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Construction and Analysis of Accurate Exchange-Correlation Potentials

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A thesis submitted in partial fulfillment of the requirements for the Doctor of Philosophy degree in Chemistry

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Abstract

Practical Kohn–Sham density-functional calculations require approximations to the exchange-correlation energy functional, $E_{\text{XC}}[\rho]$, or the exchange-correlation potential, $v_{\text{XC}}(\mathbf{r})$, defined as the functional derivative of $E_{\text{XC}}[\rho]$ with respect to the electron density, ρ . This thesis focuses on the following problems: (i) development of approximate exchange-correlation potentials by modelling the exchange-correlation charge distribution; (ii) accurate approximation of functional derivatives of orbital-dependent functionals; (iii) generation of exchange-correlation potentials from many-electron wavefunctions; (iv) analysis of accurate exchange-correlation potentials in atoms and molecules.

The advantage of modelling the exchange-correlation potential through the exchange-correlation charge distribution, $q_{\text{XC}}(\mathbf{r})$, is that it produces potentials with correct asymptotic behavior. We present an important caveat for attempts to enforce Coulombic asymptotics of $v_{\text{XC}}(\mathbf{r})$ by normalizing the exchange-correlation charge distribution. We also formulate integrability conditions that a model $q_{\text{XC}}(\mathbf{r})$ must satisfy in order for the corresponding $v_{\text{XC}}(\mathbf{r})$ to be a functional derivative of some density functional.

Functional derivatives of orbital-dependent functionals cannot be derived in closed form and have to be evaluated numerically using the optimized effective potential (OEP) method. We propose a way to avoid the OEP equation in finite-basis-set Kohn–Sham calculations employing orbital-dependent functionals. To this end, we develop a hierarchy of approximations to the functional derivative of a given orbital-dependent exchange-correlation functional. The highest level in the hierarchy is practically indistinguishable from the true OEP and is obtained from the requirement that the Kohn–Sham and the generalized Kohn–Sham densities be equal. By imposing the same requirement on the Kohn–Sham and wavefunction densities we devise and implement a method for calculating $v_{\text{XC}}(\mathbf{r})$ from a given electronic wavefunction. Our method is free from numerical limitations and basis-set artifacts of conventional schemes that fit the effective potential $v_{\text{XC}}(\mathbf{r})$ to a given ground-state electron density. In the remainder of the thesis, we apply our techniques to elucidate the mechanism of formation of the step structure of the exact $v_{\text{XC}}(\mathbf{r})$ and analyze exchange-correlation potentials derived from restricted Hartree–Fock wavefunctions of stretched diatomic molecules.

Keywords: quantum chemistry, density-functional theory, exchange-correlation potential, exchange-correlation charge distribution, sum rules, functional derivative, orbital-dependent functionals, optimized effective potential, *ab initio* calculations, correlated wavefunctions

Co-Authorship Statement

This thesis summarizes results of scientific research conducted by the author, Sviataslau V. Kohut, under the supervision of Prof. Viktor N. Staroverov and in collaboration with the former members of Prof. Staroverov’s group—Dr. Ilya G. Ryabinkin, Dr. Rogelio Cuevas Saavedra, and Alexander M. Polgar—and Prof. Paul W. Ayers of McMaster University.

Chapter 2 and Sec. 1.6 of Chapter 1 are based on the article “[Apparent violation of the sum rule for exchange-correlation charges by generalized gradient approximations](#)” [J. Chem. Phys. **139**, 164117 (2013)] by S. V. Kohut and V. N. Staroverov. Sviataslau Kohut discovered the main result, programmed the script for evaluating the total exchange-correlation charges, carried out all the derivations, performed all the calculations, and drafted the manuscript, which was revised by Prof. Staroverov.

Chapter 4 is based on the article “[Hierarchy of model Kohn–Sham potentials for orbital-dependent functionals: A practical alternative to the optimized effective potential method](#)” [J. Chem. Phys. **140**, 18A535 (2014)] by S. V. Kohut, I. G. Ryabinkin, and V. N. Staroverov. The main idea of the method was conceived by Dr. Ryabinkin and Prof. Staroverov. Sviataslau Kohut participated in the development of the method, wrote and optimized a computer code for generation of the potentials, obtained all the reported results, and co-wrote the manuscript.

Chapter 5 is based on the articles “[Reduction of electronic wave functions to Kohn–Sham effective potentials](#)” [Phys. Rev. Lett. **115**, 083001 (2015)] by I. G. Ryabinkin, S. V. Kohut, and V. N. Staroverov, and “[Response to “Comment on ‘Kohn–Sham exchange-correlation potentials from second-order reduced density matrices’”](#)” [J. Chem. Phys. **145**, 037101 (2016)]” [J. Chem. Phys. **145**, 037101 (2016)] by I. G. Ryabinkin, S. V. Kohut, R. Cuevas-Saavedra, P. W. Ayers, and V. N. Staroverov. Dr. Ryabinkin and Prof. Staroverov proposed the methodology. Sviataslau Kohut took part in the development of the method, wrote and optimized computer codes for all the calculations, and numerically discovered the key results, such as that the method is Kohn-Sham compliant in the basis-set limit and that it is not identical to the iterative Coulomb potential update procedure. Sviataslau Kohut also obtained all the reported data and, together with Dr. Ryabinkin, contributed to revising the manuscripts, both prepared by Prof. Staroverov. Dr. Cuevas Saavedra and Prof. Ayers contributed to revising the manuscript of the second article.

Chapter 6 is based on the article “[Origin of the step structure of molecular exchange-correlation potentials](#)” [Phys. Chem. Chem. Phys. **18**, 20938 (2016)] by S. V. Kohut, A. M. Polgar, and V. N. Staroverov. Alexander Polgar experimented with calculations of the average local electron energy. Sviataslau Kohut performed the final calculations

of the average local electron energy, generated the exchange-correlation potentials, and prepared the first draft of the manuscript, which was finalized by Prof. Staroverov.

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I acquired a great deal of what I represent as a scientist and as an individual while working in Belarusian State University. I thank all my former colleagues—Dr. Gennady Kabo, Dr. Andrey Blokhin, Dr. Yauheni Paulechka, Dr. Olga Voitkevich, Dr. Elena Stepurko, and others—for sharing their expertise with me and for insightful conversations.

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Светлой памяти моих дедушек,

Козута Григория Петровича

и Корнаевича Василия Ивановича

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List of Abbreviations

<i>N</i> -RDM	—	<i>N</i> -electron reduced density matrix
ALEE	—	average local electron energy
B88	—	Becke-88
BLYP	—	Becke–Lee–Yang–Parr
C	—	correlation
CAS	—	complete active space
CEDA	—	common energy denominator approximation
CI	—	configuration interaction
DCEP	—	density-consistent effective potential
DFA	—	density-functional approximation
DFT	—	density-functional theory
ECMV	—	Engel–Chevary–Macdonald–Vosko
EKT	—	extended Koopmans theorem
ELP	—	effective local potential
FCI	—	full configuration interaction
GGA	—	generalized gradient approximation
GKS	—	generalized Kohn–Sham
GLLB	—	Gritsenko–van Lenthe–van Leeuwen–Baerends
H	—	Hartree
HF	—	Hartree–Fock
HFXC	—	Hartree–Fock exchange–correlation
HOMO	—	highest-occupied molecular orbital
KLI	—	Krieger–Li–Iafrate
KS	—	Kohn–Sham
LB94	—	van Leeuwen–Baerends-94
LC- ω PBE	—	long-range corrected Perdew–Burke–Ernzerhof
LDA	—	local density approximation
LHF	—	localized Hartree–Fock
LUMO	—	lowest-unoccupied molecular orbital
M06-2X	—	Minnesota-06 with double the amount of non-local exchange
MCSCF	—	multiconfigurational self-consistent field
mRKS	—	modified Ryabinkin–Kohut–Staroverov
NPA	—	natural population analysis
OAEP	—	orbital-averaged effective potential
OCEP	—	orbital-consistent effective potential
OEP	—	optimized effective potential
PBE	—	Perdew–Burke–Ernzerhof
PBE0	—	Perdew–Burke–Ernzerhof hybrid
RHF	—	restricted Hartree–Fock
RKS	—	Ryabinkin–Kohut–Staroverov
SAOP	—	statistical average of (model) orbital potentials
SCF	—	self-consistent field

List of Abbreviations (*continued*)

TDDFT	—	time-dependent density-functional theory
UGBS	—	universal Gaussian basis set
UHF	—	unrestricted Hartree–Fock
WF	—	wavefunction
WFT	—	wavefunction theory
X	—	exchange
XC	—	exchange-correlation

List of Symbols

a_0	—	atomic unit of length (1 bohr = 0.529177 Å)
e	—	atomic unit of charge (1 e = 1.60218×10^{-19} C)
E	—	total energy
E_C	—	correlation energy
E_X	—	exchange energy
E_{XC}	—	exchange-correlation energy
E_h	—	atomic unit of energy (1 hartree = 2625.50 kJ mol ⁻¹ = 27.2114 eV)
f_{XC}	—	general exchange-correlation energy density
f_i	—	eigenfunction of the symmetrized generalized Fock operator
$F[\rho]$	—	general density functional
$F(x)$	—	enhancement factor of an exchange GGA
\hat{G}	—	generalized Fock operator
\hat{h}	—	one-electron core Hamiltonian
I	—	ionization potential
\bar{I}	—	average local ionization energy
J	—	Coulomb repulsion energy
\hat{K}	—	exchange operator of the Hartree–Fock theory
M	—	number of nuclei
N	—	number of electrons
q	—	atomic charge
q_{XC}	—	exchange-correlation charge distribution
Q_{XC}	—	total exchange-correlation charge
\mathbf{r}	—	position vector
\mathbf{R}	—	position vector of a nucleus
R_e	—	equilibrium internuclear separation
T	—	kinetic energy of electrons
v_C	—	correlation potential
$v_{c,kin}$	—	kinetic correlation potential
v_{ext}	—	external potential
v_{eff}	—	Kohn–Sham potential
v_H	—	Hartree (electrostatic) potential
v_{resp}	—	response potential
v_S	—	Slater potential
v_X	—	exchange potential
v_{XC}	—	exchange-correlation potential
v_{XC}^{hole}	—	exchange-correlation hole potential
V_{ee}	—	energy of electron–electron interaction
x	—	reduced density gradient
Z	—	nuclear charge
$\gamma(\mathbf{r}, \mathbf{r}')$	—	one-electron reduced density matrix
$\Gamma(\mathbf{r}, \mathbf{r}_2; \mathbf{r}', \mathbf{r}'_2)$	—	two-electron reduced density matrix

List of Symbols (*continued*)

$\delta(\mathbf{r})$	—	Dirac delta function
$\delta\rho(\mathbf{r})$	—	density difference profile
$\Delta\rho$	—	integrated density difference
ϵ	—	molecular orbital eigenvalue
$\bar{\epsilon}$	—	average local electron energy
λ_i	—	eigenvalue of the symmetrized generalized Fock operator
ρ	—	electron density
$\rho_{\text{XC}}^{\text{WF}}$	—	exchange-correlation hole density
τ	—	positive-definite kinetic energy density
τ_L	—	Laplacian kinetic energy density
τ_P	—	Pauli kinetic energy density
τ_W	—	von Weizäcker kinetic energy density
ϕ_i	—	molecular orbital
Ψ	—	ground-state electronic wavefunction

Chapter 1

Theoretical background

“A journey of a thousand miles begins
with a single step.”

— LAOZI, *Tao Te Ching*

1.1 Density-functional theory

Density-functional theory (DFT) has become the standard tool for electronic structure calculations of atoms, molecules, and periodic systems. The secret of its success lies in the attractive ratio of accuracy to computational cost. The foundation of modern-day DFT was laid out in a landmark paper [1] by Pierre Hohenberg and Walter Kohn in 1964.

Historically, DFT was preceded by wavefunction theory (WFT). Electronic wavefunctions can be obtained by solving the time-independent non-relativistic Schrödinger equation in the fixed-nuclei approximation,

$$\hat{H}\Psi = E\Psi, \tag{1.1}$$

where $\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)$ is the ground-state N -electron wavefunction, \hat{H} is the electronic Hamiltonian, E is the ground-state electronic energy, and $\mathbf{x}_i \equiv (\mathbf{r}_i, \sigma_i)$ signify space and spin coordinates of an electron. The wavefunction Ψ has a probabilistic interpretation and encompasses all information about the system. Because electrons are fermions, any legitimate Ψ must change its sign after an interchange of coordinates of any two electrons, a fundamental property of fermionic wavefunctions known as antisymmetry:

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = -\Psi(\mathbf{x}_2, \mathbf{x}_1, \dots, \mathbf{x}_N). \tag{1.2}$$

In the absence of external fields, the Hamiltonian for an N -electron system in the field of M nuclear point charges is given by

$$\hat{H} = \hat{T} + \hat{V}_{\text{ee}} + \hat{V}_{\text{en}} = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 + \sum_{i<j}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{i=1}^N v_{\text{ext}}(\mathbf{r}_i). \quad (1.3)$$

In this equation \hat{T} describes the kinetic energy of the electrons, \hat{V}_{ee} is the electron-electron repulsion component of the Hamiltonian, and \hat{V}_{en} is a contribution due to the external Coulomb potential of the nuclei,

$$v_{\text{ext}}(\mathbf{r}) = - \sum_{j=1}^M \frac{Z_j}{|\mathbf{r} - \mathbf{R}_j|}, \quad (1.4)$$

acting on each electron. Each nucleus is characterized by the charge Z_j and the position vector \mathbf{R}_j . For brevity, atomic units are employed here and below [2].

