{r}) - v_{\text{H}}(\mathbf{r}). \tag{2.22}$$
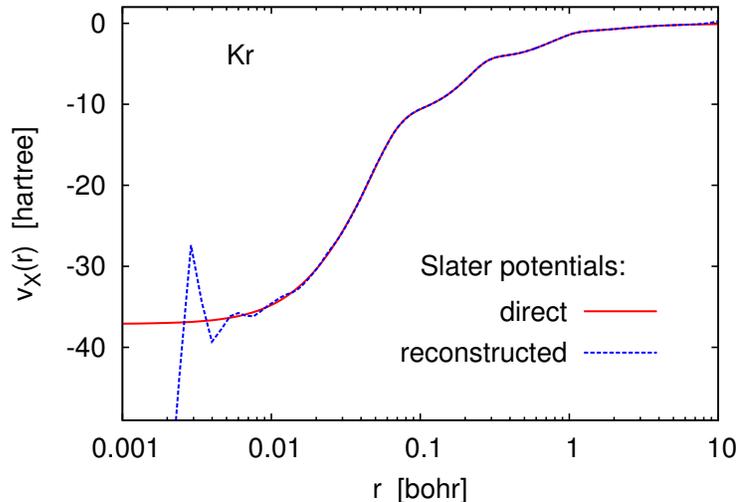
Figure 2.2: Slater potentials constructed from self-consistent Hartree–Fock UGBS orbitals by Eqs. (3.5) and (2.22). The 'smoothened' potential was obtained from the dashed curve by subtracting the LDA-X oscillation profile of Fig. 2.1. The dotted curve is almost exactly on top of the solid curve.

Calculation of the Slater potential by Eq. (2.22) is comparable in efficiency to insertion of the resolution of the identity into Eq. (3.5) [35], Equation (2.22) has been also discussed (in a different context) by Bulat *et al.*[36].

Numerical verification of Eq. (2.22) is made in Fig. 2.2, where we show Slater potentials constructed by definition (3.5) and by the Kohn–Sham inversion formula (2.22), before and after smoothening. The agreement between the two methods (after smoothening) is almost perfect.

Obviously, the Kohn–Sham inversion formula can be used to construct orbital-averaged potentials for *any* orbital-dependent functional. Examples of orbital-averaged Hartree–Fock (Slater), TPSS and PBE0 exchange potentials are shown in Fig. 2.3. Here each $\bar{v}_X(\mathbf{r})$ was obtained by substituting into Eq. (2.15) the self-consistent Kohn–Sham orbitals and orbital eigenvalues obtained by diagonalizing the corresponding exchange-only Kohn–Sham Hamiltonian. Also shown is the PBE exchange potential constructed by Eq. (2.8). These potentials are compared to the exact-exchange optimized effective potential (OEP) taken from the work of Engel

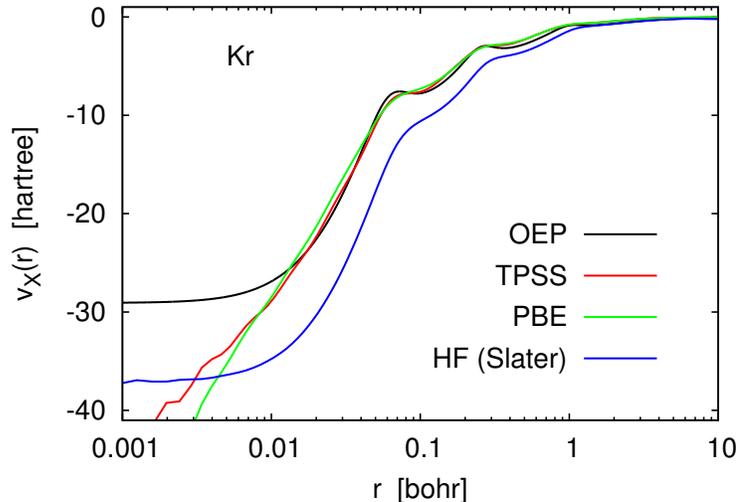Figure 2.3: Various orbital-averaged exchange potentials computed in the UGBS in comparison with the numerical exchange-only OEP. Most basis-set artifacts in the reconstructed potentials were removed by subtracting the LDA-X oscillation profile of Figure 2.1 according to Eq. (2.12).

and coworkers [37, 38], It is interesting to note that the PBE-X and orbital-averaged TPSS-X potentials are better approximations to the OEP than the PBE0-X potential. Note also that the orbital-averaged PBE0-X potential in Fig. 2.3 appears to tend to $-\infty$ as $r \to 0$. This is correct because Kohn–Sham potentials derived from GGAs are in fact singular at the nucleus [7, 8], A similar behavior is observed for the orbital-averaged TPSS-X potential, although to a lesser extent.

Kohn–Sham inversion can be also used to construct correlation potentials. Examples of such potentials for several explicit and orbital-dependent functionals are shown in Fig. 2.4. Here each $v_C(\mathbf{r})$ was obtained as the difference $v_{XC}(\mathbf{r}) - v_X(\mathbf{r})$, where $v_{XC}(\mathbf{r})$ and $v_X(\mathbf{r})$ were constructed using the same density. Specifically, each $v_{XC}(\mathbf{r})$ was obtained by the Kohn–Sham inversion procedure of Eq. (2.8) from the corresponding self-consistent orbitals and orbital eigenvalues. Each $v_X(\mathbf{r})$ was obtained by substituting into Eq. (2.8) the Kohn–Sham orbitals and orbital eigenvalues obtained by diagonalizing the corresponding exchange-only Kohn–Sham Hamiltonian constructed with the self-consistent exchange-correlation orbitals. The advantage of
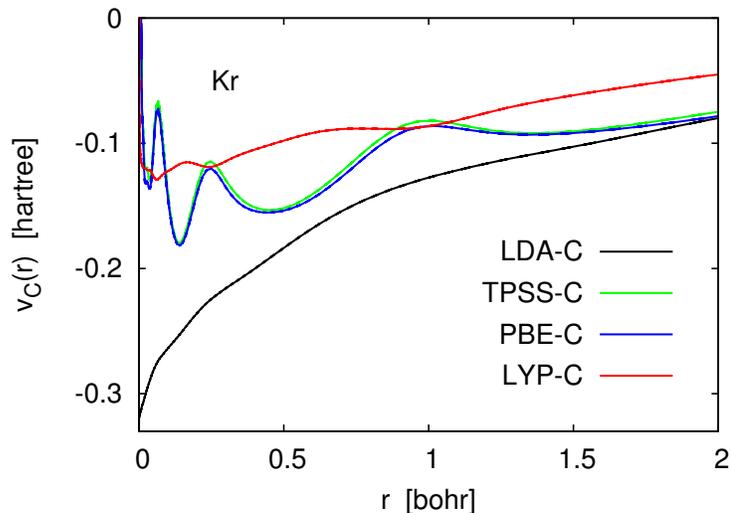
Figure 2.4: Various correlation potentials constructed as the difference $v_{\mathrm{XC}}(\mathbf{r}) - v_{\mathrm{X}}(\mathbf{r})$, where $v_{\mathrm{XC}}(\mathbf{r})$ and $v_{\mathrm{X}}(\mathbf{r})$ were obtained by Kohn–Sham inversion using the UGBS.

computing LDA-C, PBE-C, TPSS-C, and LYP-C potentials in this way is that it requires much less work than direct evaluation of the functional derivatives of the corresponding functionals. Observe that the correlation potentials in Fig. 2.4 have no spurious oscillations because the basis-set artifacts present in $v_{\mathrm{XC}}(\mathbf{r})$ and $v_{\mathrm{X}}(\mathbf{r})$ cancel each other automatically when taking the difference.

To summarize the content of this section, we showed that orbital-averaged potentials defined by Eq. (2.16) can be always constructed simply by inverting the Kohn–Sham equations using Eq. (2.15). This observation should be useful for practical calculations involving the Slater potential and other orbital-dependent potentials derived from hybrid functionals and meta-GGAs.

2.3 Discussion

2.3.1 The role of orbital eigenvalues in the Kohn–Sham inversion formula

The Kohn–Sham inversion formula (3.10) is related to another exact expression involving the potential $v_{\text{eff}}(\mathbf{r})$ and occupied Kohn–Sham orbitals—the differential virial theorem for noninteracting electrons [39–41], also known as the force balance equation [42, 43], In Refs. [44] and [45] we showed that this theorem can be written as

$$\nabla v_{\text{eff}}(\mathbf{r}) = -\frac{\nabla \tau_L(\mathbf{r}) + \sum_{i=1}^{N} \nabla^2 \phi_i(\mathbf{r}) \nabla \phi_i^*(\mathbf{r})}{\rho(\mathbf{r})}, \tag{2.23}$$

where ϕ_i are canonical Kohn–Sham orbitals. Unlike Eq. (3.10), Eq. (2.23) does not contain orbital eigenvalues. The absence of eigenvalues in Eq. (2.23) means that the occupied Kohn–Sham orbitals alone determine, up to a vertical shift, the potential $v_{\text{eff}}(\mathbf{r})$ and, if the external potential is known, the potential $v_{\text{XC}}(\mathbf{r})$. In practice, the presence of orbital eigenvalues in Eq. (3.10) is beneficial because it affords direct access to $v_{\text{eff}}(\mathbf{r})$, whereas Eq. (2.23) yields only the gradient of $v_{\text{eff}}(\mathbf{r})$.