Unfortunately, it is impossible to solve the Schrödinger equation with the Hamiltonian of Eq. (1.3) analytically, except for $N = 1$. This means that many-electron wavefunctions have to be approximated in all practical realizations of WFT. The cornerstone of approximate WFT methods, the Hartree–Fock (HF) theory, uses an antisymmetrized product of spin orbitals $\{\phi_i(\mathbf{x}_i)\}$, or a Slater determinant, as an ansatz for the unknown wavefunction $\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)$:

$$\begin{aligned} \Psi_{\text{HF}}(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) &= \hat{\mathcal{A}} \left[\prod_{i=1}^N \phi_i(\mathbf{x}_i) \right] \\ &= (N!)^{-1/2} \begin{vmatrix} \phi_1(\mathbf{x}_1) & \phi_2(\mathbf{x}_1) & \cdots & \phi_N(\mathbf{x}_1) \\ \phi_1(\mathbf{x}_2) & \phi_2(\mathbf{x}_2) & \cdots & \phi_N(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(\mathbf{x}_N) & \phi_2(\mathbf{x}_N) & \cdots & \phi_N(\mathbf{x}_N) \end{vmatrix}, \end{aligned} \quad (1.5)$$

where $(N!)^{-1/2}$ is a normalization factor and $\hat{\mathcal{A}}$ is the antisymmetrizer operator. The spatial part of the spin orbitals is usually expanded using a set of auxiliary basis functions whose coefficients are variationally optimized. More advanced methods [3–6] use a linear combination of Slater determinants to represent the wavefunction. This generally improves the accuracy of calculations, but at the same time adds extra computational cost. Such methods scale unfavorably with the system’s size, which makes them computationally expensive for large systems relevant to chemists, for example, polymers and biomolecules. It is the advent of DFT and its rapid development that caused a break-

through in computational quantum chemistry. At present, accurate DFT calculations can be routinely performed on hundreds of atoms using personal computers, and linear scaling techniques for DFT in conjunction with supercomputing facilities allow one to study systems that involve millions of atoms [7, 8].

To understand the main idea of DFT, let us take a closer look at Eq. (1.3). Observe that the external potential, v_{ext} , is one of the two quantities that encode system-specific information in the Hamiltonian, the other one being the total number of electrons, N . Because these quantities suffice to set up the Hamiltonian, they implicitly determine the ground-state wavefunction and hence the ground-state energy of the system:

$$E = E[v_{\text{ext}}, N], \quad (1.6)$$

where the square brackets indicate that E is a functional of v_{ext} and N . Hohenberg and Kohn proved a theorem [1] that states: the external potential is uniquely determined by the ground-state electron density,

$$\rho(\mathbf{r}) = N \int \cdots \int |\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)|^2 d\sigma_1 d\mathbf{x}_2 \dots d\mathbf{x}_N. \quad (1.7)$$

For simplicity, we will refer to this quantity as “electron density” or “density” and will keep in mind that, unless noted otherwise, it corresponds to the ground state. Because the electron density integrates to the total number of electrons, the Hamiltonian and, as a consequence, the ground-state wavefunction together with all associated properties are also unique functionals of the electron density. In particular, for the ground-state energy one can write

$$E = E[\rho], \quad (1.8)$$

which means that there exists a unique functional that relates the electron density to the ground-state energy. One can further partition Eq. (1.8) as

$$E[\rho] = \int v_{\text{ext}}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + F[\rho], \quad (1.9)$$

where $F[\rho]$ is the *universal* density functional in the sense that it does not contain any system-specific information. However, an analytical expression for $F[\rho]$ in terms of the density is unknown, and it has to be approximated.

Hohenberg and Kohn [1] also justified the use of the variational principle for the energy functional of Eq. (1.9):

$$E_0 \leq E[\tilde{\rho}], \quad (1.10)$$

where $\tilde{\rho}$ is a trial density and E_0 denotes the exact ground-state energy. Eq. (1.10) suggests that the ground-state energy can be obtained (or approximated) by searching over a set of admissible densities. In case an input density minimizes the energy functional, it is guaranteed to be the ground-state density, and its corresponding energy is then the ground-state energy. Importantly, the variational principle only holds for densities that have an associated external potential (v -representable densities) [9].

1.2 Kohn–Sham method

By analogy with the Hamiltonian of Eq. (1.3), one can split $F[\rho]$ as

$$F[\rho] = T[\rho] + V_{ee}[\rho], \quad (1.11)$$

where T is the kinetic energy of electrons and V_{ee} is the energy due to the electron-electron repulsion. Neither of these functionals is known as an explicit functional of the electron density. Using the fact that the major piece of V_{ee} is the classical Coulomb repulsion,

$$J[\rho] = \frac{1}{2} \iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}, \quad (1.12)$$

one can convert Eq. (1.11) into

$$F[\rho] = T[\rho] + J[\rho] + E_{\text{ncl}}[\rho], \quad (1.13)$$

where $E_{\text{ncl}}[\rho]$ is a term that includes non-classical effects of electron exchange and correlation. Thus, the problem reduces to approximating $T[\rho]$ and $E_{\text{ncl}}[\rho]$ of which $T[\rho]$ constitutes a much larger contribution to $F[\rho]$.

Kohn and Sham [10] proposed to approximate the unknown $T[\rho]$ using a fictitious system of non-interacting electrons whose electron density is the same as the density of the real (interacting) system. One of the properties of this non-interacting system (to be denoted by the subscript “s”) is that its *exact* wavefunction can be represented by a Slater determinant for which the kinetic energy of N electrons is equal to

$$T_s[\rho] = -\frac{1}{2} \sum_{i=1}^N \int \phi_i^*(\mathbf{r}) \nabla^2 \phi_i(\mathbf{r}) d\mathbf{r} \quad (1.14)$$

and the N -electron density is given by

$$\rho(\mathbf{r}) = \sum_{i=1}^N |\phi_i(\mathbf{r})|^2. \quad (1.15)$$

For an interacting and a non-interacting system with a shared density, the non-interacting kinetic energy is, of course, not equal to its interacting counterpart. However, Eq. (1.14) can approximate the interacting kinetic energy to very good accuracy. This is the starting point of the Kohn–Sham (KS) theory.

The next step is to rewrite Eq. (1.13) as

$$F[\rho] = T_s[\rho] + J[\rho] + E_{\text{XC}}[\rho], \quad (1.16)$$

where $E_{\text{XC}}[\rho]$ is the exchange-correlation energy functional defined as

$$E_{\text{XC}}[\rho] = E_{\text{ncl}}[\rho] + T[\rho] - T_s[\rho]. \quad (1.17)$$

A perfect description of the quantity E_{XC} is given in a popular DFT textbook [11] by Wolfram Koch and Max Holthausen: “a junkyard where everything is stowed away which we do not know how to handle exactly”. Observe that, contrary to its name, it contains a non-negligible kinetic energy component. Kohn and Sham proceed by minimizing the total energy functional of Eq. (1.9) with $F[\rho]$ given by Eq. (1.16) with respect to ρ . This gives a set of N one-electron Schrödinger equations known as the canonical KS equations:

$$\left[-\frac{1}{2}\nabla^2 + v_{\text{eff}}(\mathbf{r}) \right] \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r}). \quad (1.18)$$

The orbitals $\{\phi_i\}$ are related to the electron density by Eq. (1.15). The local effective potential $v_{\text{eff}}(\mathbf{r})$ is called the KS potential and includes the following components:

$$v_{\text{eff}}(\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + v_{\text{H}}(\mathbf{r}) + v_{\text{XC}}(\mathbf{r}). \quad (1.19)$$

Here, v_{H} is the Hartree (electrostatic) potential,

$$v_{\text{H}}(\mathbf{r}) = \frac{\delta J[\rho]}{\delta \rho(\mathbf{r})} = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}', \quad (1.20)$$

and v_{XC} is a functional derivative of the exchange-correlation energy functional, or the

exchange-correlation potential,

$$v_{\text{XC}}(\mathbf{r}) = \frac{\delta E_{\text{XC}}[\rho]}{\delta \rho(\mathbf{r})}. \quad (1.21)$$

The KS potential depends on the density constructed from the KS orbitals $\{\phi_i\}$, so the KS equations must be solved iteratively through the following steps: (i) compute the external potential of the system and set up an initial guess for $\{\phi_i\}$; (ii) calculate ρ using Eq. (1.15) and construct the v_{XC} and v_{H} terms; (iii) solve Eq. (1.18) to obtain a new set of $\{\phi_i\}$; (iv) repeat steps (ii) and (iii) until self-consistency is reached.

The KS orbitals generally have no direct physical meaning, except for the highest-occupied orbital whose eigenvalue is equal to the negative of the ionization potential of the system [12–14]. This is because they are introduced merely as a mathematical construct to obtain the correct density. At the same time, it was empirically found that $\{\phi_i\}$ have an interpretive value. In particular, accurate KS eigenvalues agree quite well with experimental vertical ionization potentials [15].

The beauty of the KS theory is that it effectively replaces the N -electron Schrödinger equation with a more tractable one-electron problem. The KS equations are formally exact. In practice, however, one has to approximate the unknown v_{XC} . This constitutes the main challenge of the KS method because no systematic way to improve the accuracy of such approximations exists.

1.3 Functionals and functional derivatives

The mathematical formulation of DFT employs the concepts of the functional and the functional derivative. Here, we introduce these objects and briefly discuss their properties.

Loosely speaking, a function is a rule for assigning a number (a set of numbers) to another number. A functional is a prescription that maps a function (a set of functions) into a number. In simple terms, a functional is a function that takes another function (several functions) as an argument, which is formally written as

$$f \mapsto F[f]. \quad (1.22)$$

Many physical theories deal with the problem of finding extrema of a given functional in a domain of functions. This is the subject of calculus of variations. Recall that the extremum of a function can be found using its derivative. Similarly, in order to find the

extremal function for a functional, one needs to calculate its functional derivative.

Consider a density-functional approximation to some component of the electronic energy, $F[\rho]$. The functional derivative of F , $\delta F[\rho]/\delta\rho(\mathbf{r})$, is defined by

$$\int \frac{\delta F[\rho]}{\delta\rho(\mathbf{r})} h(\mathbf{r}) d\mathbf{r} = \lim_{\epsilon \rightarrow 0} \frac{F[\rho + \epsilon h] - F[\rho]}{\epsilon}, \quad (1.23)$$

where ϵ is a real number, h is an arbitrary integrable function, and the product ϵh is called the variation of ρ . The right-hand side of the above equation is known as the Gâteaux differential in the direction h [16]:

$$D_h F[\rho] = \lim_{\epsilon \rightarrow 0} \frac{F[\rho + \epsilon h] - F[\rho]}{\epsilon}. \quad (1.24)$$

If this limit exists for all functions h , the functional F is said to be Gâteaux differentiable at a point ρ , and one can write

$$D_h F[\rho] = \left\{ \frac{d}{d\epsilon} (F[\rho + \epsilon h]) \right\}_{\epsilon=0}. \quad (1.25)$$

The Gâteaux differential is analogous to the directional derivative in ordinary vector calculus, and the functional derivative can be thought of as an extension of the gradient of a function of several variables to an infinite number of variables:

$$\frac{\delta F[\rho]}{\delta\rho(\mathbf{r})} \longleftarrow \nabla F(x_1, x_2, \dots, x_n) = \left(\frac{\partial F}{\partial x_1}, \frac{\partial F}{\partial x_2}, \dots, \frac{\partial F}{\partial x_n} \right). \quad (1.26)$$

Eqs. (1.23)–(1.25) suggest a two-step method for obtaining the functional derivative of a given functional $F[\rho]$. First, evaluate its Gâteaux differential as prescribed by Eq. (1.25). Second, cast the result in the form

$$D_h F[\rho] = \int v(\mathbf{r}) h(\mathbf{r}) d\mathbf{r}. \quad (1.27)$$

The term $v(\mathbf{r})$ is the sought-for functional derivative, that is, $\delta F[\rho]/\delta\rho(\mathbf{r})$. It is itself a functional of ρ for each value of \mathbf{r} , which is sometimes indicated by writing $v([\rho]; \mathbf{r})$. Let us now illustrate this method with two examples.

Consider the Thomas–Fermi approximation for the kinetic energy,

$$T_{\text{TF}}[\rho] = C_{\text{TF}} \int \rho^{5/3}(\mathbf{r}) d\mathbf{r}, \quad (1.28)$$

where C_{TF} is a constant. Using Eq. (1.25) we write (the arguments of h and ρ are omitted

for brevity here and in the next example)

$$\begin{aligned} D_h T_{\text{TF}}[\rho] &= \left\{ \frac{d}{d\epsilon} C_{\text{TF}} \int (\rho + \epsilon h)^{5/3} d\mathbf{r} \right\}_{\epsilon=0} = \left\{ \frac{5}{3} C_{\text{TF}} \int (\rho + \epsilon h)^{2/3} d\mathbf{r} \right\}_{\epsilon=0} \\ &= \frac{5}{3} C_{\text{TF}} \int \rho^{2/3} h d\mathbf{r}. \end{aligned} \quad (1.29)$$

Comparing this with Eq. (1.27) we obtain the functional derivative of $T_{\text{TF}}[\rho]$:

$$\frac{\delta T_{\text{TF}}[\rho]}{\delta \rho(\mathbf{r})} = \frac{5}{3} C_{\text{TF}} \rho^{2/3}(\mathbf{r}). \quad (1.30)$$

The exchange-correlation energy functional of Eq. (1.17) is usually approximated in the form of an integral involving density-dependent ingredients. Let us derive a general expression for the functional derivative of an approximate $E_{\text{XC}}[\rho]$ given by

$$E_{\text{XC}}[\rho] = \int f_{\text{XC}}(\rho, \nabla \rho, \nabla^2 \rho) d\mathbf{r}, \quad (1.31)$$

where $f_{\text{XC}}(\rho, \nabla \rho, \nabla^2 \rho)$ is a model function termed the exchange-correlation energy density.