It is known [46, 47] that canonical exchange-only OEP orbitals are similar to the canonical Hartree–Fock orbitals. By Eq. (2.23), the similarity of OEP and Hartree–Fock orbitals implies that the Kohn–Sham potentials corresponding to OEP and Hartree–Fock densities also should be similar. However, if we substitute Hartree–Fock orbitals and orbital energies into Eq. (2.15), we obtain the Slater potential of Eq. (2.22), which is much more negative than the OEP (see Fig. 2.3). This suggests that, from the point of view of Eq. (2.15), the difference between the OEP and the Slater potential lies mostly in the orbital energies. Therefore, we should be able to turn the Slater potential built with Hartree–Fock orbitals into a good OEP approximation simply by varying the values of ϵ_i in Eq. (2.15) while keeping the orbitals

Figure 2.5: Model exchange potentials for the Kr atom constructed by the Kohn–Sham inversion formula using the same set of orbitals (Hartree–Fock) and various sets of self-consistent orbital eigenvalues. Basis set: UGBS. The reference OEP-X potential (black line) is from Refs. [37, 38].

fixed.

Figure 2.5 demonstrates that one can indeed obtain good approximations to the OEP by substituting into Eq. (2.15) a set of Hartree–Fock orbitals and OEP-like orbital energies obtained from LDA-X or TPSS-X calculations. This approach works because the LDA-X and TPSS-X orbital energies are closer to the corresponding OEP eigenvalues than the Hartree–Fock energies. Conversely, one can start with a good approximation to the OEP (e.g., the orbital-averaged TPSS-X potential) and turn it into a Slater-like potential simply by using Hartree–Fock orbital energies instead of TPSS-X eigenvalues (see Fig. 2.6).

2.3.2   Approximation of functional derivatives of orbital-dependent functionals

The above analysis suggests that the shape of a Kohn–Sham potential as defined by Eq. (2.8) or (2.15) can be effectively controlled by varying orbital eigenvalues. Let us seize this idea and develop it into a practical approximation to the exact-exchange
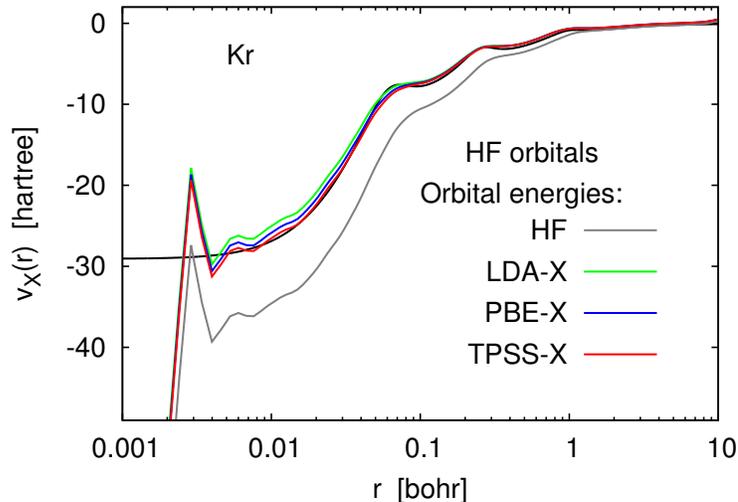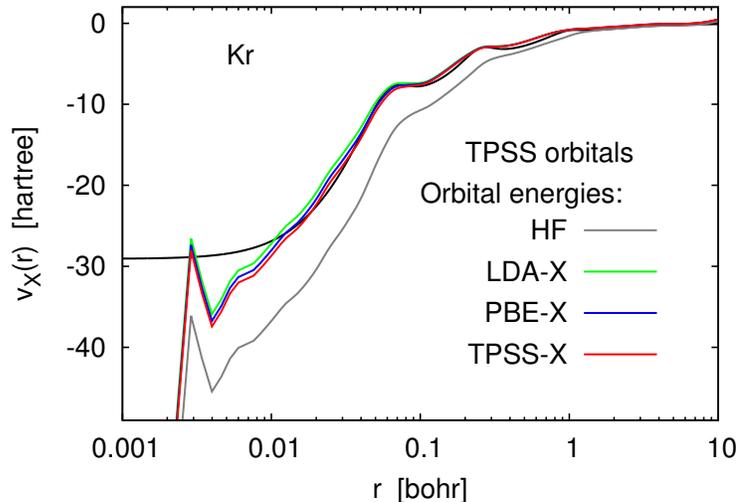
Figure 2.6: Model exchange potentials for the Kr atom constructed by the Kohn–Sham inversion formula using the same set of orbitals (TPSS-X) and various sets of self-consistent orbital eigenvalues. Basis set: UGBS. The reference OEP-X potential (black line) is from Refs. [37, 38].

OEP.

Following Della Sala and Görling, [35] we assume that the occupied eigenfunctions of the Kohn–Sham OEP Hamiltonian are the same as the eigenfunctions of the Hartree–Fock Hamiltonian, i.e., $\phi_i = \phi_i^{\mathrm{HF}}$. Under this assumption, we can use the Kohn–Sham inversion formula to approximate the OEP with the model potential

$$v_{\mathrm{X}}^{\mathrm{model}} = \frac{-\tau_L^{\mathrm{HF}} + \sum_{i=1}^{N} \epsilon_i |\phi_i^{\mathrm{HF}}|^2}{\rho^{\mathrm{HF}}} - v - v_{\mathrm{H}}^{\mathrm{HF}}, \qquad (2.24)$$

where $v_{\mathrm{H}}^{\mathrm{HF}}$ is the Hartree potential built from the Hartree–Fock orbitals and ϵ_i are approximate eigenvalues of the OEP orbitals which at this point are unknown.

Next consider a different potential constructed in the same manner as $v_{\mathrm{X}}^{\mathrm{model}}$ but using Hartree–Fock orbitals *and* orbital energies. As explained in Sec. 2.2.2, this is the Slater potential built from the Hartree–Fock orbitals,

$$v_{\mathrm{X}}^{\mathrm{S,HF}} = \frac{-\tau_L^{\mathrm{HF}} + \sum_{i=1}^{N} \epsilon_i^{\mathrm{HF}} |\phi_i^{\mathrm{HF}}|^2}{\rho^{\mathrm{HF}}} - v - v_{\mathrm{H}}^{\mathrm{HF}}. \qquad (2.25)$$

According to Eqs. (2.24) and (2.25), the only difference between v_X^{model} and $v_X^{\text{S,HF}}$ is in the orbital energies. We already know that $v_X^{\text{S,HF}}$ is not a good approximation to the OEP, but expect v_X^{model} to be much better with a proper choice of ϵ_i values.

Now let us subtract Eq. (2.25) from Eq. (2.24) and write the result as

$$v_X^{\text{model}}(\mathbf{r}) = v_X^{\text{S,HF}}(\mathbf{r}) + \frac{1}{\rho^{\text{HF}}(\mathbf{r})} \sum_{i=1}^{N} (\epsilon_i - \epsilon_i^{\text{HF}})|\phi_i^{\text{HF}}(\mathbf{r})|^2. \tag{2.26}$$

A model exchange potential of this form (with ϕ_i in place of ϕ_i^{HF}) was discussed by Nagy [48] as an equivalent of the Krieger–Li–Iafrate [49] (KLI) potential. Equation (2.26) suggests that we define ϵ_i as the eigenvalues of v_X^{model}. In that case, one can determine them by iterative solution of the Kohn–Sham equations with v_X^{model}, continuing until the potential is self-consistent.

The idea that led us to Eq. (2.26) can be readily extended to any orbital-dependent functional. In general, we obtain a model potential of the form

$$v_{\text{XC}}^{\text{model}}(\mathbf{r}) = \bar{v}_{\text{XC}}^0(\mathbf{r}) + \frac{1}{\rho^0(\mathbf{r})} \sum_{i=1}^{N} (\epsilon_i - \epsilon_i^0)|\phi_i^0(\mathbf{r})|^2, \tag{2.27}$$

where ϕ_i^0 and ϵ_i^0 are solutions of the orbital-specific Kohn–Sham Eq. (2.13), $\bar{v}_{\text{XC}}^0$ is the orbital-averaged potential built from ϕ_i^0, and ϵ_i are the eigenvalues of $v_{\text{XC}}^{\text{model}}$ which are initially unknown but can be determined iteratively. By analogy with Eq. (2.26), which defines a KLI-like approximation to the exact-exchange OEP, we expect Eq. (2.27) to yield good approximations to the functional derivatives of hybrid and meta-GGA exchange-correlation energy functionals such as PBE0 and TPSS. Our approach is more practical than the suggestion to set up and solve an OEP-like integral equation for the functional derivative of an orbital-dependent functional [50].

2.4 Conclusion

We have shown that inversion of Kohn–Sham equations provides a convenient practical method for computing functional derivatives of explicit density functionals and for constructing orbital-averaged potentials for orbital-dependent functionals. The orbital-averaged exchange potential $\bar{v}_X$ corresponding to the exact-exchange functional (the Slater potential) is a crude approximation to the exchange-only OEP (the true functional derivative of the exact-exchange energy functional), but for hybrid and kinetic-energy-density-dependent functionals such as PBE0 and TPSS, the agreement between $\bar{v}_X$ and $\delta E_X/\delta\rho$ is significantly better (see Fig. 2.3). We believe that the orbital-averaged potentials for the PBE0 and TPSS functionals are shown in this work for the first time.

Orbital-averaged potentials constructed by Kohn–Sham inversion from a fixed set of orbitals can vary considerably depending on the choice of eigenvalues. This observation gave us a valuable insight into the structure of the OEP which we used for constructing explicit approximations to functional derivatives of orbital-dependent functionals. In the case of the exact-exchange functional, this idea leads to the model exchange potential of Eq. (2.26) whose analytic structure is similar to that of the KLI approximation. In our future work, we plan to investigate eigenvalue-dependent model potentials of Eq. (2.27) as approximations to the functional derivatives of hybrid functionals and meta-GGAs.

Bibliography

[1] W. Kohn and L. J. Sham, "Self-consistent equations including exchange and correlation effects", *Phys. Rev.* **140**, A1133 (1965).

[2] P. Hohenberg, W. Kohn, and L. Sham, "The beginnings and some thoughts on the future", *Adv. Quant. Chem.* **21**, 7 (1990).

[3] E. Engel and R. M. Dreizler, *Density Functional Theory: An Advanced Course*, Springer, Berlin, Berlin (2011).

[4] R. Leeuwen, O. V. Gritsenko, and E. J. Baerends, "Analysis and modelling of atomic and molecular Kohn–Sham potentials", *Top. Curr. Chem.* **180**, 107 (1996).

[5] O. Gritsenko, P. Schipper, and E. Baerends, "Approximation of the exchange-correlation Kohn–Sham potential with a statistical average of different orbital model potentials", *Chem. Phys. Lett.* **302**, 199 (1999).

[6] V. N. Staroverov, "A family of model Kohn–Sham potentials for exact exchange", *J. Chem. Phys.* **129**, 134103 (2008).

[7] C. J. Umrigar and X. Gonze, "Accurate exchange-correlation potentials and total-energy components for the helium isoelectronic series", *Phys. Rev. A* **50**, 3827 (1994).

[8] C. Filippi, X. Gonze, and C. J. Umrigar, *Recent Developments and Applications of Modern Density Functional Theory*, Theoretical and Computational Chemistry, Elsevier Science (1996).

[9] O. V. Gritsenko and E. J. Baerends, "Electron correlation effects on the shape of the Kohn–Sham molecular orbital", *Theor. Chem. Acc.* **96**, 44 (1997).

[10] P. R. T. Schipper, O. V. Gritsenko, and E. J. Baerends, "Kohn–Sham potentials corresponding to slater and gaussian basis set densities", *Theor. Chem. Acc.* **98**, 16 (1997).

[11] M. E. Mura, P. J. Knowles, and C. A. Reynolds, "Accurate numerical determination of Kohn–Sham potentials from electronic densities: I. two-electron systems", *J. Chem. Phys.* **106**, 9659 (1997).

[12] P. de Silva and T. A. Wesolowski, "Pure-state noninteracting v-representability of electron densities from Kohn–Sham calculations with finite basis sets", *Phys. Rev. A* **85**, 032518 (2012).

[13] M. J. G. Peach, D. G. J. Griffiths, and D. J. Tozer, "On the evaluation of the non-interacting kinetic energy in density functional theory", *J. Chem. Phys.* **136**, 144101 (2012).

[14] R. van Leeuwen and E. J. Baerends, "Exchange-correlation potential with correct asymptotic behavior", *Phys. Rev. A* **49**, 2421 (1994).

[15] O. V. Gritsenko, R. van Leeuwen, and E. J. Baerends, "Molecular Kohn–Sham exchange-correlation potential from the correlated *ab initio* electron density", *Phys. Rev. A* **52**, 1870 (1995).

[16] R. A. King and N. C. Handy, "Kinetic energy functionals from the Kohn–Sham potential", *Phys. Chem. Chem. Phys.* **2**, 5049 (2000).

[17] J. D. Goodpaster, N. Ananth, F. R. Manby, and T. F. Miller, "Exact nonadditive kinetic potentials for embedded density functional theory", *J. Chem. Phys.* **133**, 084103 (2010).

[18] J. P. Perdew, K. Burke, and M. Ernzerhof, "Generalized gradient approximation made simple", *Phys. Rev. Lett.* **77**, 3865 (1996).

[19] C. R. Jacob, "Unambiguous optimization of effective potentials in finite basis sets", *J. Chem. Phys.* **135**, 244102 (2011).

[20] E. V. R. de Castro and F. E. Jorge, "Accurate universal gaussian basis set for all atoms of the periodic table", *J. Chem. Phys.* **108**, 5225 (1998).

[21] A. P. Gaiduk, I. G. Ryabinkin, and V. N. Staroverov, "Removal of basis-set artifacts in Kohn–Sham potentials recovered from electron densities", *J. Chem. Theory and Comput.* **accepted** (2013).

[22] T. Grabo, T. Kreibich, S. Kurth, and E. K. U. Gross, *Strong Coulomb Correlations in Electronic Structure Calculations: Beyond the Local Density Approximation*, Advances in Condensed Matter Science, Gordon and Breach Science Publishers (2000).

[23] E. Engel, *A Primer in Density Functional Theory*, Lecture Notes in Physics, Springer (2003).

[24] S. Kümmel and L. Kronik, "Orbital-dependent density functionals: Theory and applications", *Rev. Mod. Phys.* **80**, 3 (2008).

[25] M. Ernzerhof and G. E. Scuseria, "Assessment of the Perdew–Burke–Ernzerhof exchange-correlation functional", *J. Chem. Phys.* **110**, 5029 (1999).

[26] C. Adamo and V. Barone, "Toward reliable density functional methods without adjustable parameters: The PBE0 model", *J. Chem. Phys.* **110**, 6158 (1999).

[27] J. Tao, J. P. Perdew, V. N. Staroverov, and G. E. Scuseria, "Climbing the density functional ladder: Nonempirical meta-generalized gradient approximation designed for molecules and solids", *Phys. Rev. Lett.* **91**, 146401 (2003).

[28] R. Neumann, R. H. Nobes, and N. C. Handy, "Exchange functionals and potentials", *Mol. Phys.* **87**, 1 (1996).

[29] A. V. Arbuznikov, M. Kaupp, V. G. Malkin, R. Reviakine, and O. L. Malkina, "Validation study of meta-gga functionals and of a model exchange-correlation potential in density functional calculations of epr parameters", *Phys. Chem. Chem. Phys.* **4**, 5467 (2002).

[30] A. V. Arbuznikov and M. Kaupp, "The self-consistent implementation of exchange-correlation functionals depending on the local kinetic energy density", *Chem. Phys. Lett.* **381**, 495 (2003).

[31] A. V. Arbuznikov, M. Kaupp, and H. Bahmann, "From local hybrid functionals to "localized local hybrid" potentials: Formalism and thermochemical tests", *J. Chem. Phys.* **124**, 204102 (2006).

[32] A. Arbuznikov, "Hybrid exchange correlation functionals and potentials: Concept elaboration", *J. Struct. Chem.* **48**, S1 (2007).

[33] A. D. Becke, "A density-functional approximation for relativistic kinetic energy", *The Journal of Chemical Physics* **131**, 244118 (2009).

[34] J. C. Slater, "A simplification of the Hartree–Fock method", *Phys. Rev.* **81**, 385 (1951).

[35] F. Della Sala and A. Görling, "Efficient localized Hartree–Fock methods as effective exact-exchange Kohn–Sham methods for molecules", *J. Chem. Phys.* **115**, 5718 (2001).

[36] F. A. Bulat, M. Levy, and P. Politzer, "Average local ionization energies in the Hartree–Fock and Kohn–Sham theories", *Phys. Chem. A* **113**, 1384 (2009).

[37] E. Engel and S. H. Vosko, "Accurate optimized-potential-model solutions for spherical spin-polarized atoms: Evidence for limitations of the exchange-only local spin-density and generalized-gradient approximations", *Phys. Rev. A* **47**, 2800 (1993).

[38] E. Engel and R. M. Dreizler, "From explicit to implicit density functionals", *J. Comput. Chem.* **20**, 31 (1999).

[39] R. Baltin, "Hypervirial relations between ground-state particle density, kinetic energy density, and potential in three dimensions", *Phys. Lett. A* **117**, 317 (1986).

[40] A. Holas and N. H. March, "Exact exchange-correlation potential and approximate exchange potential in terms of density matrices", *Phys. Rev. A* **51**, 2040 (1995).

[41] A. Holas and N. H. March, "Exact theorems concerning noninteracting kinetic energy density functional in d dimensions and their implications for gradient expansions", *Int. J. Quantum Chem.* **56**, 371 (1995).

[42] N. March, "Localization via density functionals", *Top. Curr. Chem.* **203**, 201 (1999).

[43] V. Sahni, *Quantal Density Functional Theory*, Springer, Berlin (2004).

[44] I. G. Ryabinkin and V. N. Staroverov, "Determination of Kohn–Sham effective potentials from electron densities using the differential virial theorem", *J. Chem. Phys.* **137**, 164113 (2012).

[45] I. G. Ryabinkin and V. N. Staroverov, "Exact relations between the electron

density and external potential for systems of interacting and noninteracting electrons", *Int. J. Quant. Chem.* **113**, 1626 (2013).