We start by evaluating the Gâteaux differential:

$$\begin{aligned} D_h E_{\text{XC}}[\rho] &= \left\{ \frac{d}{d\epsilon} \int f_{\text{XC}}(\rho + \epsilon h, \nabla(\rho + \epsilon h), \nabla^2(\rho + \epsilon h)) d\mathbf{r} \right\}_{\epsilon=0} \\ &= \int \left[\frac{\partial f_{\text{XC}}}{\partial \rho} h + \frac{\partial f_{\text{XC}}}{\partial \nabla \rho} \cdot \nabla h + \frac{\partial f_{\text{XC}}}{\partial \nabla^2 \rho} \nabla^2 h \right] d\mathbf{r}. \end{aligned} \quad (1.32)$$

We then apply integration by parts to the second term,

$$\int \frac{\partial f_{\text{XC}}}{\partial \nabla \rho} \cdot \nabla h d\mathbf{r} = - \int \nabla \cdot \left(\frac{\partial f_{\text{XC}}}{\partial \nabla \rho} \right) h d\mathbf{r}, \quad (1.33)$$

and to the third term (two integration steps are needed in this case),

$$\int \frac{\partial f_{\text{XC}}}{\partial \nabla^2 \rho} \nabla^2 h d\mathbf{r} = \int \nabla^2 \left(\frac{\partial f_{\text{XC}}}{\partial \nabla^2 \rho} \right) h d\mathbf{r}. \quad (1.34)$$

Here, we assumed that $h(\mathbf{r})$ is a well-behaved function that vanishes at infinity. Combining Eqs. (1.32)–(1.34) we get

$$D_h E_{\text{XC}}[\rho] = \int \left[\frac{\partial f_{\text{XC}}}{\partial \rho} - \nabla \cdot \left(\frac{\partial f_{\text{XC}}}{\partial \nabla \rho} \right) + \nabla^2 \left(\frac{\partial f_{\text{XC}}}{\partial \nabla^2 \rho} \right) \right] h d\mathbf{r}. \quad (1.35)$$

Therefore,

$$\frac{E_{\text{XC}}[\rho]}{\delta\rho(\mathbf{r})} = \frac{\partial f_{\text{XC}}}{\partial\rho} - \nabla \cdot \left(\frac{\partial f_{\text{XC}}}{\partial\nabla\rho} \right) + \nabla^2 \left(\frac{\partial f_{\text{XC}}}{\partial\nabla^2\rho} \right), \quad (1.36)$$

which implies that the functional derivative of the functional of Eq. (1.31) may depend on the density derivatives up to the fourth order.

Properties of the functional derivative resemble those of the ordinary derivative:

(i) linearity,

$$\frac{\delta(aF + bG)[f]}{\delta f(\mathbf{r})} = a \frac{\delta F[f]}{\delta f(\mathbf{r})} + b \frac{\delta G[f]}{\delta f(\mathbf{r})}, \quad (1.37)$$

where a and b are constants, (ii) the product rule,

$$\frac{\delta(FG)[f]}{\delta f(\mathbf{r})} = \frac{\delta F[f]}{\delta f(\mathbf{r})} G[f] + \frac{\delta G[f]}{\delta f(\mathbf{r})} F[f], \quad (1.38)$$

and (iii) the chain rule,

$$\frac{\delta F[f]}{\delta f(\mathbf{r})} = \int \frac{\delta F[G]}{\delta G(\mathbf{r}')} \frac{\delta G[f](\mathbf{r}')}{\delta f(\mathbf{r})} d\mathbf{r}'. \quad (1.39)$$

If the argument of F depends on a parameter λ , that is, $f \equiv f(\mathbf{r}, \lambda)$, we have

$$\frac{\partial F}{\partial\lambda} = \int \frac{\delta F[f]}{\delta f(\mathbf{r})} \frac{\partial f(\mathbf{r})}{\partial\lambda} d\mathbf{r}, \quad (1.40)$$

which follows from Eq. (1.39).

1.4 Explicit and implicit density functionals

We have seen that KS DFT is in principle an exact theory, which in practice requires an approximation to the unknown v_{XC} . The conventional approach is to model it *indirectly* through E_{XC} and then derive v_{XC} according to Eq. (1.21) using the method explained in the previous section. It is customary to partition E_{XC} into the exchange contribution, E_{X} , and the correlation contribution, E_{C} , and approximate them separately.

The simplest density-functional approximation is the local density approximation (LDA),

$$E_{\text{XC}}^{\text{LDA}}[\rho] = \int f_{\text{XC}}^{\text{LDA}}(\rho(\mathbf{r})) d\mathbf{r}, \quad (1.41)$$

whose exchange-correlation energy density function, $f_{\text{XC}}^{\text{LDA}} = f_{\text{X}}^{\text{LDA}} + f_{\text{C}}^{\text{LDA}}$, depends *only* on the electron density. This function is obtained from the uniform electron gas theory: either in the form of an exact analytic expression [17] (LDA for exchange) or as an accurate parametrization [18] of the exact numerical values from quantum Monte-Carlo

simulations (LDA for correlation). The LDA is generally more accurate than the HF theory in calculations of thermochemical properties and predicts reasonable equilibrium molecular geometries and lattice constants of solids.

The exact exchange-correlation functional is highly non-local, which means that it is sensitive to changes of the density not only at a point \mathbf{r} , but also at remote points. This suggests that the next level of accuracy can be reached by incorporating this non-locality in density-functional approximations. The successor of the LDA, the generalized gradient approximation (GGA), achieves this by the use of the density gradient, $\nabla\rho$, that contains information about the behavior of the density in an infinitesimal neighborhood of a point \mathbf{r} :

$$E_{\text{XC}}^{\text{GGA}}[\rho] = \int f_{\text{XC}}^{\text{GGA}}(\rho(\mathbf{r}), \nabla\rho(\mathbf{r}))d\mathbf{r}. \quad (1.42)$$

The GGA-based approximate functionals, or GGAs, are vastly better than the LDA. In fact, it is the development of the first GGAs that marked the wide acceptance of DFT by the chemical community. Nevertheless, GGAs remain far from the chemical accuracy (1 kcal/mol) and have serious flaws, for example, the inability to describe non-covalent interactions [19, 20].

The LDA and GGAs are similar in the sense they are both *explicit* functionals of the electron density. This feature can be viewed as a restriction because one is free to use quantities that are indirectly determined by the density, for example, the KS orbitals. Such a strategy brings us to *implicit*, or orbital-dependent functionals,

$$E_{\text{XC}}[\rho] = \int f(\{\phi_i\})d\mathbf{r}, \quad (1.43)$$

where $\{\phi_i\}$ is the set of the N occupied KS orbitals and f is an analytic expression written in terms of $\{\phi_i\}$. The function f must satisfy two properties: (i) it must be invariant with respect to a unitary transformation of the orbitals; (ii) it must be gauge-independent. The idea to use orbitals is in perfect alignment with the spirit of KS DFT that originates from the proposal to introduce the orbital-dependent kinetic energy functional T_s of Eq. (1.14).

The most important orbital-dependent functional in the KS theory is the exact-exchange functional,

$$E_{\text{X}}^{\text{exact}}[\rho] = -\frac{1}{4} \int d\mathbf{r} \int \frac{|\gamma(\mathbf{r}, \mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}', \quad (1.44)$$

where

$$\gamma(\mathbf{r}, \mathbf{r}') = \sum_{i=1}^N \phi_i(\mathbf{r})\phi_i^*(\mathbf{r}') \quad (1.45)$$

is the KS one-electron reduced density matrix (1-RDM). Equation (1.44) is the exact formula for the exchange energy of the KS determinant. The same expression for exchange is also used in the HF theory, where it is evaluated using the HF orbitals. The exact-exchange functional is normally combined with local and semilocal approximations for exchange and correlation. Such combinations, called hybrid functionals [21], have the following form in the simplest case:

$$E_{\text{XC}}[\rho] = a_0 E_{\text{X}}^{\text{exact}}[\rho] + (1 - a_0) E_{\text{X}}^{\text{DFA}}[\rho] + E_{\text{C}}^{\text{DFA}}[\rho], \quad (1.46)$$

where a_0 is an adjustable parameter and the superscript ‘‘DFA’’ indicates that $E_{\text{X}}^{\text{DFA}}$ and $E_{\text{C}}^{\text{DFA}}$ are approximations to the corresponding exact density functionals.

Another group of orbital-dependent functionals includes the so-called meta-GGAs of the form

$$E_{\text{XC}}^{\text{mGGA}}[\rho] = \int f_{\text{XC}}^{\text{mGGA}}(\rho(\mathbf{r}), \nabla\rho(\mathbf{r}), \nabla^2\rho(\mathbf{r}), \tau(\mathbf{r})) d\mathbf{r}, \quad (1.47)$$

where $\nabla^2\rho(\mathbf{r})$ is the Laplacian of the electron density, and

$$\tau(\mathbf{r}) = \frac{1}{2} \sum_{i=1}^N |\nabla\phi_i(\mathbf{r})|^2 \quad (1.48)$$

is the KS positive-definite kinetic energy density with the property that it integrates to the KS kinetic energy T_s of Eq. (1.14). The other form of the KS kinetic energy density is the Laplacian kinetic energy density,

$$\tau_L(\mathbf{r}) = \tau(\mathbf{r}) - \frac{\nabla^2\rho(\mathbf{r})}{4} = -\frac{1}{2} \sum_{i=1}^N \phi_i^*(\mathbf{r}) \nabla^2\phi_i(\mathbf{r}), \quad (1.49)$$

with the same property.

The advantage of orbital-dependent functionals is that they offer more freedom in the design of new approximations. However, they also have one fundamental shortcoming compared to explicit functionals. Recall that, in order to set up the KS equations for an approximate E_{XC} , one needs to obtain its functional derivative with respect to the electron density. For orbital-dependent functionals, this quantity cannot be evaluated in closed form by functional differentiation. To understand where the difficulty arises, let us apply the chain rule for functional derivatives to an arbitrary orbital-dependent

functional (we write it here as $E_{\text{XC}}[\{\phi_i\}]$ to emphasize the dependence on the orbitals):

$$v_{\text{XC}}(\mathbf{r}) = \frac{\delta E_{\text{XC}}[\{\phi_i\}]}{\delta \rho(\mathbf{r})} = \sum_{i=1}^N \int \frac{\delta E_{\text{XC}}}{\delta \phi_i(\mathbf{r}')} \frac{\delta \phi_i(\mathbf{r}')}{\delta \rho(\mathbf{r}')} d\mathbf{r}' + \text{c.c.}, \quad (1.50)$$

where ‘‘c.c.’’ denotes the complex conjugate of the preceding sum. Working out the first factor inside the integral, $\delta E_{\text{XC}}/\delta \phi_i$, is a trivial task, while the remainder, $\delta \phi_i/\delta \rho$, cannot be obtained in closed form by functional differentiation because there is no explicit mapping between i th orbital and the electron density. Fortunately, one can evaluate the functional derivative of Eq. (1.50) *numerically* using the optimized effective potential (OEP) method.

The OEP method was devised in 1953 by Sharp and Horton [22] who developed an approximation to the non-local exchange operator of the HF theory by having posed the following question: What is the effective local potential that minimizes the HF energy expression? They showed that such a potential satisfies an integral equation, now called the OEP equation. Numerical solutions of the OEP equation to spherical atoms were reported by Talman and Shadwick [23] in 1976. A few years later, Sahni and coworkers [24] demonstrated that the OEP potential is the exact exchange potential of KS DFT, that is, the functional derivative of the exact-exchange functional of Eq. (1.44).

Several equivalent forms of the OEP equation have been derived [25–28]. The most common one is the following:

$$\sum_{i=1}^N \int \phi_i^*(\mathbf{r}') [v_{\text{XC}}^{\text{OEP}}(\mathbf{r}') - \hat{u}_{\text{XC}}] G_{\text{KS},i}(\mathbf{r}, \mathbf{r}') \phi_i(\mathbf{r}) d\mathbf{r}' + \text{c.c.} = 0, \quad (1.51)$$

where the KS Green’s function, $G_{\text{KS},i}(\mathbf{r}, \mathbf{r}')$, is given by:

$$G_{\text{KS},i}(\mathbf{r}, \mathbf{r}') = \sum_{\substack{j=1 \\ j \neq i}}^{\infty} \frac{\phi_j(\mathbf{r}) \phi_j^*(\mathbf{r}')}{\epsilon_j - \epsilon_i}, \quad (1.52)$$

and \hat{u}_{XC} is a non-local operator such that

$$\hat{u}_{\text{XC}} \phi_i(\mathbf{r}) = \frac{\delta E_{\text{XC}}[\{\phi_i\}]}{\delta \phi_i^*(\mathbf{r})}. \quad (1.53)$$

It is important to note that the OEP equation is not limited to the exact exchange and is applicable to any orbital-dependent functional. However, the term ‘‘OEP’’ is often

(loosely) used to denote the functional derivative of the exact-exchange functional for historical reasons.

There are two reasons why the OEP method does not eliminate completely the main challenge of orbital-dependent functionals—the evaluation of their functional derivatives. First, existing methods for solving the OEP equation directly [29, 30] are not numerically reliable. Second, the OEP problem is ill-posed in finite basis sets, which means that the finite-basis-set representation of the OEP cannot be uniquely determined [31]. As a result, the OEP equation is often avoided in practical calculations with orbital-dependent functionals.

One way to circumvent the OEP equation is to replace the functional derivative $\delta E_{\text{XC}}[\{\phi_i\}]/\delta\rho(\mathbf{r})$ by the non-local orbital-specific operator of Eq. (1.53), an approach called the generalized Kohn–Sham (GKS) scheme [32]. When applied for the exact-exchange functional, the GKS scheme leads to the one-electron equations of the HF theory. The advantage of this approach is that it can be easily implemented and works quite well for total energies. However, the eigenvalue spectrum of the non-local operator \hat{u}_{XC} is not the same as that of the multiplicative operator $v_{\text{XC}}^{\text{OEP}}(\mathbf{r}) = \delta E_{\text{XC}}[\{\phi_i\}]/\delta\rho(\mathbf{r})$.

Another approach is to solve the OEP equation in an approximate way. The simplest approximation to the exact exchange potential was suggested [22] by the creators of the OEP method, Sharp and Horton, and goes back to an earlier result of Slater [33]. This approximation is called the Slater potential and has the following form:

$$v_{\text{X}}^{\text{OEP}}(\mathbf{r}) \approx v_{\text{S}}^{\text{HF}}(\mathbf{r}) = -\frac{1}{2\rho^{\text{HF}}(\mathbf{r})} \int \frac{|\gamma^{\text{HF}}(\mathbf{r}, \mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}', \quad (1.54)$$

where the HF electron density, $\rho^{\text{HF}}(\mathbf{r})$, and the HF 1-RDM, $\gamma^{\text{HF}}(\mathbf{r}, \mathbf{r}')$, are given by the same equations as their KS counterparts (Eqs. (1.15) and (1.45), respectively) but are constructed using the HF orbitals. The accuracy of the Slater potential is not adequate for practical purposes. Nevertheless, it is conceptually significant and serves as a building block for more accurate approximations.

The first truly successful approximation to the exact-exchange OEP was developed by Krieger, Li, and Iafrate [34] in 1990 and is known under the name “the KLI potential”:

$$v_{\text{X}}^{\text{OEP}}(\mathbf{r}) \approx v_{\text{X}}^{\text{KLI}}(\mathbf{r}) = v_{\text{S}}^{\text{HF}}(\mathbf{r}) + \frac{1}{\rho(\mathbf{r})} \sum_{i=1}^{\text{occ.}} |\phi_i(\mathbf{r})|^2 \left\langle \phi_i | v_{\text{X}}^{\text{KLI}} - \hat{K} | \phi_i \right\rangle, \quad (1.55)$$

where the operator \hat{K} is nothing but \hat{u}_{XC} of Eq. (1.53) evaluated for the exact-exchange functional and the orbitals $\{\phi_i\}$ are obtained self-consistently with $v_{\text{X}}^{\text{KLI}}$. The KLI po-

tential retains all important analytical features of the exact exchange potential but is considerably simpler to compute. Observe that the KLI potential is the sum of the Slater potential and the correction term. Competitors of the KLI approximation that appeared later [35–37] only differ by this correction term and have comparable accuracy.

1.5 Potential-driven Kohn–Sham density-functional theory

We have outlined the approach that dominates KS DFT: constructing an approximate $E_{\text{XC}}[\rho]$ whose functional derivative, v_{XC} , is subsequently used to solve the KS equations. An appealing alternative is to model v_{XC} directly and then integrate it to obtain the corresponding exchange-correlation energy. This approach is often referred to as potential-driven KS DFT, and approximations to the exchange-correlation potential are called *model* potentials. Compared to the conventional functional-based approach, working directly with the exchange-correlation potential makes it easier to reproduce desired properties of the exact v_{XC} . These properties usually include the Coulombic asymptotic decay [14, 38, 39], the shell structure [40], and the derivative discontinuity [12, 13, 41].

The long-range behavior of the exact v_{XC} is Coulombic [14, 38, 39, 42],

$$v_{\text{XC}}(\mathbf{r}) \sim -\frac{1}{r} \quad (r \rightarrow \infty), \quad (1.56)$$

where the asymptotic notation $f(x) \sim g(x)$ ($x \rightarrow \infty$) means that $\lim_{x \rightarrow \infty} [f(x)/g(x)] = 1$. At the same time, functional derivatives of common DFAs fall off faster (exponentially). The exponential asymptotic decay distorts the shape and energies of the highest occupied molecular orbital (HOMO) and of the other molecular orbitals, which leads to the incorrect description of molecular response properties such as the ionization potential (if approximated by the negative of the HOMO energy of the neutral system), electronic excitation energies, and polarizabilities. Several model potentials [43–45] were specifically designed to mimic the Coulombic decay of the exact v_{XC} . The most prominent example of such potentials is the approximation of van Leeuwen and Baerends (LB94) [43]. Their idea was to modify the exponentially decaying LDA potential for exchange,

$$v_{\text{X}}^{\text{LDA}}(\mathbf{r}) = -\frac{4}{3}C_{\text{X}}\rho^{1/3}(\mathbf{r}), \quad (1.57)$$

where $C_{\text{X}} = (3/4)(3/\pi)^{1/3}$, by adding a gradient-dependent term (the position variable

is suppressed for brevity):

$$v_{\text{X}}^{\text{LB94}} = v_{\text{X}}^{\text{LDA}} - \rho^{1/3} \frac{\beta \xi x^2}{1 + 3\beta \xi x \sinh^{-1}(\xi x)}, \quad (1.58)$$

where $x = |\nabla\rho|/\rho^{4/3}$ is a dimensionless reduced density gradient, β is an empirical parameter, and the factor $\xi = 2^{1/3}$ arises from conversion to the spin-unpolarized form. Besides the $-1/r$ decay, the gradient correction imparts the LB94 exchange potential with the pronounced shell structure.

The most important methodological question of potential-driven KS DFT is how to assign an energy to a given model potential. To this end, one needs to recover the corresponding energy functional by means of functional integration. The basic technique for integration of model potentials was pointed out by van Leeuwen and Baerends [46]. In their technique, known as the line integral method, the potential is integrated along a path in the space of electron densities,

$$E_{\text{XC}}[\rho] = \int d\mathbf{r} \int_0^1 v_{\text{XC}}([\rho_\lambda], \mathbf{r}) \frac{\rho_\lambda(\mathbf{r})}{\partial\lambda} d\lambda, \quad (1.59)$$

where $\rho_\lambda(\mathbf{r}) \equiv \rho(\mathbf{r}, \lambda)$ is a density parameterization which defines the path. Let us now define two classes of model potentials. An *integrable* potential is a potential that can be derived from some density functional. In other words, an integrable potential is a functional derivative. A *non-integrable* or *stray* potential, on the contrary, does not have a parent functional. In fact, most existing model potentials are stray [47], including the LB94 exchange potential of Eq. (1.58). The final result of Eq. (1.59) depends on whether a potential is integrable or stray. For integrable potentials, Eq. (1.59) will always produce the same exchange-correlation energy regardless of the chosen density path $\rho_\lambda(\mathbf{r})$. This is not the case for stray potentials for which such an energy depends on a path and hence cannot be uniquely assigned [48]. The path dependence of the exchange-correlation energy is not the only problem of stray potentials. They also lack translational and rotational invariance [49], cannot be used for geometry optimizations [47], and may lead to unphysical results [50–52] in calculations of molecular response properties. Thus, it is crucial to be able to identify stray potentials and make them integrable.

The basic integrability test for model exchange-correlation potentials was derived by Ou-Yang and Levy [53] and reads:

$$\frac{\delta v_{\text{XC}}(\mathbf{r})}{\delta\rho(\mathbf{r}')} = \frac{\delta v_{\text{XC}}(\mathbf{r}')}{\delta\rho(\mathbf{r})}. \quad (1.60)$$

This result of Ou-Yang and Levy can be understood as follows: in order for a potential to be a functional derivative of some density functional, the functional derivative of this potential with respect to the electron density must be a symmetric function with respect to the interchange of its variables \mathbf{r} and \mathbf{r}' . Gaiduk and Staroverov [54] later considered the explicitly density-dependent potential of the type

$$v_{\text{XC}} \equiv v_{\text{XC}}(\rho, \nabla\rho, \nabla^2\rho) \quad (1.61)$$

and demonstrated that in this case Eq. (1.60) is equivalent to

$$\frac{\partial v_{\text{XC}}}{\partial \nabla\rho} = \nabla \frac{\partial v_{\text{XC}}}{\partial \nabla^2\rho}. \quad (1.62)$$

The condition of Eq. (1.62) is satisfied for any integrable model potential of the type (1.61) and is violated otherwise. The significance of this equation is that it can be converted into a practical recipe [54] for turning stray potentials into functional derivatives.

The area where the use of model potentials has been most fruitful [55–58] is calculation of molecular response properties and particularly vertical electronic excitation spectra for atoms and molecules. Electronic excitation energies are either approximated as orbital energy differences or, more commonly, computed using adiabatic linear-response time-dependent density-functional theory (TDDFT) [59]. Popular density functionals severely underestimate [57, 60] high-lying (Rydberg) transitions, a failure that can be corrected by model potentials. Gaiduk *et al.* [61, 62] recently proposed a method for generation of model potentials from standard density functional approximations by the HOMO depopulation. Their scheme amounts to correcting the mid- and long-range behavior of $v_{\text{XC}}(\mathbf{r})$ and improves the accuracy of Rydberg excitations by an order of magnitude without affecting valence transitions. Another recent illustration of utility of model potentials in calculations of excitation energies was reported by Chai and coworkers [63]. They showed that asymptotically corrected model potentials can be reliably used to estimate Rydberg excitation energies and their accuracy is comparable to that of sophisticated multiparameter empirical functionals (for example, the M06-2X functional of Ref. 64) specifically tuned to reproduce these properties. Unfortunately, available model potentials still need to be improved [63, 65] for accurate description of charge-transfer excitations.

The superior performance of model potentials in terms of molecular response properties results from the high quality of the KS orbitals they produce. Baerends, Gritsenko, and coworkers [66–68] analyzed eigenspectra of the exact exchange-correlation potential, an accurate model potential (the statistical average of orbital potentials (SAOP) [56]),

and approximate density functionals. They found that the SAOP approximates the true $v_{\text{XC}}(\mathbf{r})$ much better than local, semilocal, and hybrid functionals. This is reflected in good agreement between experimental vertical excitation energies and virtual-occupied orbital energy gaps, reasonable shapes of virtual orbitals, and the single-orbital nature of most excitations, meaning that the transition density is dominated by one occupied-virtual orbital transition. One might expect the same picture for any other accurate model potential. Importantly, the use of hybrid functionals leads to the unoccupied orbitals that are too diffuse. This is because such functionals are normally applied using the GKS scheme discussed in Sec. 1.4. Recall that in this scheme the multiplicative operator $v_{\text{XC}}(\mathbf{r})$ is replaced by non-local orbital-specific potentials. In the case of global hybrids, Kim and coworkers [69] demonstrated that the transition to the KS scheme with the local OEP potential significantly improves the shape of the unoccupied KS orbitals and, as a result, the accuracy of TDDFT excited state calculations, and does not impact ground-state properties such as atomization energies and potential energy barrier heights.

Finally, we note that exchange-correlation potentials are important not only in the framework of potential-driven DFT but can also guide the development of approximate density functionals. Recall that in the conventional functional-based approach one approximates the exchange-correlation energy density. This quantity is such that its corresponding exchange-correlation energy remains unchanged upon addition of an arbitrary function that integrates to zero. On the other hand, $v_{\text{XC}}(\mathbf{r})$ is uniquely determined by the electron density and can be plotted as a function of \mathbf{r} . In many cases, failures of an approximate density functional can be understood by analyzing the shape of its functional derivative, $v_{\text{XC}}(\mathbf{r})$. Accurate exchange-correlation potentials can also be directly used to design new density functionals. For example, one can generate $v_{\text{XC}}(\mathbf{r})$ from correlated *ab initio* densities [70, 71] and use these potentials to constrain the functional derivative of a flexible functional form whose expansion coefficients are subsequently optimized [72–74].

1.6 Electrostatic approach to modelling the exchange-correlation potential¹

An alternative to the direct design of asymptotically correct model potentials is to approximate the so-called exchange-correlation charge distribution, $q_{\text{XC}}(\mathbf{r})$, defined [75–77]

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in terms of the exchange-correlation potential by the Poisson equation,

$$q_{\text{XC}}(\mathbf{r}) = -\frac{1}{4\pi} \nabla^2 v_{\text{XC}}(\mathbf{r}). \quad (1.63)$$

The quantity $q_{\text{XC}}(\mathbf{r})$ specifies a fictitious charge distribution whose electrostatic potential is equal to $v_{\text{XC}}(\mathbf{r})$, that is,

$$v_{\text{XC}}(\mathbf{r}) = \int \frac{q_{\text{XC}}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'. \quad (1.64)$$

Because Eqs. (1.63) and (1.64) are borrowed from electrostatics where they link the electric potential with its corresponding charge distribution, this approach is called the electrostatic approach to modelling the exchange-correlation potential.

The exchange-correlation charge distribution has many interesting properties [78–82], one of which is the following. Let

$$Q_{\text{XC}} = \int q_{\text{XC}}(\mathbf{r}) d\mathbf{r} \quad (1.65)$$

be the total exchange-correlation charge. Then the value of Q_{XC} determines the rate of asymptotic decay of the corresponding $v_{\text{XC}}(\mathbf{r})$. Specifically, using the big- O notation,

$$v_{\text{XC}}(\mathbf{r}) = \frac{Q_{\text{XC}}}{r} + O(r^{-m}) \quad (r \rightarrow \infty), \quad (1.66)$$

where $m > 1$. To understand the physical origin of this result, consider a spatially localized but otherwise arbitrary charge distribution $q(\mathbf{r})$. At a point \mathbf{r} such that $r \gg r'$, the electrostatic potential induced by this distribution can be represented by the multipole expansion [83]

$$v(\mathbf{r}) = \frac{Q}{r} + \frac{\mathbf{r} \cdot \mathbf{Q}^{(1)}}{r^3} + \frac{\mathbf{r} \cdot \mathbf{Q}^{(2)} \cdot \mathbf{r}}{r^5} + \dots, \quad (1.67)$$

where $Q = \int q(\mathbf{r}') d\mathbf{r}'$ is the total charge or the monopole moment (a rank-zero tensor), $\mathbf{Q}^{(1)} = \int \mathbf{r}' q(\mathbf{r}') d\mathbf{r}'$ is the dipole moment (a rank-one tensor), $\mathbf{Q}^{(2)}$ is the quadrupole moment (a rank-two tensor), and so forth. According to Eq. (1.67), the leading term in the asymptotic expansion of $v(\mathbf{r})$ is Q/r . If $Q = 0$, then $v(\mathbf{r})$ must decay faster than any Coulombic potential [84].