[46] A. Görling and M. Ernzerhof, "Energy differences between Kohn–Sham and Hartree–Fock wave functions yielding the same electron density", *Phys. Rev. A* **51**, 4501 (1995).

[47] A. Holas and N. March, "Exchange and correlation in density functional theory of atoms and molecules", *Top. Curr. Chem.* **180**, 57 (1996).

[48] A. Nagy, "Alternative derivation of the Krieger–Li–Iafrate approximation to the optimized-effective-potential method", *Phys. Rev. A* **55**, 3465 (1997).

[49] J. B. Krieger, Y. Li, and G. J. Iafrate, "Construction and application of an accurate local spin-polarized Kohn–Sham potential with integer discontinuity: Exchange-only theory", *Phys. Rev. A* **45**, 101 (1992).

[50] M. Miao, "Density-functional derivatives from exact orbital functionals", *Chem. Phys. Lett.* **324**, 447 (2000).

Chapter 3

Accurate and efficient approximation to the optimized effective potential for exchange

3.1 Introduction

In this chapter we suggest an essentially exact, robust, practical method for construct-
ing the optimized effective potential (OEP) [1] of the exact-exchange Kohn–Sham
scheme. OEPs naturally arise in the theory of orbital-dependent functionals [2]—one
of the most promising modern density-functional techniques—and are of significant
practical interest because they afford qualitatively better description of molecular
properties than local and semilocal approximations [1, 2].

The exchange-only OEP is defined [3] as the multiplicative potential $v_{\mathrm{X}}^{\mathrm{QEP}}(\mathbf{r})$
that minimizes the Hartree–Fock (HF) total energy expression within the Kohn–
Sham scheme. Equivalently [4], the OEP is the functional derivative $v_{\mathrm{X}}^{\mathrm{QEP}}(\mathbf{r}) \equiv$
$\delta E_{\mathrm{X}}^{\mathrm{exact}}/\delta\rho(\mathbf{r})$, where $E_{\mathrm{X}}^{\mathrm{exact}}$ is the HF exchange energy expression written in terms
of Kohn–Sham orbitals (an implicit density functional) and $\rho(\mathbf{r})$ is the electron den-

sity. To obtain $v_X^{\mathrm{OEP}}(\mathbf{r})$ in a formally correct manner, one has to solve the OEP integral equation [1]. Unfortunately, every attempt to do this runs into severe numerical difficulties because the problem is ill-posed [5] and has infinitely many solutions in finite basis sets [5, 6]. Recent advances in OEP methods [7–14] have alleviated some of these difficulties but, even today, flawless OEPs can be obtained only case by case, with painstaking effort.

In the absence of an efficient OEP solver, various approximations to the OEP have long been used as pragmatic alternatives. These include the Krieger–Li–Iafrate (KLI) [15], localized Hartree–Fock (LHF) [16], and related approximations [17–20], as well as model potentials for exact exchange [21–25], of which the Becke–Johnson (BJ) approximation [23] is the most popular. The LHF method is equivalent [20] to the common energy denominator approximation (CEDA) [17] and to the effective local potential (ELP) scheme [19].

In a parallel development, several workers studied [26–29] the HF method as a density-functional problem and occasionally observed [30, 31] that Kohn–Sham exchange-correlation potentials corresponding to HF electron densities (HFXC potentials for short) were very close to OEPs. However, this observation had little impact on the OEP impasse because existing methods for determining exchange-correlation potentials from densities (see, for instance, Refs. [32–36]) face the same basis-set artifacts [37] and numerical challenges [38] as attempts to solve the OEP equation.

In this work, we devise a practical, artifact-free procedure which allows one to compute the HFXC potential efficiently for any atom or molecule. Then we use our method to show, on a variety of systems, that HFXC potentials are not just close but practically indistinguishable from OEPs. The significance of our approach is that it has the same reliability and computational cost as the KLI, LHF, and BJ schemes, but its accuracy is vastly superior.

The proposed method originated with our observation that the quantity ($\tau^{\mathrm{HF}} -$

$\tau)/\rho$, where τ and τ^{HF} are the Kohn–Sham and HF kinetic energy densities, reproduces that part of atomic shell structure of exact-exchange potentials which is missing in the KLI and LHF approximations. While searching for a rigorous explanation, we realized that we were dealing with the HFXC potential and arrived at the following argument.

3.2   The HFXC potential

Consider the HF description of a closed-shell N-electron system. The exchange energy of this system is

$$E_{\mathrm{X}}^{\mathrm{HF}} = -\frac{1}{4} \int d\mathbf{r} \int \frac{|\gamma^{\mathrm{HF}}(\mathbf{r},\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|} \, d\mathbf{r}', \tag{3.1}$$

where $\gamma^{\mathrm{HF}}(\mathbf{r},\mathbf{r}') = \sum_{i=1}^{N} \phi_i^{\mathrm{HF}}(\mathbf{r})\phi_i^{\mathrm{HF}*}(\mathbf{r}')$ is the spinless reduced density matrix and ϕ_i^{HF} is the spatial part of the ith canonical HF spin-orbital. The HF electron density is given by $\rho^{\mathrm{HF}}(\mathbf{r}) = \sum_{i=1}^{N} |\phi_i^{\mathrm{HF}}(\mathbf{r})|^2$. The orbitals ϕ_i^{HF} are the lowest-eigenvalue solutions of the HF equations

$$\left[-\frac{1}{2}\nabla^2 + v(\mathbf{r}) + v_{\mathrm{H}}(\mathbf{r}) + \hat{K} \right] \phi_i^{\mathrm{HF}}(\mathbf{r}) = \epsilon_i^{\mathrm{HF}} \phi_i^{\mathrm{HF}}(\mathbf{r}), \tag{3.2}$$

where $v(\mathbf{r})$ is the external potential (e.g., the potential of the nuclei), $v_{\mathrm{H}}(\mathbf{r}) = \int \rho^{\mathrm{HF}}(\mathbf{r}')|\mathbf{r}-\mathbf{r}'|^{-1} \, d\mathbf{r}'$ is the Hartree (electrostatic) potential of $\rho^{\mathrm{HF}}(\mathbf{r})$, and $\hat{K}$ is the Fock exchange operator defined by

$$\hat{K}\phi_i^{\mathrm{HF}}(\mathbf{r}) = \frac{\delta E_{\mathrm{X}}^{\mathrm{HF}}}{\delta \phi_i^{\mathrm{HF}*}(\mathbf{r})} = -\frac{1}{2} \int \frac{\gamma^{\mathrm{HF}}(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \phi_i^{\mathrm{HF}}(\mathbf{r}') \, d\mathbf{r}'. \tag{3.3}$$

Let us multiply Eq. (3.2) by $\phi_i^{\mathrm{HF}*}$, sum over i from 1 to N, and divide through by

ρ^{HF}. The result is

$$\frac{\tau_L^{\mathrm{HF}}}{\rho^{\mathrm{HF}}} + v + v_{\mathrm{H}} + v_{\mathrm{S}}^{\mathrm{HF}} = \frac{1}{\rho^{\mathrm{HF}}} \sum_{i=1}^{N} \epsilon_i^{\mathrm{HF}} |\phi_i^{\mathrm{HF}}|^2, \tag{3.4}$$

where $\tau_L^{\mathrm{HF}}(\mathbf{r}) = -\frac{1}{2} \sum_{i=1}^{N} \phi_i^{\mathrm{HF*}}(\mathbf{r}) \nabla^2 \phi_i^{\mathrm{HF}}(\mathbf{r})$ is the Laplacian form of the HF kinetic energy density and

$$v_{\mathrm{S}}^{\mathrm{HF}}(\mathbf{r}) = -\frac{1}{2\rho^{\mathrm{HF}}(\mathbf{r})} \int \frac{|\gamma^{\mathrm{HF}}(\mathbf{r}, \mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r}'. \tag{3.5}$$

is the Slater potential (the orbital-averaged $\hat{K}$ operator) [39] built from the HF orbitals. The quantity on the right-hand side of Eq. (3.4) is known as the HF average local ionization energy [40],

$$\bar{I}^{\mathrm{HF}}(\mathbf{r}) = \frac{1}{\rho^{\mathrm{HF}}(\mathbf{r})} \sum_{i=1}^{N} \epsilon_i^{\mathrm{HF}} |\phi_i^{\mathrm{HF}}(\mathbf{r})|^2. \tag{3.6}$$

Note that $\tau_L^{\mathrm{HF}} = \tau^{\mathrm{HF}} - \frac{1}{4} \nabla^2 \rho^{\mathrm{HF}}$, where

$$\tau^{\mathrm{HF}}(\mathbf{r}) = \frac{1}{2} \sum_{i=1}^{N} |\nabla \phi_i^{\mathrm{HF}}(\mathbf{r})|^2 \tag{3.7}$$

is the positive-definite form of the HF kinetic energy density. In practical calculations, it is much better to deal with τ^{HF} than with τ_L^{HF} because the former is always finite, whereas the latter becomes infinite at the nuclei. With these definitions we rewrite Eq. (3.4) as

$$\frac{\tau^{\mathrm{HF}}}{\rho^{\mathrm{HF}}} - \frac{1}{4} \frac{\nabla^2 \rho^{\mathrm{HF}}}{\rho^{\mathrm{HF}}} + v + v_{\mathrm{H}} + v_{\mathrm{S}}^{\mathrm{HF}} = \bar{I}^{\mathrm{HF}}. \tag{3.8}$$

Now, let us pose the following problem: Find the multiplicative exchange-correlation potential of the Kohn–Sham scheme which generates the same electron density as the HF method. This HFXC potential, $v_{\mathrm{XC}}^{\mathrm{HF}}(\mathbf{r})$, is defined by the Kohn–

Sham equations

$$\left[-\frac{1}{2}\nabla^2 + v(\mathbf{r}) + v_{\mathrm{H}}(\mathbf{r}) + v_{\mathrm{XC}}^{\mathrm{HF}}(\mathbf{r}) \right] \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r}), \tag{3.9}$$

where v and v_{H} are the same as in Eq. (3.2) and the eigenfunctions ϕ_i are such that $\rho(\mathbf{r}) \equiv \sum_{i=1}^{N} |\phi_i(\mathbf{r})|^2 = \rho^{\mathrm{HF}}(\mathbf{r})$. An important point here is that the equality $\rho = \rho^{\mathrm{HF}}$ does *not* imply that $\phi_i = \phi_i^{\mathrm{HF}}$. In fact, the canonical orbitals ϕ_i and ϕ_i^{HF} are known to be slightly different [28].