For example, the *exact* $v_{\text{XC}}(\mathbf{r})$ in an atom or molecule decays Coulombically [Eq. (1.56)]. This immediately suggests that the exact $q_{\text{XC}}(\mathbf{r})$ satisfies the sum rule [75–78]

$$Q_{\text{XC}} \equiv \int q_{\text{XC}}(\mathbf{r}) d\mathbf{r} = -1. \quad (1.68)$$

The exact correlation potential is known to fall off as [14, 85]

$$v_{\text{C}}(\mathbf{r}) \sim -\frac{\alpha}{2r^4} \quad (r \rightarrow \infty), \quad (1.69)$$

where α is a system-dependent constant. This means that the exact correlation charge distribution $q_{\text{C}}(\mathbf{r})$, defined in terms of $v_{\text{C}}(\mathbf{r})$ by analogy with Eq. (1.63), has the normalization property [78]

$$Q_{\text{C}} \equiv \int q_{\text{C}}(\mathbf{r}) d\mathbf{r} = 0. \quad (1.70)$$

Finally, Eqs. (1.56) and (1.69) together imply that the exact exchange potential is Coulombic [85],

$$v_{\text{X}}(\mathbf{r}) \sim -\frac{1}{r} \quad (r \rightarrow \infty) \quad (1.71)$$

and hence the exact exchange charge satisfies [76, 78]

$$Q_{\text{X}} \equiv \int q_{\text{X}}(\mathbf{r}) d\mathbf{r} = -1 \quad (1.72)$$

since $Q_{\text{XC}} = Q_{\text{X}} + Q_{\text{C}}$.

The promise of the electrostatic approach is that it is well suited for enforcing correct asymptotic behavior of $v_{\text{XC}}(\mathbf{r})$. The sum rule of Eq. (1.68) suggests the following strategy: (i) find a suitable analytic expression for $q_{\text{XC}}(\mathbf{r})$ that integrates to -1 ; (ii) insert it into Eq. (1.64) to obtain an approximate exchange-correlation potential. This strategy has already been used [86, 87] to develop model potentials with correct long-range decay.

1.7 Outline of the study

The goal of my graduate research was to explore a promising direction in potential-driven KS DFT (electrostatic approach of Sec. 1.6) as well as to advance several existing problems in this field. The scope of this thesis includes four domains: (i) development of approximate exchange-correlation potentials by modelling the exchange-correlation charge distribution, (ii) accurate approximation of functional derivatives of orbital-dependent functionals, (iii) generation of exact exchange-correlation potentials, and (iv) analysis of accurate exchange-correlation potentials in atoms and molecules.

In Chapter 2, we revisit the sum rules for exchange-correlation charge distributions and discuss practical implications of an important caveat that arises during evaluation of the total exchange-correlation charge for functional derivatives of GGAs. In Chapter 3, we derive an integrability test for the exchange-correlation potential expressed in the form

of an explicitly density-dependent exchange-correlation charge distribution. Chapter 4 describes a method for constructing a hierarchy of model potentials approximating the functional derivative of a given orbital-dependent exchange-correlation functional with respect to the electron density. The accuracy of the highest ladder in the proposed hierarchy is such that it can be regarded as the finite-basis-set OEP for all practical purposes. In Chapter 5, we present an algorithm for calculating the exchange-correlation potential from a given electronic wavefunction. Our algorithm is free from numerical instabilities of conventional density fitting schemes and can be used to probe the functional derivative of the true exchange-correlation functional. In Chapter 6, we apply the method of Chapter 5 to study the origin of the step structure of the exact exchange-correlation potential in heteronuclear diatomic molecules. Finally, the focus of Chapter 7 is on the step structure of exchange-correlation potentials reconstructed from restricted Hartree–Fock wavefunctions of stretched diatomic molecules and, specifically, its relation to spurious fractional charges in stretched diatomic molecules.

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Chapter 2

Apparent violation of the sum rule for exchange-correlation charges by generalized gradient approximations

2.1 Introduction

It is well known [1] that exchange-correlation potentials derived from the local density approximation (LDA) and all commonly used generalized gradient approximations (GGAs) decay faster than $-\text{const}/r$. This implies that exchange-correlation charge distribution [Eq. (1.63)] derived from the LDA or any common GGA must be such that the total exchange-correlation charge, Q_{XC} , integrates to 0. However, Liu *et al.* [2] reported values $Q_{\text{XC}} < 0$ for exchange-correlation potentials reconstructed from LDA and GGA electron densities by the Zhao–Morrison–Parr method [3]. This inconsistency was one of the original motivations for this work.

Another reason for revisiting the sum rules expressed by Eqs. (1.68), (1.70), and (1.72) has to do with recent advances in the theory of model Kohn–Sham potentials. It is now firmly established that the proper Coulombic decay of $v_{\text{XC}}(\mathbf{r})$ is crucial for accurate description of excited states and many ground-state properties [4–9]. According to Eq. (1.56), any approximate exchange-correlation potential with $Q_{\text{XC}} = -1$ should decay as $-1/r$. This suggests using the function $q_{\text{XC}}(\mathbf{r})$ as a handle on the asymptotic behavior of $v_{\text{XC}}(\mathbf{r})$. In fact, several workers have already attempted to devise approximate exchange potentials with proper $-1/r$ decay by modeling the corresponding ex-

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change charge and then enforcing the sum rule of Eq. (1.72). For example, Andrade and Aspuru-Guzik [10] altered the shape of the $q_X(\mathbf{r})$ corresponding to the exchange LDA potential [Eq. (1.57)] to enforce Eq. (1.72) and obtained an asymptotically corrected model potential that produced accurate fundamental energy gaps in atoms and molecules. Gidopoulos and Lathiotakis [11] have employed Eq. (1.72) as a constraint within the optimized effective potential method to obtain approximate Kohn–Sham potentials with correct asymptotic decay.

Here we uncover and discuss an important caveat that must be taken into consideration when using the sum rules for exchange and correlation charges as constraints for devising model Kohn–Sham potentials. Our findings concern all GGAs and other types of density-functional approximations whose functional derivatives are singular at the nuclei.

2.2 Numerical tests of the sum rules

Our first objective is to test Eqs. (1.68), (1.70), and (1.72) for exchange and correlation charge distributions derived from density-functional *approximations*. To simplify the task we restrict ourselves to spherically symmetric atoms, for which the exchange–correlation potential is effectively one-dimensional and Eq. (1.63) reduces to

$$q_{XC}(r) = -\frac{1}{4\pi r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial v_{XC}}{\partial r} \right). \quad (2.1)$$

The total exchange charge is then given by

$$Q_{XC} = 4\pi \int r^2 q_{XC}(r) dr, \quad (2.2)$$

Similar equations hold, of course, for exchange and correlation separately.

We selected the following density-functional approximations: LDA for exchange (LDAX), LDA for correlation (LDAc) in the Perdew–Wang parametrization [12], the exchange part of the model potential of van Leeuwen and Baerends [13] (LB94x), the exchange part of the Perdew–Burke–Ernzerhof [14] (PBEx) GGA, and Becke’s 1988 exchange [15] (B88x) GGA. For each approximation, the exchange–correlation charge distribution was derived by Eq. (2.1) from the corresponding potential. The LDAX, LDAc, PBEx, and B88x potentials were obtained as functional derivatives of the respective functionals using Eq. (13) of Ref. 16, whereas the LB94x potential was used as is (since it has no parent functional [13, 17]).

Table 2.1: Total exchange (correlation) charges for various density-functional approximations obtained by numerical integration of the corresponding exchange (correlation) charge distributions. The results are for Hartree–Fock–Roothaan electron densities expanded in Slater-type basis sets [18]. All reported significant figures are accurate.

Atom	LDAX	LDAc	LB94x	PBE _x	B88 _x
H	0.000000	0.000000	−1.000000	0.036513	0.039568
He	0.000000	0.000000	−1.000000	0.040220	0.042832
Be	0.000000	0.000000	−1.000000	0.037994	0.040885
Ne	0.000000	0.000000	−1.000000	0.036788	0.039814
Mg	0.000000	0.000000	−1.000000	0.036576	0.039624
Ar	0.000000	0.000000	−1.000000	0.036017	0.039123
Ca	0.000000	0.000000	−1.000000	0.036090	0.039189
Kr	0.000000	0.000000	−1.000000	0.035685	0.038824
Sr	0.000000	0.000000	−1.000000	0.035648	0.038791
Xe	0.000000	0.000000	−1.000000	0.035456	0.038617

All tests were performed for the Hartree–Fock–Roothaan ground-state atomic electron densities, which were constructed from the Slater-type basis-set orbital expansions reported by Bunge *et al.* [18]. The asymptotic tail of every trial density used in this work is therefore truly exponential,

$$\rho(\mathbf{r}) = O(e^{-ar}) \quad (r \rightarrow \infty), \quad (2.3)$$

where $a = 2\zeta$, and ζ is the exponent of the most diffuse Slater-type orbital. Starting from the basis-set representation of the input density, $v_{\text{XC}}(\mathbf{r})$ and $q_{\text{XC}}(\mathbf{r})$ were computed analytically using the MATHEMATICA [19] program. The resulting distributions $q_{\text{XC}}(\mathbf{r})$ were integrated numerically using the built-in function `NIntegrate` whose parameters were adjusted to ensure an absolute accuracy of 10^{-7} in Q_{XC} values. The results appear in Table 2.1.

Consider first the LDAX values. The spin-unpolarized form of the LDAX potential is given by Eq. (1.57). In the tail of an atomic density, where Eq. (2.3) holds, this potential is exponential,

$$v_{\text{X}}^{\text{LDA}}(\mathbf{r}) = -O(e^{-ar/3}) \quad (r \rightarrow \infty). \quad (2.4)$$

For reasons explained in Sec. 2.1, we expect $Q_{\text{X}}^{\text{LDA}} = 0$ for all atoms. The data of Table 2.1 confirm this prediction.

The LDAc potential is given by $v_C^{\text{LDA}} = \partial(\rho\epsilon_C^{\text{LDA}})/\partial\rho$, where ϵ_C^{LDA} is the LDAc energy per electron as defined by Eqs. (8)–(10) of Ref. 12. It is straightforward to show that the asymptotic form of the LDAc potential for an exponential density of Eq. (2.3) is again exponential,

$$v_C^{\text{LDA}}(\mathbf{r}) = -O(e^{-ar/3}) \quad (r \rightarrow \infty). \quad (2.5)$$

Therefore, Q_C^{LDA} should be zero for all atoms, which is what we obtained (Table 2.1).

The spin-unpolarized form of the gradient-corrected LB94x potential is defined by Eq. (1.58). The LB94x potential was specifically designed [13] to have the asymptotic behavior of the exact exchange potential,

$$v_X^{\text{LB94}}(\mathbf{r}) \sim -\frac{1}{r} \quad (r \rightarrow \infty). \quad (2.6)$$

Therefore, the total LB94x charge should be -1 for all atoms. Actual numerical calculations reproduce this value to all digits of accuracy (Table 2.1).

Now let us try to rationalize the results for the GGAs. Every GGA for the exchange energy has the form

$$E_X^{\text{GGA}}[\rho] = \int \epsilon_X^{\text{LDA}}(\rho) F(x) d\mathbf{r}, \quad (2.7)$$

where $x = |\nabla\rho|/\rho^{4/3}$ is a dimensionless reduced density gradient, $\epsilon_X^{\text{LDA}}(\rho) = -C_X\rho^{4/3}$, and $F_X(x)$ is an enhancement factor in the spin-unpolarized form. For PBE_x,

$$F_X^{\text{PBE}}(x) = 1 + \frac{\mu x^2}{1 + \mu x^2/\kappa}, \quad (2.8)$$

where $\mu = 0.21951/4(3\pi^2)^{2/3}$ and $\kappa = 0.804$. Using this definition one finds that, for $\rho(\mathbf{r}) = O(e^{-ar})$,

$$v_X^{\text{PBE}}(\mathbf{r}) = -O(e^{-ar/3}) \quad (r \rightarrow \infty). \quad (2.9)$$

The potential decays faster than const/r and so, according to Eq. (1.66), Q_X^{PBE} should be zero. However, our calculations give $Q_X^{\text{PBE}} > 0$ for all atoms (Table 2.1).

Similarly, for the B88x functional [15] with

$$F_X^{\text{B88}}(x) = 1 + \frac{1}{C_X} \frac{b\xi x^2}{1 + 6b\xi x \sinh^{-1}(\xi x)}, \quad (2.10)$$

where $b = 0.0042$, one finds [20] that, for $\rho(\mathbf{r}) = O(e^{-ar})$,

$$v_X^{\text{B88}}(\mathbf{r}) = -O(r^{-2}) \quad (r \rightarrow \infty). \quad (2.11)$$

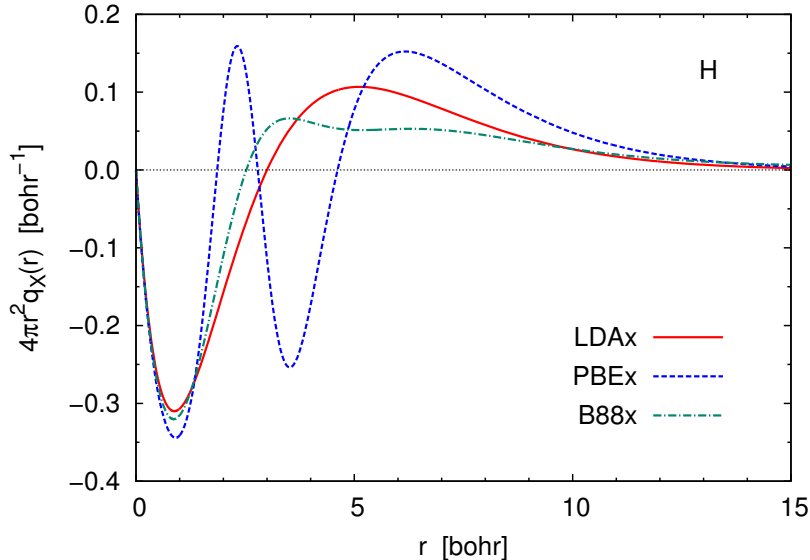


Figure 2.1: Radial exchange-charge distributions derived from the LDAx and two GGAs for the exact hydrogenic density. All three distributions can be reliably integrated, but only the LDAx curve yields the correct total charge $Q_X = 0$ (Table 2.1).

Thus, we should have $Q_X^{\text{B88}} = 0$, but actual numerical calculations yield $Q_X^{\text{B88}} > 0$ for all atoms (Table 2.1), manifestly at odds with theory.

2.3 Resolution of the paradox

To account for the apparent violation of the sum rule for the PBEx and B88x exchange charges, we first considered the possibility that the non-zero values of Q_X^{PBE} and Q_X^{B88} in Table 2.1 are results of numerical integration errors. Such errors are not inconceivable and in fact unavoidable when one attempts to integrate a pathological function with singularities or rapid oscillations. Figures 2.1 and 2.2 show, however, that the PBEx and B88x radial distributions $4\pi r^2 q_X(r)$ are as well-behaved as the LDAx distribution, for which the accuracy of our numerical integration is beyond doubt.

Then we observed that, unlike the LDAx, LDAc and LB94x potentials, the functional derivatives of GGAs are singular at the nucleus. Specifically, one can show [21] that for exchange GGAs in an atom,

$$v_X^{\text{GGA}}(\mathbf{r}) \sim -\frac{c}{r} \quad (r \rightarrow 0), \quad (2.12)$$

where $c > 0$ is a system-dependent constant (see Ref. 16 for a fully worked-out expres-

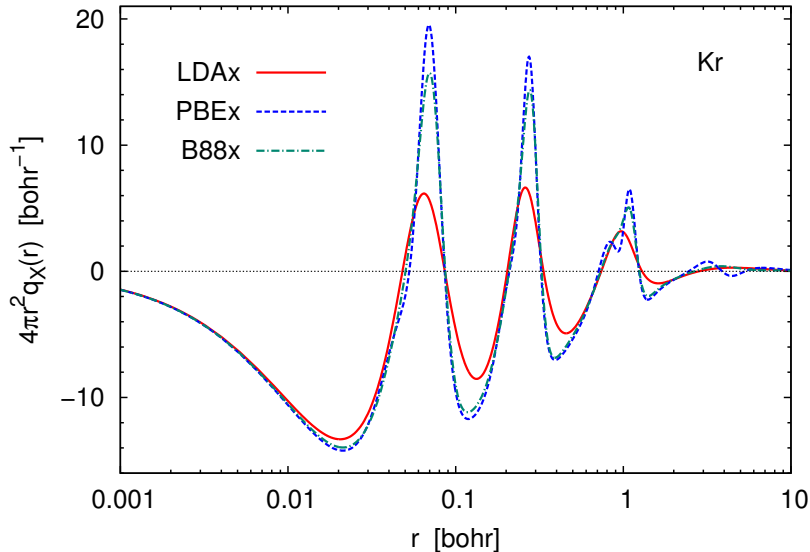


Figure 2.2: Same as in Fig. 2.1 for a Hartree–Fock–Roothaan density of the ground-state krypton atom.

sion). This allows us to express a GGA exchange potential in an atom

$$v_X^{\text{GGA}}(\mathbf{r}) = \tilde{v}_X(\mathbf{r}) - \frac{c}{r}, \quad (2.13)$$

where $\tilde{v}_X(\mathbf{r})$ is the singularity-free part. Let us substitute this expression into Eq. (1.63) and recall that

$$\frac{1}{4\pi} \nabla^2 \left(-\frac{1}{r} \right) = \delta(\mathbf{r}), \quad (2.14)$$

where $\delta(\mathbf{r})$ is Dirac’s δ -function. It transpires that the exchange-correlation charge corresponding to a GGA potential has the general form

$$q_X^{\text{GGA}}(\mathbf{r}) = \tilde{q}_X(\mathbf{r}) - c\delta(\mathbf{r}), \quad (2.15)$$

where $\tilde{q}_X(\mathbf{r})$ is a well-behaved function arising from the singularity-free part $\tilde{v}_X(\mathbf{r})$, and $-c\delta(\mathbf{r})$ is the contribution arising from the singularity of $v_X^{\text{GGA}}(\mathbf{r})$ at the nucleus. Standard numerical integration algorithms deliver the charge $\tilde{Q}_X = \int \tilde{q}_X(\mathbf{r}) d\mathbf{r}$, but cannot sample the point-charge contribution at $r = 0$, because $v_X^{\text{GGA}}(\mathbf{r})$ is undefined there. As a result, the sum rule appears to be violated.

This shows that to evaluate the total exchange for a GGA correctly, it is not enough to integrate the distribution $q_X^{\text{GGA}}(\mathbf{r})$ numerically. One must also determine the value of

c and combine it with the numerical integral,

$$Q_X = \tilde{Q}_X - c. \quad (2.16)$$

The point charge c is approximation- and system-dependent and, for a given density, can be determined as

$$c = -\lim_{r \rightarrow 0} r v_X^{\text{GGA}}(\mathbf{r}). \quad (2.17)$$

As an illustration, let us calculate the value of c for the PBE exchange potential using the exact density of the hydrogen atom, $\rho(\mathbf{r}) = e^{-2r}/\pi$. Substituting this $\rho(\mathbf{r})$ into the spin-polarized analytic expression for the PBE exchange potential and using Eq. (2.17) we obtain

$$c_X^{\text{PBE}} = \frac{2^{8/3} \pi^{1/3} C_X \kappa^2 \mu}{(\kappa + 2^{4/3} \pi^{2/3} \mu)^2} \approx 0.036513, \quad (2.18)$$

where C_X , κ , and μ are parameters of the PBE exchange functional defined above. This value exactly matches the apparent total PBE exchange charge \tilde{Q}_X^{PBE} shown in Table 2.1. By Eq. (2.16), the true PBE exchange charge for the hydrogen atom is zero, consistent with the exponential decay of the PBE exchange potential. A similar calculation for the B88 exchange charge in the H atom gives $c_X^{\text{B88}} \approx 0.039568$, also in perfect agreement with Table 2.1. Thus, the paradox of nonzero apparent exchange charges obtained from the PBE and B88 potentials is fully resolved.

One should keep in mind that, although all common GGAs give rise to potentials that decay quadratically or faster, the GGA form by itself does not preclude the $-1/r$ decay of $v_X(\mathbf{r})$. GGAs leading to exchange potentials with correct asymptotic behavior have been constructed, for instance, in Refs. 20 and [22]. Such GGAs are not common because they give poor exchange energies but, in the present context, serve as very interesting test cases that provide further insights into the relationship between the apparent and true total exchange charges and the behavior of $v_X(\mathbf{r})$ at large and small r .

Consider, for instance, the (impractical) exchange GGA suggested by the analysis of Engel, Chevary, Macdonald, and Vosko [20] (ECMV). The enhancement factor for this GGA may be written as

$$F_X^{\text{ECMV}}(x) = 1 + \frac{x}{2C_X}. \quad (2.19)$$

Using Eq. (2.19) one can show [16, 20] that, in the tail of an exponential density,

$$v_X^{\text{ECMV}}(\mathbf{r}) \sim -\frac{1}{r} \quad (r \rightarrow \infty). \quad (2.20)$$

According to Eq. (1.66), we should have $Q_X^{\text{ECMV}} = -1$. In reality, accurate numerical

integration of $q_X^{\text{ECMV}}(\mathbf{r})$ for all atoms gives a total charge of zero (not shown in Table 2.1), as if $v_X^{\text{ECMV}}(\mathbf{r})$ were an exponentially decaying potential. This does not mean, of course, that Eq. (1.66) is wrong, but that we are missing a large point-charge contribution to Q_X^{ECMV} . One can show that the ECMV potential is purely Coulombic near the nucleus,

$$v_X^{\text{ECMV}}(\mathbf{r}) \sim -\frac{1}{r} \quad (r \rightarrow 0), \quad (2.21)$$

so that $c_X^{\text{ECMV}} = 1$. Upon inclusion of the point-charge contribution we obtained $Q_X^{\text{ECMV}} = -1$ for every atom, as it should be.

2.4 Conclusion

We have shown analytically and numerically that the value of the total exchange-correlation charge, Q_{XC} , determines the rate of the asymptotic decay the corresponding exchange-correlation potential via Eq. (1.66). The subtle aspect of applying this rule is that, to obtain the correct values of Q_{XC} it is necessary to analyze the behavior of the potential at the nucleus (every nucleus in a molecule). If the potential has a Coulombic singularity at a nucleus (as GGAs do), the corresponding exchange-correlation charge will contain a non-zero point charge contribution which cannot be accounted for by numerical quadratures. This point charge contribution must be evaluated explicitly by Eq. (2.17).

As for the nonzero values of Q_{XC} reported by Liu *et al.* [2] for the LDA and GGA exchange-correlation potentials, we believe that they were a combined result of numerical errors of the Zhao–Morrison–Parr procedure and residual contributions of the Coulombically decaying Fermi–Amaldi potential which was used as a fixed reference to represent each $v_{\text{XC}}(\mathbf{r})$. This explanation is consistent with the fact that most values of Q_{XC} in Table I of Ref. 2 are close to -1 .

The relationship between the magnitude of Q_{XC} and the asymptotic behavior of $v_{\text{XC}}(\mathbf{r})$ has important practical implications. For example, to construct a model exchange-correlation potential with the correct $-1/r$ asymptotic decay, it is sufficient to model a distribution $q_{\text{XC}}(\mathbf{r})$ that integrates to -1 . This can be accomplished by taking an exchange-correlation charge distribution that integrates to zero (e.g., LDAx) and reshaping it [10], or by adding a point exchange-correlation charge at the nucleus (in which case $v_{\text{XC}}(\mathbf{r})$ will be singular at $r = 0$). The overall effect of the latter approach should be qualitatively similar to the effect of depopulating the highest-occupied molecular orbital of the system in a self-consistent Kohn–Sham calculation [23, 24]. At the same time, it is not possible to obtain a Coulombic potential by taking the LDA exchange-correlation

charge distribution and simply scaling it, because the total exchange-correlation charge will remain zero.

An approximate Kohn–Sham potential obtained from a model exchange-correlation charge distribution using Eq. (1.63) will generally not be a functional derivative of any energy expression. Although it is possible to assign reasonable energy values to non-integrable Kohn–Sham potentials in many different ways [25–27], a better strategy would be to find the constraints on $q_{XC}(\mathbf{r})$ which ensure that the corresponding $v_{XC}(\mathbf{r})$ is a functional derivative. In Chapter 3, we derive these constraints in the form of an analytical test that a model function $q_{XC}(\mathbf{r})$ must pass in order for the corresponding $v_{XC}(\mathbf{r})$ to be a functional derivative of some energy functional.

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Chapter 3

Integrability conditions for model potentials constructed using the exchange-correlation charge distribution

3.1 Introduction

Two methodological challenges of potential-driven KS DFT are: (i) how to assign an energy to a given model potential and (ii) how to identify and construct integrable model potentials. The first problem was solved by the line integral method [1] of van Leeuwen and Baerends [Eq. (1.59)]. The second problem was addressed by Ou-Yang and Levy [2] followed by van Leeuwen and Baerends [1] who derived the basic integrability condition for model potentials:

$$\frac{\delta v_{\text{XC}}(\mathbf{r})}{\delta \rho(\mathbf{r}')} = \frac{\delta v_{\text{XC}}(\mathbf{r}')}{\delta \rho(\mathbf{r})}. \quad (3.1)$$

The above equation can serve as the starting point for deriving more practical integrability conditions for potentials restricted to certain analytic forms. Consider, for example, an explicitly density-dependent potential, $v_{\text{XC}} \equiv v_{\text{XC}}(\rho, \nabla \rho, \nabla^2 \rho)$. For such a potential, evaluating both sides of Eq. (3.1), followed by their comparison, leads to the integrability condition of Eq. (1.62) [3].

In this chapter, we derive analytic integrability conditions for model potentials expressed in the form of the electrostatic integral of Eq. (1.64). To this end, we first obtain integrability conditions for a broad class of non-local potentials. Next, we apply these conditions to work out integrability constraints on the exchange-correlation charge dis-

tribution. Derivations presented in this work require the knowledge of several properties of the Dirac delta function and its derivatives, which are summarized in Appendix A.

3.2 Integrability conditions for non-local model potentials

Consider a model potential of the form

$$v_{\text{XC}}(\mathbf{r}) = \int g(\mathbf{r}, \mathbf{r}') d\mathbf{r}', \quad (3.2)$$

where $g(\mathbf{r}, \mathbf{r}')$ is some function of the electron density and its derivatives. Such a potential is said to be *non-local* because it contains information about the density not only at a point \mathbf{r} but also at all other points \mathbf{r}' . Approximations of this type have not been proposed to date. Their development is one of the most promising routes in potential-driven KS DFT. This is because functional derivatives of common density-functional approximations (DFAs) fail to reproduce the nonlocality of the exact $v_{\text{XC}}(\mathbf{r})$ [4]. Here, we derive analytic integrability conditions for $v_{\text{XC}}(\mathbf{r})$ of the type (3.2).