To find $v_{\mathrm{XC}}^{\mathrm{HF}}(\mathbf{r})$, we perform the same manipulations on Eq. (3.9) that led from Eq. (3.2) to Eq. (3.8) and arrive at

$$\frac{\tau}{\rho} - \frac{1}{4}\frac{\nabla^2 \rho}{\rho} + v + v_{\mathrm{H}} + v_{\mathrm{XC}}^{\mathrm{HF}} = \bar{I}, \tag{3.10}$$

where $\tau(\mathbf{r}) = \frac{1}{2}\sum_{i=1}^{N} |\nabla\phi_i(\mathbf{r})|^2$ is the positive-definite Kohn–Sham kinetic energy density, and

$$\bar{I}(\mathbf{r}) = \frac{1}{\rho(\mathbf{r})} \sum_{i=1}^{N} \epsilon_i |\phi_i(\mathbf{r})|^2 \tag{3.11}$$

is the Kohn–Sham average local ionization energy. Finally, we subtract Eq. (3.8) from (3.10) and write

$$v_{\mathrm{XC}}^{\mathrm{HF}}(\mathbf{r}) = v_{\mathrm{S}}^{\mathrm{HF}}(\mathbf{r}) + \bar{I}(\mathbf{r}) - \bar{I}^{\mathrm{HF}}(\mathbf{r}) + \frac{\tau^{\mathrm{HF}}(\mathbf{r})}{\rho^{\mathrm{HF}}(\mathbf{r})} - \frac{\tau(\mathbf{r})}{\rho(\mathbf{r})}, \tag{3.12}$$

where $\rho = \rho^{\mathrm{HF}}$, but $\tau \neq \tau^{\mathrm{HF}}$ and $\bar{I} \neq \bar{I}^{\mathrm{HF}}$.

Equation (3.12) is the key result of this work. It gives the HFXC potential exactly (in a complete basis). Analogous but less practical expressions for $v_{\mathrm{XC}}^{\mathrm{HF}}$ were presented earlier in Refs. [41–43].

We propose to treat Eq. (3.12) as the definition of a model Kohn–Sham potential for exact exchange. To turn this definition into a practical method we observe that $\bar{I}$ and τ are determined by $v_{\mathrm{XC}}^{\mathrm{HF}}$ and hence are initially unknown. Therefore, Eq. (3.12)

has to be solved iteratively. The algorithm we suggest is as follows.

1. Perform an HF calculation on the system of interest and construct ρ^{HF}, $v_{\mathrm{S}}^{\mathrm{HF}}$, τ^{HF}, and $\bar{I}^{\mathrm{HF}}$.

2. Choose an initial guess for the occupied Kohn–Sham orbitals $\{\phi_i\}$ and their eigenvalues $\{\epsilon_i\}$ (e.g., HF orbitals and orbital energies).

3. Shift all ϵ_i simultaneously to satisfy the condition $\epsilon_N = \epsilon_N^{\mathrm{HF}}$. This is needed to ensure that $v_{\mathrm{XC}}^{\mathrm{HF}}$ retains the correct $-1/r$ asymptotic behavior of $v_{\mathrm{S}}^{\mathrm{HF}}$.

4. Construct $v_{\mathrm{XC}}^{\mathrm{HF}}$ by substituting the current $\{\phi_i\}$ and $\{\epsilon_i\}$ into Eq. (3.12). To facilitate convergence, we found it essential to compute the terms $\bar{I}$ and τ/ρ using the density $\rho = \sum_{i=1}^{N} |\phi_i|^2$ rather than ρ^{HF}.

5. Solve the Kohn–Sham equations (3.9) using the current $v_{\mathrm{XC}}^{\mathrm{HF}}$. This gives a new set of $\{\phi_i\}$ and $\{\epsilon_i\}$.

6. Return to Step 3. Iterate until $v_{\mathrm{XC}}^{\mathrm{HF}}$ is self-consistent, i.e., until $\{\phi_i\}$ and $\{\epsilon_i\}$ on input and output agree within a desired threshold.

For spin-polarized systems, there will be two HFXC potentials (spin-up and spin-down) and hence two sets of all quantities except v and v_{H}. The entire scheme described above was implemented in GAUSSIAN 09 [44].

The most computationally intensive step in the HFXC approach, as in the KLI, LHF, BJ, and related approximations, is the construction of the Slater potential. It helps that in our method the Slater potential has to be computed only once (at the start of iterations). To eliminate every possible source of errors unrelated to the HFXC approximation, here we constructed $v_{\mathrm{S}}^{\mathrm{HF}}(\mathbf{r})$ by using Eq. (3.5). For routine applications, we recommend resolution-of-the-identity techniques or the method proposed in Chapter 2.

3.3　HFXC potential for atoms and molecules

To assess the quality of HFXC potentials produced by our method we compared them to the exact (numerical) OEPs, some of the best existing OEP approximations (KLI, ELP=LHF=CEDA, and BJ), and finite-basis-set OEPs obtained by the Wu–Yang OEP (WY-OEP) method [45]. The OEP and KLI results were taken from the work of Engel and coworkers [46, 47] (for spherical atoms) and from Makmal *et al.* [48] (for molecules); these are exact fully numerical solutions of the OEP and KLI equations. The BJ, ELP, and WY-OEP results were obtained earlier by one of the authors [49]. To simulate the basis-set limit in the HFXC, BJ, ELP, and WY-OEP calculations we employed the large universal Gaussian basis set (UGBS) of Ref. [50] for atoms and UGBS1P (UGBS augmented with one set of polarization functions for each exponent) for molecules. The accuracy of the UGBS is such that total atomic HF energies computed in this basis are converged to 7 significant figures with respect to the basis-set limit [50].

In all cases where the UGBS (UGBS1P) was used, we found that HFXC potentials are virtually indistinguishable from exact OEPs (Figs. 3.1 and 3.2) and are dramatically better as approximations to OEPs than the KLI and BJ models (Fig. 3.2). Note that the performance of the LHF approximation is very similar to that of the KLI [16] scheme, so the LHF or ELP or CEDA curves (not shown in Fig. 3.2) would be almost superimposed with the KLI potentials. The excellent agreement between HFXC potentials and exact OEPs suggests that the 'correlation' part of an HFXC potential is negligibly small.

For quantitative comparison, we took the self-consistent Kohn–Sham orbitals generated by HFXC and other potentials and calculated the conventional total exchange-only energy, E_{conv}, which defined as the HF total energy expression in terms of Kohn–Sham orbitals. Table 3.1 shows that the KLI, ELP, and BJ potentials produce E_{conv} values noticeably above the exact OEP energies. By contrast, conventional energies

obtained from HFXC potentials are within 0.1 mE_h of the OEP benchmarks for most atoms—closer than E_conv values from WY-OEPs.
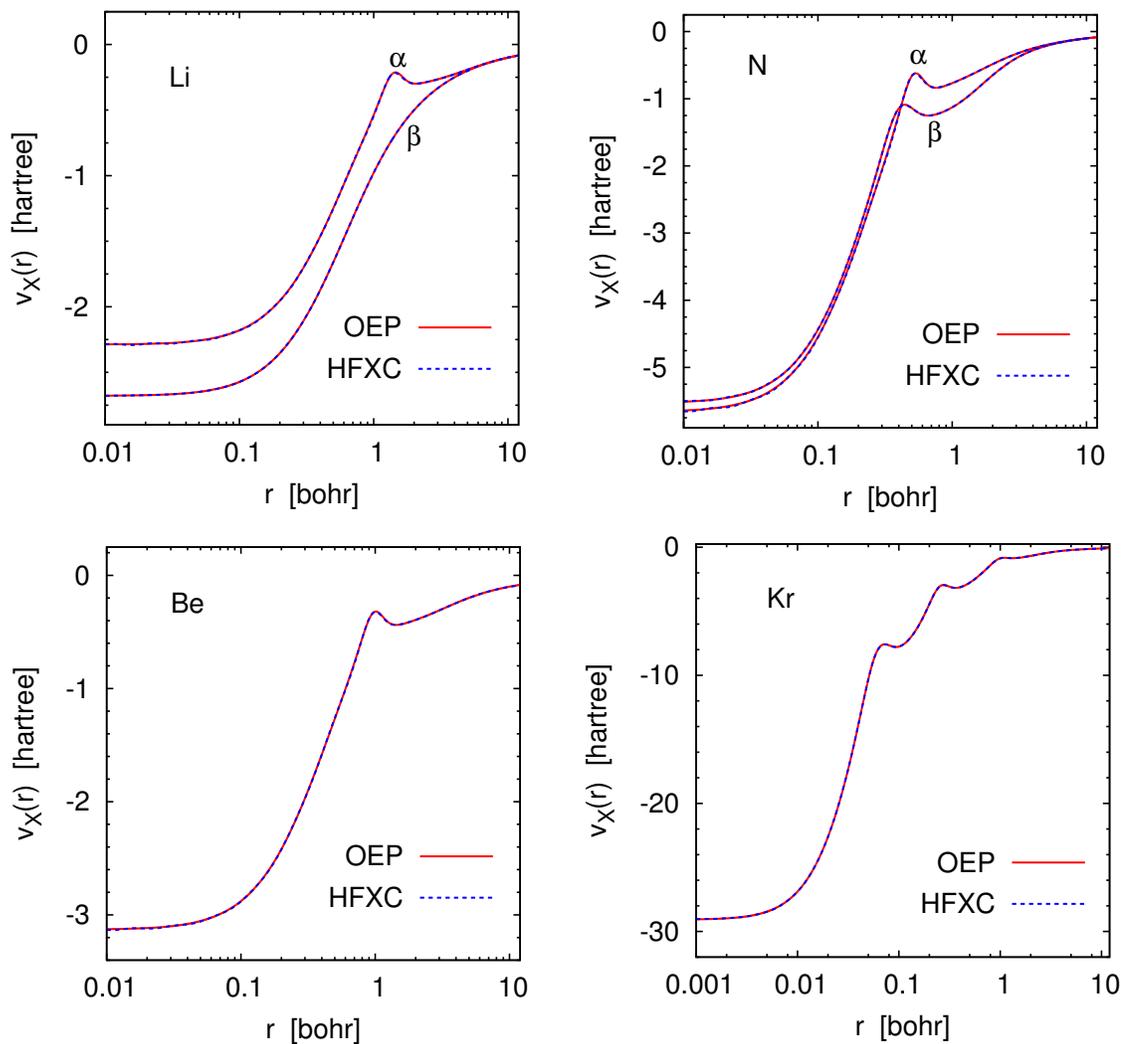

Figure 3.1: OEPs and HFXC potentials are visually indistinguishable. The same excellent agreement was observed for all atoms where comparison with OEPs was made.
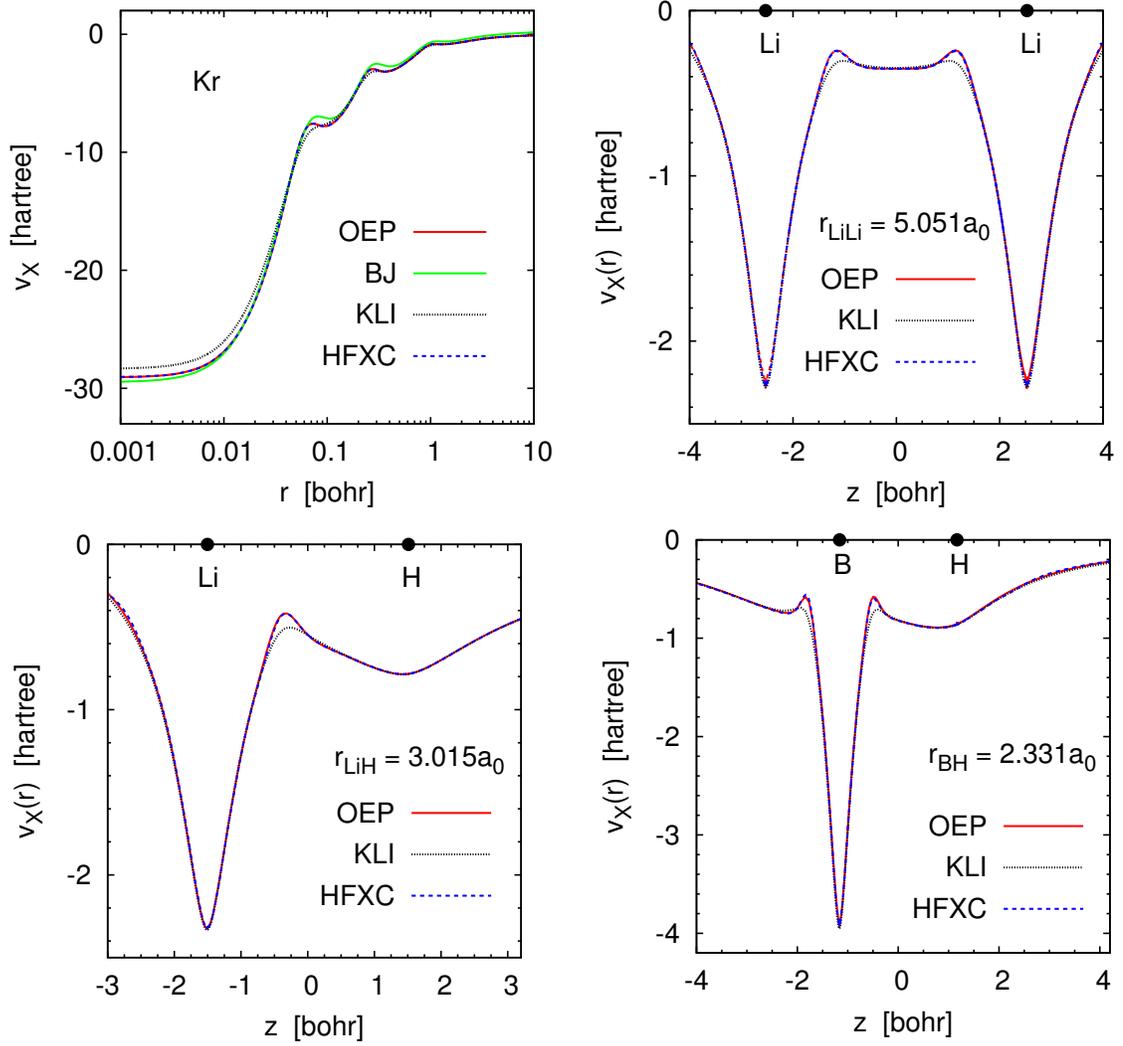
Figure 3.2: HFXC potentials are perfect representations of OEPs, unlike KLI and BJ potentials.

Table 3.1: Total ground-state energies of 12 representative atoms obtained with various exchange potentials. The numerical OEP and KLI results are from Refs. [46, 47]. All other values were computed using a large Gaussian basis set (UGBS).

| Atom | E_{OEP} (units of E_{h}) | $E_{\mathrm{conv}} - E_{\mathrm{OEP}}$ (units of mE_{h}) | | | | | $E_{\mathrm{vir}} - E_{\mathrm{conv}}$ (units of mE_{h}) | | | | |
		KLI	ELP	BJ	WY-OEP	HFXC	KLI	ELP	BJ	WY-OEP	HFXC
Li	-7.43250	0.06	0.08	1.20	0.00	0.00	-5.28	4.61	50.45	-0.01	-0.04
Be	-14.57243	0.15	0.15	0.75	0.01	-0.01	-21.20	13.85	31.68	0.07	-0.10
N	-54.40340	0.36	0.34	4.14	0.01	0.00	24.74	78.47	250.56	-0.04	-0.21
Ne	-128.54541	0.58	0.57	9.59	0.02	0.01	155.62	197.51	781.68	-0.05	-0.14
Na	-161.85664	0.73	0.73	7.71	0.02	0.00	183.10	231.84	805.90	0.22	-0.28
Mg	-199.61158	0.87	0.87	5.86	0.02	0.00	182.26	267.70	799.35	-0.64	-0.26
P	-340.71500	1.28	1.28	3.99	0.02	-0.03	144.86	376.08	904.12	1.21	-1.84
Ar	-526.81222	1.74	1.83	3.36	0.09	-0.07	124.68	512.68	1182.26	2.54	-4.08
Ca	-676.75193	2.23	1.98	3.58	-0.03	-0.13	14.94	597.73	1126.91	-2.49	-5.86
Zn	-1777.83436	3.65	3.05	10.40	-0.07	-0.07	1047.87	1238.61	2130.22	-1.21	-5.93
Kr	-2752.04295	3.18	3.44	6.52	0.26	-0.07	1468.11	1657.32	3128.48	7.85	-7.43
Cd	-5465.11441	6.04	5.58	6.46	0.92	-0.26	1883.92	2374.14	3617.48	-4.25	-6.99
mean average value		1.74	1.66	5.30	0.12	0.05	438.0	629.2	1234.1	1.76	2.76

A more stringent quality test [49] for OEP approximations is the virial energy discrepancy, $\Delta_{\mathrm{vir}} = E_{\mathrm{vir}} - E_{\mathrm{conv}}$, where E_{vir} is the total energy with the exchange contribution obtained by the Levy–Perdew virial relation [51],

$$E_{\mathrm{X}}^{\mathrm{vir}} = \int v_{\mathrm{X}}(\mathbf{r}) \left[3\rho(\mathbf{r}) + \mathbf{r} \cdot \nabla \rho(\mathbf{r}) \right] d\mathbf{r}. \tag{3.13}$$

For exact OEPs, $\Delta_{\mathrm{vir}} = 0$ [52]. Table 3.1 shows that virial energy discrepancies for HFXC potentials do not exceed a few $\mathrm{m}E_{\mathrm{h}}$, that is, are three orders of magnitude smaller than for the LHF, ELP, and BJ approximations—as small as for WY-OEPs. These discrepancies are expected to be even smaller in the basis-set limit. (The numerical OEPs have Δ_{vir} values of the order of a few μE_{h}.)