Our starting point is the function $g(\mathbf{r}, \mathbf{r}')$ of the following form:

$$g(\mathbf{r}, \mathbf{r}') \equiv g(\rho(\mathbf{r}), \rho(\mathbf{r}'), \nabla\rho(\mathbf{r}), \nabla\rho(\mathbf{r}'), \nabla^2\rho(\mathbf{r}), \nabla^2\rho(\mathbf{r}')). \quad (3.3)$$

The next step is to apply Eq. (3.1) to $v_{\text{XC}}(\mathbf{r})$ of Eq. (3.2) where $g(\mathbf{r}, \mathbf{r}')$ is given by Eq. (3.3). Let us first evaluate the right-hand side of Eq. (3.1). It is straightforward to show that

$$\begin{aligned} \frac{\delta v_{\text{XC}}(\mathbf{r})}{\delta\rho(\mathbf{r}')} &= \frac{\partial g}{\partial\rho(\mathbf{r}')} - \nabla_{\mathbf{r}'} \cdot \frac{\partial g}{\partial\nabla_{\mathbf{r}'}\rho(\mathbf{r}')} + \nabla_{\mathbf{r}'}^2 \frac{\partial g}{\partial\nabla_{\mathbf{r}'}^2\rho(\mathbf{r}')} \\ &+ (A(\mathbf{r}') - \nabla_{\mathbf{r}'} \cdot B(\mathbf{r}') + \nabla_{\mathbf{r}'}^2 C(\mathbf{r}')) \delta(\mathbf{r} - \mathbf{r}') \\ &+ (2\nabla_{\mathbf{r}'} C(\mathbf{r}') - B(\mathbf{r}')) \cdot \nabla_{\mathbf{r}'} \delta(\mathbf{r} - \mathbf{r}') + C(\mathbf{r}') \nabla_{\mathbf{r}'}^2 \delta(\mathbf{r} - \mathbf{r}'), \end{aligned} \quad (3.4)$$

where $\delta(\mathbf{r} - \mathbf{r}')$ denotes the Dirac delta function and the functions $A(\mathbf{r}')$, $B(\mathbf{r}')$, and $C(\mathbf{r}')$ are given by

$$A(\mathbf{r}') = \int \frac{\partial g'}{\partial\rho(\mathbf{r}')} d\mathbf{r}, \quad (3.5)$$

$$B(\mathbf{r}') = \int \frac{\partial g'}{\partial\nabla\rho(\mathbf{r}')} d\mathbf{r}, \quad (3.6)$$

and

$$C(\mathbf{r}') = \int \frac{\partial g'}{\partial \nabla^2 \rho(\mathbf{r}')} d\mathbf{r}, \quad (3.7)$$

respectively. Here, g' is essentially the same function as g with the exception that its variables are interchanged:

$$g' \equiv g(\mathbf{r} \rightarrow \mathbf{r}', \mathbf{r}' \rightarrow \mathbf{r}). \quad (3.8)$$

Evaluating the left-hand side of Eq. (3.1), we obtain:

$$\begin{aligned} \frac{\delta v(\mathbf{r}')}{\delta \rho(\mathbf{r})} &= \frac{\partial g'}{\partial \rho(\mathbf{r})} - \nabla_{\mathbf{r}} \cdot \frac{\partial g'}{\partial \nabla_{\mathbf{r}} \rho(\mathbf{r})} + \nabla_{\mathbf{r}}^2 \frac{\partial g'}{\partial \nabla_{\mathbf{r}}^2 \rho(\mathbf{r})} \\ &+ (A(\mathbf{r}) - \nabla_{\mathbf{r}} \cdot B(\mathbf{r}) + \nabla_{\mathbf{r}}^2 C(\mathbf{r})) \delta(\mathbf{r}' - \mathbf{r}) \\ &+ (2\nabla_{\mathbf{r}} C(\mathbf{r}) - B(\mathbf{r})) \cdot \nabla_{\mathbf{r}} \delta(\mathbf{r}' - \mathbf{r}) + C(\mathbf{r}) \nabla_{\mathbf{r}}^2 \delta(\mathbf{r}' - \mathbf{r}), \end{aligned} \quad (3.9)$$

where the functions $A(\mathbf{r})$, $B(\mathbf{r})$, and $C(\mathbf{r})$ are defined by Eqs. (3.5)–(3.7). Both Eqs. (3.4) and (3.9) are expressions that involve the Dirac delta function. In order to compare such expressions, one needs to multiply each of them by an arbitrary well-behaved function $k(\mathbf{r})$ and then integrate over \mathbf{r} . It is tedious but not difficult to verify that Eqs. (3.4) and (3.9) are equal if and only if

$$\begin{cases} \frac{\partial g}{\partial \rho(\mathbf{r}')} - \nabla_{\mathbf{r}'} \cdot \frac{\partial g}{\partial \nabla_{\mathbf{r}'} \rho(\mathbf{r}')} + \nabla_{\mathbf{r}'}^2 \frac{\partial g}{\partial \nabla_{\mathbf{r}'}^2 \rho(\mathbf{r}')} = \frac{\partial g'}{\partial \rho(\mathbf{r})} - \nabla_{\mathbf{r}} \cdot \frac{\partial g'}{\partial \nabla_{\mathbf{r}} \rho(\mathbf{r})} + \nabla_{\mathbf{r}}^2 \frac{\partial g'}{\partial \nabla_{\mathbf{r}}^2 \rho(\mathbf{r})} \\ \frac{\partial g}{\partial \nabla_{\mathbf{r}} \rho(\mathbf{r})} = \nabla_{\mathbf{r}} \frac{\partial g}{\partial \nabla_{\mathbf{r}}^2 \rho(\mathbf{r})}. \end{cases} \quad (3.10)$$

This system of equations is the integrability test for potentials of the type of Eq. (3.2) with $g(\mathbf{r}, \mathbf{r}')$ given by Eq. (3.3). It should be noted that the first equation of the system is nothing but the requirement that the function $D(\mathbf{r}, \mathbf{r}') = \frac{\partial g}{\partial \rho(\mathbf{r}')} - \nabla_{\mathbf{r}'} \cdot \frac{\partial g}{\partial \nabla_{\mathbf{r}'} \rho(\mathbf{r}')} + \nabla_{\mathbf{r}'}^2 \frac{\partial g}{\partial \nabla_{\mathbf{r}'}^2 \rho(\mathbf{r}'')}$ must be symmetric in \mathbf{r} and \mathbf{r}' . Also, note that, when $g \equiv g(\rho(\mathbf{r}), \nabla \rho(\mathbf{r}), \nabla^2 \rho(\mathbf{r}))$, the system correctly reduces to the integrability condition derived by Gaiduk and Staroverov in Ref. 3 (Eq. (1.62) of Chapter 1). Let us illustrate the use of Eq. (3.10) with an example.

Consider the following functional:

$$E[\rho] = \left(\int |\nabla_{\mathbf{r}'} \rho(\mathbf{r}')|^2 \rho(\mathbf{r}') d\mathbf{r}' \right)^2, \quad (3.11)$$

whose functional derivative is given by

$$\frac{\delta E[\rho]}{\delta \rho(\mathbf{r})} = -2 [|\nabla_{\mathbf{r}} \rho(\mathbf{r})|^2 + 2\rho(\mathbf{r}) \nabla_{\mathbf{r}}^2 \rho(\mathbf{r})] \int |\nabla_{\mathbf{r}'} \rho(\mathbf{r}')|^2 \rho(\mathbf{r}') d\mathbf{r}'. \quad (3.12)$$

Eq. (3.12) can be viewed as a non-local potential of Eq. (3.2) with

$$g(\mathbf{r}, \mathbf{r}') = -2 [|\nabla_{\mathbf{r}}\rho(\mathbf{r})|^2 + 2\rho(\mathbf{r})\nabla_{\mathbf{r}}^2\rho(\mathbf{r})] |\nabla_{\mathbf{r}'}\rho(\mathbf{r}')|^2\rho(\mathbf{r}'). \quad (3.13)$$

It is easy to see that this $g(\mathbf{r}, \mathbf{r}')$ passes the integrability test of Eq. (3.10). Let us first obtain the function $D(\mathbf{r}, \mathbf{r}') = \frac{\partial g}{\partial \rho(\mathbf{r}')} - \nabla_{\mathbf{r}'} \cdot \frac{\partial g}{\partial \nabla_{\mathbf{r}'}\rho(\mathbf{r}')} + \nabla_{\mathbf{r}'}^2 \frac{\partial g}{\partial \nabla_{\mathbf{r}'}^2\rho(\mathbf{r}'')}$ for $g(\mathbf{r}, \mathbf{r}')$ of Eq. (3.13):

$$\begin{aligned} D(\mathbf{r}, \mathbf{r}') &= \frac{\partial g}{\partial \rho(\mathbf{r}')} - \nabla_{\mathbf{r}'} \cdot \frac{\partial g}{\partial \nabla_{\mathbf{r}'}\rho(\mathbf{r}')} + \nabla_{\mathbf{r}'}^2 \frac{\partial g}{\partial \nabla_{\mathbf{r}'}^2\rho(\mathbf{r}'')} = \\ &= 2 [|\nabla_{\mathbf{r}}\rho(\mathbf{r})|^2 + 2\rho(\mathbf{r})\nabla_{\mathbf{r}}^2\rho(\mathbf{r})] [|\nabla_{\mathbf{r}'}\rho(\mathbf{r}')|^2 + 2\rho(\mathbf{r}')\nabla_{\mathbf{r}'}^2\rho(\mathbf{r}')] \end{aligned} \quad (3.14)$$

This function is symmetric in \mathbf{r} and \mathbf{r}' as required in order to pass the integrability test. Next, we show that the second condition of Eq. (3.10) is also satisfied:

$$\frac{\partial g}{\partial \nabla_{\mathbf{r}}\rho(\mathbf{r})} = \nabla_{\mathbf{r}} \frac{\partial g}{\partial \nabla_{\mathbf{r}}^2\rho(\mathbf{r})} = -4|\nabla_{\mathbf{r}'}\rho(\mathbf{r}')|^2\rho(\mathbf{r}')\nabla_{\mathbf{r}}\rho(\mathbf{r}). \quad (3.15)$$

Thus, both conditions of the Eq. (3.10) are satisfied, which is the expected result for the function $g(\mathbf{r}, \mathbf{r}')$ that corresponds to a functional derivative.

3.3 Integrability conditions at the level of the exchange-correlation charge distribution

We have demonstrated that a trial potential of Eq. (3.2) with the explicitly density-dependent $g(\mathbf{r}, \mathbf{r}')$ of Eq. (3.3) is a functional derivative of an energy functional if and only if Eq. (3.10) is satisfied. Let us adapt these integrability conditions for the exchange-correlation potential written in terms of a model exchange-correlation charge distribution $q_{\text{XC}}(\mathbf{r}')$,

$$v_{\text{XC}}(\mathbf{r}) = \int \frac{q_{\text{XC}}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}', \quad (3.16)$$

where $q_{\text{XC}}(\mathbf{r}') \equiv q_{\text{XC}}(\rho(\mathbf{r}'), \nabla\rho(\mathbf{r}'), \nabla^2\rho(\mathbf{r}'))$. The function $g(\mathbf{r}, \mathbf{r}')$ for such a potential is nothing but

$$g(\mathbf{r}, \mathbf{r}') = \frac{q_{\text{XC}}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \quad (3.17)$$

We only need to consider the first condition of Eq. (3.10) because $q_{\text{XC}}(\mathbf{r}')$ does not depend on $\rho(\mathbf{r})$, $\nabla_{\mathbf{r}}\rho(\mathbf{r})$, and $\nabla_{\mathbf{r}}^2\rho(\mathbf{r})$, and, as a result, the second condition of Eq. (3.10) is satisfied for any $q_{\text{XC}}(\mathbf{r}')$.

Using the identities

$$\nabla_{\mathbf{r}'} \left(\frac{1}{|\mathbf{r} - \mathbf{r}'|} \right) = -\nabla_{\mathbf{r}} \left(\frac{1}{|\mathbf{r}' - \mathbf{r}|} \right) = \frac{\mathbf{r} - \mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|^3} \quad (3.18)$$

and

$$\nabla_{\mathbf{r}'}^2 \left(\frac{1}{|\mathbf{r} - \mathbf{r}'|} \right) = \nabla_{\mathbf{r}}^2 \left(\frac{1}{|\mathbf{r}' - \mathbf{r}|} \right) = -4\pi\delta(\mathbf{r}' - \mathbf{r}) \quad (3.19)$$

we end up with the following expression for $D(\mathbf{r}, \mathbf{r}') = \frac{\partial g}{\partial \rho(\mathbf{r}')} - \nabla_{\mathbf{r}'} \cdot \frac{\partial g}{\partial \nabla_{\mathbf{r}'} \rho(\mathbf{r}')} + \nabla_{\mathbf{r}'}^2 \frac{\partial g}{\partial \nabla_{\mathbf{r}'}^2 \rho(\mathbf{r}')}$:

$$\begin{aligned} D(\mathbf{r}, \mathbf{r}') &= \frac{1}{|\mathbf{r} - \mathbf{r}'|} \left[\frac{\partial q_{\text{XC}}}{\partial \rho(\mathbf{r}')} - \nabla_{\mathbf{r}'} \cdot \left(\frac{\partial q_{\text{XC}}}{\partial \nabla_{\mathbf{r}'} \rho(\mathbf{r}')} \right) + \nabla_{\mathbf{r}'}^2 \left(\frac{\partial q_{\text{XC}}}{\partial \nabla_{\mathbf{r}'}^2 \rho(\mathbf{r}')} \right) \right] \\ &+ \frac{(\mathbf{r} - \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|^3} \cdot \left[2\nabla_{\mathbf{r}'} \left(\frac{\partial q_{\text{XC}}}{\partial \nabla_{\mathbf{r}'}^2 \rho(\mathbf{r}')} \right) - \frac{\partial q_{\text{XC}}}{\partial \nabla_{\mathbf{r}'} \rho(\mathbf{r}')} \right] + \frac{\partial q_{\text{XC}}}{\partial \nabla_{\mathbf{r}'}^2 \rho(\mathbf{r}')} 4\pi\delta(\mathbf{r}' - \mathbf{r}) \end{aligned} \quad (3.20)$$

or, more compactly,

$$D(\mathbf{r}, \mathbf{r}') = \frac{X(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \frac{(\mathbf{r} - \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|^3} \cdot Y(\mathbf{r}') + 4Z(\mathbf{r}')\pi\delta(\mathbf{r}' - \mathbf{r}), \quad (3.21)$$

where

$$X(\mathbf{r}') = \frac{\partial q_{\text{XC}}}{\partial \rho(\mathbf{r}')} - \nabla_{\mathbf{r}'} \cdot \left(\frac{\partial q_{\text{XC}}}{\partial \nabla_{\mathbf{r}'} \rho(\mathbf{r}')} \right) + \nabla_{\mathbf{r}'}^2 \left(\frac{\partial q_{\text{XC}}}{\partial \nabla_{\mathbf{r}'}^2 \rho(\mathbf{r}')} \right), \quad (3.22)$$

$$Y(\mathbf{r}') = 2\nabla_{\mathbf{r}'} \left(\frac{\partial q_{\text{XC}}}{\partial \nabla_{\mathbf{r}'}^2 \rho(\mathbf{r}')} \right) - \frac{\partial q_{\text{XC}}}{\partial \nabla_{\mathbf{r}'} \rho(\mathbf{r}')}, \quad (3.23)$$

and

$$Z(\mathbf{r}') = \frac{\partial q_{\text{XC}}}{\partial \nabla_{\mathbf{r}'}^2 \rho(\mathbf{r}')}. \quad (3.24)$$