Recall that to solve the OEP integral equation by the WY method one needs two sets of basis functions: a one-electron basis for the orbitals and an auxiliary basis for the OEP. The two sets must be "balanced" with respect to each other; otherwise, the resulting potential will be either suboptimal or highly oscillatory [6, 8–10]. By employing the same large basis set in both roles one can usually obtain OEPs that are smooth and correct everywhere except near the nucleus (panel in Fig. 3.3). However, the single-basis trick does not work for small and medium-sized one-electron basis sets such as 6-31G and cc-pVQZ, for which a suitable auxiliary basis can be found only in an *ad hoc* manner with considerable effort and some arbitrariness [8–10]. Such problems do not exist in our method, where we automatically obtain a smooth HFXC potential for any one-electron basis (the right panel in Fig. 3.3). Since OEPs and HFXC potentials are nearly identical in the basis-set limit, one can even operationally define a finite-basis-set OEP (a fundamentally ambiguous quantity [6]) as the corresponding HFXC potential.

The reason the HFXC scheme is very robust is because the potential $v_{\mathrm{XC}}^{\mathrm{HF}}$ is built up directly as a sum of commensurate, well-behaved terms. Apart from being a tool for generating approximate OEPs, the HFXC method can be used to determine Kohn–
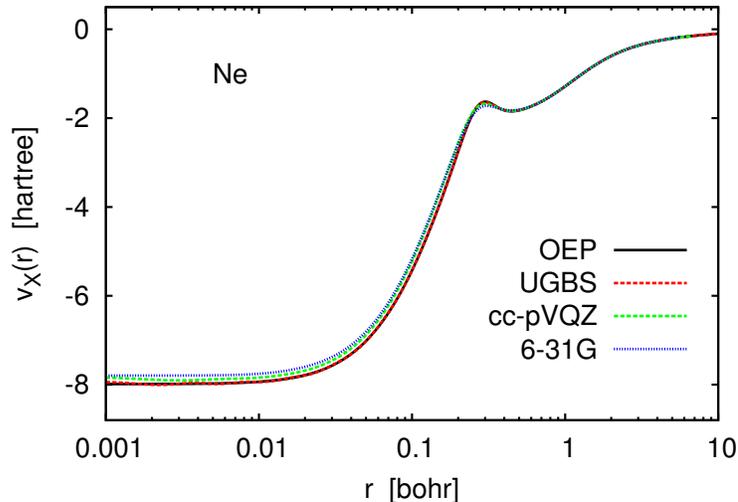
Figure 3.3: HFXC potentials obtained with small (6-31G), intermediate (cc-pVQZ), and large (UGBS) basis sets as approximations to the exact (numerical) OEP. The HFXC/UGBS curve is right on top of the OEP.

Sham potentials from HF densities, provided that the HF and Kohn–Sham orbitals are expanded in a complete (in practice, very large) basis or represented on a dense grid. In Kohn–Sham calculations using a *finite* basis set, however, the potential given by Eq. (3.12) reproduces the target $\rho^{\mathrm{HF}}(\mathbf{r})$ only approximately because Eq. (3.9) and its finite-dimensional matrix representation are not equivalent [1].

We can also identify the reason why HFXC potentials are much closer to OEPs than KLI, LHF, and related approximations. This happens because in our derivation we did *not* assume that $\phi_i = \phi_i^{\mathrm{HF}}$ for all $i \leq N$. If, for the sake of argument, we make this assumption in Eq. (3.12), we immediately obtain a different potential,

$$\tilde{v}_{\mathrm{XC}}(\mathbf{r}) = v_{\mathrm{S}}^{\mathrm{HF}}(\mathbf{r}) + \frac{1}{\rho^{\mathrm{HF}}(\mathbf{r})} \sum_{i=1}^{N} (\epsilon_i - \epsilon_i^{\mathrm{HF}}) |\phi_i^{\mathrm{HF}}(\mathbf{r})|^2, \qquad (3.14)$$

which was introduced and discussed by Nagy [42] (with ϕ_i in place of ϕ_i^{HF}) as an approximate equivalent of the KLI potential. The difference between HF and OEP

---

[1]Problems such as "find the multiplicative potential which reproduces the HF/6-31G density when the Kohn-Sham equations are solved in the 6-31G basis" are ill-posed. Using the method of Ref. [7] it is easy to construct any number of different potentials that satisfy the above requirement, but to decide which of these potentials is "the true one" is fundamentally impossible [53]

orbitals may be small, but it gives rise to the crucial $(\tau^{\mathrm{HF}} - \tau)/\rho$ term responsible for the atomic shell structure of the OEP. It follows that the KLI and LHF approximations would be greatly improved simply by including this term.

3.4 Conclusion

In conclusion, we have shown (a) how to construct HFXC potentials (i.e., model exchange-correlation potentials yielding HF densities in the basis-set limit) at the computational cost of the KLI, LHF, and BJ approximations; (b) that HFXC potentials are nearly exact approximations to exchange-only OEPs, much better than the KLI, LHF, BJ, and related models. The advantage of approximating OEPs with HFXC potentials is that it the HFXC method completely avoids the OEP equation, and so is free from numerical difficulties and basis-set artifacts that beset OEP techniques.

HFXC potentials obtained in finite basis sets exhibit no spurious oscillations and, for all intents and purposes, may be treated as solutions of the OEP equation. In this sense, the HFXC scheme solves the long-standing problem of unambiguous "black-box" construction of elusive finite-basis-set OEPs. We anticipate that our approach will be widely embraced as a practical substitute for OEP methods and as a superior alternative to existing model potentials for exact exchange.

Finally, we wish to remark that our approach can be generalized to *any* orbital-dependent exchange-correlation functional. One simply needs to start with the corresponding energy expression $E_{\mathrm{XC}}[\{\phi_i\}]$ instead of $E_{\mathrm{X}}^{\mathrm{HF}}$ and modify appropriately all the steps in the derivation. For τ-dependent functionals and hybrids (mixtures of exact exchange and semilocal approximations), this scheme is expected to produce even more accurate approximations to $\delta E_{\mathrm{XC}}[\{\phi_i\}]/\delta\rho$ than for the exact-exchange functional itself.

Bibliography

[1] T. Grabo, T. Kreibich, S. Kurth, and E. K. U. Gross, *Strong Coulomb Correlations in Electronic Structure Calculations: Beyond the Local Density Approximation*, Advances in Condensed Matter Science, Gordon and Breach Science Publishers (2000).

[2] S. Kümmel and L. Kronik, "Orbital-dependent density functionals: Theory and applications", *Rev. Mod. Phys.* **80**, 3 (2008).

[3] R. T. Sharp and G. K. Horton, "A variational approach to the unipotential many-electron problem", *Phys. Rev.* **90**, 317 (1953).

[4] V. Sahni, J. Gruenebaum, and J. P. Perdew, "Study of the density-gradient expansion for the exchange energy", *Phys. Rev. B* **26**, 4371 (1982).

[5] S. Hirata, S. Ivanov, I. Grabowski, R. J. Bartlett, K. Burke, and J. D. Talman, "Can optimized effective potentials be determined uniquely?", *J. Chem. Phys.* **115**, 1635 (2001).

[6] V. N. Staroverov, G. E. Scuseria, and E. R. Davidson, "Optimized effective potentials yielding Hartree–Fock energies and densities", *J. Chem. Phys.* **124**, 141103 (2006).

[7] S. Kümmel and J. P. Perdew, "Simple iterative construction of the optimized

effective potential for orbital functionals, including exact exchange", *Phys. Rev. Lett.* **90**, 043004 (2003).

[8] A. Hesselmann, A. W. Götz, F. Della Sala, and A. Görling, "Numerically stable optimized effective potential method with balanced gaussian basis sets", *J. Chem. Phys.* **127**, 054102 (2007).

[9] A. Görling, A. Hesselmann, M. Jones, and M. Levy, "Relation between exchange-only optimized potential and Kohn–Sham methods with finite basis sets, and effect of linearly dependent products of orbital basis functions", *J. Chem. Phys.* **128**, 104104 (2008).

[10] T. Heaton-Burgess, F. A. Bulat, and W. Yang, "Optimized effective potentials in finite basis sets", *Phys. Rev. Lett.* **98**, 256401 (2007).

[11] C. Kollmar and M. Filatov, "Optimized effective potential method: Is it possible to obtain an accurate representation of the response function for finite orbital basis sets?", *J. Chem. Phys.* **127**, 114104 (2007).

[12] C. Kollmar and M. Filatov, "The role of orbital products in the optimized effective potential method", *J. Chem. Phys.* **128**, 064101 (2008).

[13] C. R. Jacob, "Unambiguous optimization of effective potentials in finite basis sets", *J. Chem. Phys.* **135**, 244102 (2011).

[14] N. I. Gidopoulos and N. N. Lathiotakis, "Nonanalyticity of the optimized effective potential with finite basis sets", *Phys. Rev. A* **85**, 052508 (2012).

[15] J. B. Krieger, Y. Li, and G. J. Iafrate, "Construction and application of an accurate local spin-polarized Kohn–Sham potential with integer discontinuity: Exchange-only theory", *Phys. Rev. A* **45**, 101 (1992).

[16] F. Della Sala and A. Görling, "Efficient localized Hartree–Fock methods as effective exact-exchange Kohn–Sham methods for molecules", *J. Chem. Phys.* **115**, 5718 (2001).

[17] M. Grüning, O. V. Gritsenko, and E. J. Baerends, "Exchange potential from the common energy denominator approximation for the Kohn–Sham Green's function: Application to (hyper)polarizabilities of molecular chains", *J. Chem. Phys.* **116**, 6435 (2002).

[18] A. Holas and M. Cinal, "Exact and approximate exchange potentials investigated in terms of their matrix elements with the Kohn–Sham orbitals", *Phys. Rev. A* **72**, 032504 (2005).

[19] V. N. Staroverov, G. E. Scuseria, and E. R. Davidson, "Effective local potentials for orbital-dependent density functionals", *J. Chem. Phys.* **125**, 081104 (2006).

[20] A. F. Izmaylov, V. N. Staroverov, G. E. Scuseria, E. R. Davidson, G. Stoltz, and E. Cancès, "The effective local potential method: Implementation for molecules and relation to approximate optimized effective potential techniques", *J. Chem. Phys.* **126**, 084107 (2007).

[21] R. Leeuwen, O. V. Gritsenko, and E. J. Baerends, "Analysis and modelling of atomic and molecular Kohn–Sham potentials", *Top. Curr. Chem.* **180**, 107 (1996).

[22] O. Gritsenko, P. Schipper, and E. Baerends, "Approximation of the exchange-correlation Kohn–Sham potential with a statistical average of different orbital model potentials", *Chem. Phys. Lett.* **302**, 199 (1999).

[23] A. D. Becke and E. R. Johnson, "A simple effective potential for exchange", *J. Chem. Phys.* **124**, 221101 (2006).

[24] V. N. Staroverov, "A family of model Kohn–Sham potentials for exact exchange", *J. Chem. Phys.* **129**, 134103 (2008).

[25] E. Räsänen, S. Pittalis, and C. R. Proetto, "Universal correction for the Becke–Johnson exchange potential", *J. Chem. Phys.* **132**, 044112 (2010).

[26] P. W. Payne, "Density functionals in unrestricted Hartree–Fock theory", *J. Chem. Phys.* **71**, 490 (1979).

[27] A. Holas, N. H. March, Y. Takahashi, and C. Zhang, "Hartree–Fock method posed as a density-functional theory: Application to the Be atom", *Phys. Rev. A* **48**, 2708 (1993).

[28] A. Görling and M. Ernzerhof, "Energy differences between Kohn–Sham and Hartree–Fock wave functions yielding the same electron density", *Phys. Rev. A* **51**, 4501 (1995).

[29] A. Holas and N. March, "Exchange and correlation in density functional theory of atoms and molecules", *Top. Curr. Chem.* **180**, 57 (1996).

[30] J. Chen, R. O. Esquivel, and M. J. Stott, "Exchange-correlation potential for small atoms", *Philos. Mag. B* **69**, 1001 (1994).

[31] C. Filippi, C. J. Umrigar, and X. Gonze, "Separation of the exchange-correlation potential into exchange plus correlation: An optimized effective potential approach", *Phys. Rev. A* **54**, 4810 (1996).

[32] Q. Zhao, R. C. Morrison, and R. G. Parr, "From electron densities to Kohn–Sham kinetic energies, orbital energies, exchange-correlation potentials, and exchange-correlation energies", *Phys. Rev. A* **50**, 2138 (1994).

[33] R. van Leeuwen and E. J. Baerends, "Exchange-correlation potential with correct asymptotic behavior", *Phys. Rev. A* **49**, 2421 (1994).

[34] D. J. Tozer, V. E. Ingamells, and N. C. Handy, "Exchange-correlation potentials", *J. Chem. Phys.* **105**, 9200 (1996).

[35] Q. Wu and W. Yang, "A direct optimization method for calculating density functionals and exchange–correlation potentials from electron densities", *J. Chem. Phys.* **118**, 2498 (2003).

[36] I. G. Ryabinkin and V. N. Staroverov, "Determination of Kohn–Sham effective potentials from electron densities using the differential virial theorem", *J. Chem. Phys.* **137**, 164113 (2012).

[37] P. R. T. Schipper, O. V. Gritsenko, and E. J. Baerends, "Kohn–Sham potentials corresponding to slater and gaussian basis set densities", *Theor. Chem. Acc.* **98**, 16 (1997).

[38] F. A. Bulat, T. Heaton-Burgess, A. J. Cohen, and W. Yang, "Optimized effective potentials from electron densities in finite basis sets", *J. Chem. Phys.* **127**, 174101 (2007).

[39] J. C. Slater, "A simplification of the Hartree–Fock method", *Phys. Rev.* **81**, 385 (1951).

[40] F. A. Bulat, M. Levy, and P. Politzer, "Average local ionization energies in the Hartree–Fock and Kohn–Sham theories", *Phys. Chem. A* **113**, 1384 (2009).

[41] A. Holas and N. H. March, "Correction to slater exchange potential to yield exact Kohn–Sham potential generating the Hartree-Fock density", *Phys. Rev. B* **55**, 1295 (1997).

[42] A. Nagy, "Alternative derivation of the Krieger–Li–Iafrate approximation to the optimized-effective-potential method", *Phys. Rev. A* **55**, 3465 (1997).

[43] M. S. Miao, "A direct derivation of the optimized effective potential using orbital perturbation theory", *Philos. Mag. B* **80**, 409 (2000).

[44] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, "Gaussian 09, Revision A.1", Gaussian Inc., Wallingford, CT (2009).

[45] Q. Wu and W. Yang, "Algebraic equation and iterative optimization for the optimized effective potential in density functional theory", *J. Theor. Comput. Chem.* **2**, 627 (2003).

[46] E. Engel and S. H. Vosko, "Accurate optimized-potential-model solutions for spherical spin-polarized atoms: Evidence for limitations of the exchange-only local spin-density and generalized-gradient approximations", *Phys. Rev. A* **47**, 2800 (1993).

[47] E. Engel and R. M. Dreizler, "From explicit to implicit density functionals", *J. Comput. Chem.* **20**, 31 (1999).

[48] A. Makmal, S. Kümmel, and L. Kronik, "Fully numerical all-electron solutions of the optimized effective potential equation for diatomic molecules", *J. Chem. Theory Comput.* **5**, 1731 (2009).

[49] A. P. Gaiduk and V. N. Staroverov, "Virial exchange energies from model exact-exchange potentials", *J. Chem. Phys.* **128**, 204101 (2008).

[50] E. V. R. de Castro and F. E. Jorge, "Accurate universal gaussian basis set for all atoms of the periodic table", *J. Chem. Phys.* **108**, 5225 (1998).

[51] M. Levy and J. P. Perdew, "Hellmann–Feynman, virial, and scaling requisites for the exact universal density functionals. shape of the correlation potential and diamagnetic susceptibility for atoms", *Phys. Rev. A* **32**, 2010 (1985).

[52] H. Ou-Yang and M. Levy, "Theorem for exact local exchange potential", *Phys. Rev. Lett.* **65**, 1036 (1990).

[53] J. E. Harriman, "Densities, operators, and basis sets", *Phys. Rev. A* **34**, 29 (1986).

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Alexei

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Curriculum Vitæ

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- Devised efficient and accurate approximations to Optimized effective potential

2009–2013, Content developer, Competentum Group, Inc., Minsk, Belarus
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2006–2011, Member, Methodological Commission for the Belarus National Chemistry Olympiad, Minsk, Belarus
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2. Ilya G. Ryabinkin, **Alexei A. Kananenka**, and Viktor N. Staroverov, "Accurate and efficient approximation to the optimized effective potential for exchange", *Phys. Rev. Lett.* **111**, 013001 (2013)

1. Vadim E. Matulis, Oleg A. Ivashkevich, **Alexei A. Kananenka**, "Quantum-chemical Investigation of the *cis-trans* isomerization mechanism of *bis*(tetrazol-5-yl)diazenes", *Vestnik Bel. Gos. Univ.* **2**, 3 (2010)

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2. "Thermodynamics of 2-methyl-3-buten-2-ol", 19th Mendeleev Conference of Young Researchers, St.-Petersburg, Russia, June 29–July 3, 2009 (poster).

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2006–2011, Coach for the Belarus team, International and National Chemistry Olympiads, Minsk, Belarus

- Taught students how to solve olympiad problems in physical chemistry, organic chemistry, analytical chemistry

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2010 6th Place, First Student Chemistry Olympiad "Oxygen-2010", Minsk, Belarus

2009 2nd Place, Second International Chemistry Olympiad of University Students, Moscow, Russia

2006 President's Fund Scholarship

2005 Bronze Medal, 37th International Chemistry Olympiad, Taipei, Taiwan

2005 President's Fund Scholarship

2005 Gold Medal, 39th International Mendeleev Chemistry Olympiad, Dushanbe, Tajikistan

2004 1st Prize, 1st International Chemistry Olympiad of the Nations of the Commonwealth of Independent States and the Baltic Region, Moscow, Russia