In order for a trial potential of the type (3.16) to be a functional derivative of some energy expression, the function $D(\mathbf{r}, \mathbf{r}')$ of Eq. (3.21) must be symmetric with respect to the interchange of the variables. Therefore, in order to find explicit integrability constraints on X , Y , and Z , one needs to solve the following equation:

$$D(\mathbf{r}, \mathbf{r}') = D(\mathbf{r}', \mathbf{r}), \quad (3.25)$$

where $D(\mathbf{r}', \mathbf{r})$ is obtained from $D(\mathbf{r}, \mathbf{r}')$ by the simple interchange of the variables. The function D of Eq. (3.21) is an expression involving the Dirac delta function. Recall that comparison of such expressions can only be made after one multiplies both of them by an arbitrary well-behaved function $k(\mathbf{r})$ and integrates over \mathbf{r} . By doing so, we obtain

the following solution to Eq. (3.25) after some algebra:

$$\begin{cases} Y(\mathbf{r}') = -Y(\mathbf{r}) \\ X(\mathbf{r}') = X(\mathbf{r}) \end{cases} \quad (3.26)$$

which is equivalent to

$$\begin{cases} Y(\mathbf{r}') = 0 \\ X(\mathbf{r}') = \text{constant} \end{cases} \quad (3.27)$$

Observe that there is no restrictions on the function Z . This is because the term $4Z(\mathbf{r}')\pi\delta(\mathbf{r}' - \mathbf{r})$ is symmetric in \mathbf{r}' and \mathbf{r} for *any* $Z(\mathbf{r}')$ owing to the properties of the Dirac delta function.

The above equation permits us to conclude that the integrability constraints on a model function $q_{\text{XC}}(\rho, \nabla\rho, \nabla^2\rho)$ are as follows:

$$\begin{cases} 2\nabla \left(\frac{\partial q_{\text{XC}}}{\partial \nabla^2 \rho} \right) = \frac{\partial q_{\text{XC}}}{\partial \nabla \rho} \\ \frac{\partial q_{\text{XC}}}{\partial \rho} - \nabla \cdot \left(\frac{\partial q_{\text{XC}}}{\partial \nabla \rho} \right) + \nabla^2 \left(\frac{\partial q_{\text{XC}}}{\partial \nabla^2 \rho} \right) = \text{constant}. \end{cases} \quad (3.28)$$

To simplify Eq. (3.28), we insert the first equation of the system into the second one to obtain:

$$\begin{cases} 2\nabla \left(\frac{\partial q_{\text{XC}}}{\partial \nabla^2 \rho} \right) = \frac{\partial q_{\text{XC}}}{\partial \nabla \rho} \\ \frac{\partial q_{\text{XC}}}{\partial \rho} - \frac{1}{2} \nabla \cdot \left(\frac{\partial q_{\text{XC}}}{\partial \nabla \rho} \right) = \text{constant} \end{cases} \quad (3.29)$$

This set of conditions is a ready-to-use analytic integrability test for model potentials of Eq. (3.16).

Consider, for instance, the LDA exchange potential of Eq. (1.57). The exchange charge distribution associated with $v_{\text{X}}^{\text{LDA}}$ can be derived using Eq. (1.63) and reads:

$$q_{\text{X}}^{\text{LDA}} = \gamma\rho^{-\frac{2}{3}}\nabla^2\rho - \frac{2}{3}\gamma\rho^{-\frac{5}{3}}|\nabla\rho|^2, \quad (3.30)$$

where $\gamma = \frac{1}{9\pi}C_{\text{X}}$. Partial derivatives of $q_{\text{X}}^{\text{LDA}}$ with respect to the density ingredients are equal to

$$\frac{\partial q_{\text{X}}^{\text{LDA}}}{\partial \rho} = -\frac{2}{3}\gamma\rho^{-\frac{5}{3}}\nabla^2\rho + \frac{10}{9}\gamma\rho^{-\frac{8}{3}}|\nabla\rho|^2, \quad (3.31)$$

$$\frac{\partial q_{\text{X}}^{\text{LDA}}}{\partial \nabla \rho} = -\frac{4}{3}\gamma\rho^{-\frac{5}{3}}\nabla\rho, \quad (3.32)$$

and

$$\frac{\partial q_X^{\text{LDA}}}{\partial \nabla^2 \rho} = \gamma \rho^{-\frac{2}{3}}. \quad (3.33)$$

It is easy to see that Eq. (3.29) is satisfied for the LDA exchange charge distribution,

$$\begin{cases} 2 \left(-\frac{2}{3} \gamma \rho^{-\frac{5}{3}} \nabla \rho \right) = -\frac{4}{3} \gamma \rho^{-\frac{5}{3}} \nabla \rho \\ -\frac{2}{3} \gamma \rho^{-\frac{5}{3}} \nabla^2 \rho + \frac{10}{9} \gamma \rho^{-\frac{8}{3}} |\nabla \rho|^2 - \frac{1}{2} \left(-\frac{4}{3} \gamma \rho^{-\frac{5}{3}} \nabla^2 \rho + \frac{20}{9} \gamma \rho^{-\frac{8}{3}} |\nabla \rho|^2 \right) = 0 = \text{constant}, \end{cases} \quad (3.34)$$

which is consistent with the fact that the LDA exchange potential is a functional derivative of the LDA exchange energy functional. The test is also passed by the functional derivative of the Coulomb repulsion energy, the Hartree electrostatic potential of Eq. (1.20), that can be cast in the form of Eq. (3.16) ($q_H = \rho$):

$$\begin{cases} \frac{\partial q_H}{\partial \nabla \rho} = 0 \\ \frac{\partial q_H}{\partial \nabla^2 \rho} = 0 \\ \frac{\partial q_H}{\partial \rho} = 1 = \text{constant} \end{cases} \quad (3.35)$$

3.4 Conclusion

The exchange-correlation potential obtained from a model exchange-correlation charge distribution with the proper normalization is unlikely to be a functional derivative of some energy functional on its own. Potentials that are not functional derivatives often lead to the wrong description [5–9] of observable physical properties. Therefore, it is desirable to impose the integrability constraint when developing exchange-correlation potentials by modelling the exchange-correlation charge distribution.

We have devised analytic integrability conditions that allow one to tell if a model exchange-correlation charge function gives rise to an integrable exchange-correlation potential. Our conditions can be converted into a method for explicit construction of functional derivatives starting from model exchange-correlation charge distributions using the approach of Ref. 3.

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Chapter 4

Hierarchy of model Kohn–Sham potentials approximating functional derivatives of orbital-dependent functionals

4.1 Introduction

Although orbital-dependent functionals offer many advantages over local density approximations (LDAs) and generalized gradient approximations (GGAs), they also pose distinctive challenges. In particular, proper implementation of the Kohn–Sham (KS) density-functional scheme with an orbital-dependent functional requires computing the multiplicative effective exchange–correlation potential, $v_{\text{XC}}(\mathbf{r}) = \delta E_{\text{XC}}/\delta\rho(\mathbf{r})$. If the functional E_{XC} is implicit, this potential cannot be obtained by direct functional differentiation of E_{XC} with respect to $\rho(\mathbf{r})$ and has to be determined indirectly by solving the optimized effective potential (OEP) integral equation [1, 2]. Unfortunately, the structure of the OEP equation is such that it is not well-suited for solving in finite (Gaussian) basis sets [3–13].

There are two pragmatic alternatives to the OEP method in basis-set calculations with orbital-dependent functionals. One is to use OEP approximations such as the Krieger–Li–Iafrate [14] (KLI) potential, the Becke–Johnson potential [15], and others [16–29]. However, existing OEP approximations are not always sufficiently accurate, cannot be

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assigned energy values in an unambiguous manner [30–34], and cannot be improved systematically. The other strategy is to abandon the effective potential $v_{\text{XC}}(\mathbf{r})$ altogether and replace it by a functional derivative of E_{XC} with respect to the orbitals [35–38]. This approach is not always satisfactory either because the derivatives $\delta E_{\text{XC}}/\delta\phi_i(\mathbf{r})$ are different for different orbitals, so the resulting eigenvalue spectrum is qualitatively distinct from the spectrum obtained with a multiplicative potential.

In this work, we present a fresh take on the problem. We describe a method for constructing a ladder of increasingly accurate model KS potentials for various orbital-dependent functionals including exact exchange, hybrid functionals, and meta-GGAs. The distinctive feature of our approach is that the model potentials at the top of the proposed hierarchy require self-consistent solutions of the generalized KS equations as input, and are practically indistinguishable from OEPs.

Throughout this work, we compare all our models to the exact numerical solutions of the OEP and KLI equations reported by Engel and coworkers [39–41] for atoms and by Makmal *et al.* [42] for molecules. To simulate the basis-set limit represented by these KLI and OEP benchmarks we use the original universal Gaussian basis set [43] (UGBS) and its polarized versions, UGBS n O, with $n = 1$ or 2. A UGBS n O basis is a UGBS augmented with polarization functions using the “old” scheme as implemented in GAUSSIAN 09, Revision B.1 [44].

4.2 Problem statement

If $E_{\text{XC}}[\rho]$ is an orbital-dependent functional, one cannot derive a closed-form expression for $v_{\text{XC}}(\mathbf{r})$ by straightforward functional differentiation. Formally, $v_{\text{XC}}(\mathbf{r})$ can be found by solving the OEP integral equation, but nearly all existing implementations of hybrid functionals and meta-GGAs do not even attempt that approach. Instead, they tacitly adopt the generalized KS (GKS) formalism [35–38] in which the KS equations are replaced with the eigenvalue problem of the Hartree–Fock (HF) type,

$$\left[-\frac{1}{2}\nabla^2 + v_{\text{ext}}(\mathbf{r}) + v_{\text{H}}(\mathbf{r}) + \hat{u}_{\text{XC}} \right] \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r}), \quad (4.1)$$

where \hat{u}_{XC} is a one-electron operator defined by Eq. (1.53). In the case of the exact-exchange functional, the GKS approach is equivalent to the HF self-consistent field (SCF) scheme. Just like the KS equation, the GKS equations are solved by iteration until self-consistency. (In finite-basis-set calculations, one does not have to compute v_{XC} and $\hat{u}_{\text{XC}}\phi_i$ but only their matrix elements, which is a simpler task [45]. However, this does

not resolve the problem that the functional derivative $\delta E_{\text{XC}}/\delta\rho$ for implicit functionals cannot be evaluated in closed form.)

The switch to the GKS scheme is usually made as a matter of convenience because the quantity $\hat{u}_{\text{XC}}\phi_i$ can be evaluated for any orbital-dependent functional. However, the self-consistent GKS orbitals and orbital eigenvalues are not identical to their KS counterparts except for one- and closed-shell two-electron systems.

Does it matter in practice that the KS scheme is replaced with the GKS scheme when dealing with orbital-dependent functionals? The answer depends on the application. Total electronic energies computed by the KS and GKS methods typically differ by a few parts per million—much less than either the KS or GKS energy varies with the one-electron basis set. Therefore, for the purpose of computing total energies, the KS approach offers no practical advantage over the GKS scheme. At the same time, KS orbital eigenvalues are often quite different from the corresponding GKS orbital eigenvalues. The energy gap between the highest-occupied and lowest-unoccupied molecular orbitals (HOMO–LUMO gap) is often significantly smaller in the KS method than in the GKS formalism, and the very nature of the frontier orbitals in the GKS and KS schemes can be different (Table 4.1). This means that if one is interested in properties whose calculation involves orbital eigenvalues (excitation energies, band structure, polarizabilities etc.), then it may be essential to use a multiplicative exchange-correlation potential of the KS scheme.

All in all, it is highly desirable to be able to compute KS effective potentials for orbital-dependent functionals without having to cope with the OEP integral equation. So far, this challenge has been tackled either by evaluating the functional derivative $v_{\text{XC}}^{\text{OEP}}(\mathbf{r}) = \delta E_{\text{XC}}[\{\phi_i\}]/\delta\rho(\mathbf{r})$ approximately [14, 16–23, 48] or by devising functional-specific “model potentials”—direct approximations to $v_{\text{XC}}^{\text{OEP}}(\mathbf{r})$ in terms of KS orbitals and, possibly, other ingredients [15, 24–29].

$$v_{\text{XC}}^{\text{model}}(\mathbf{r}) \approx v_{\text{XC}}^{\text{OEP}}(\mathbf{r}). \quad (4.2)$$

The following section presents a new proposal which combines the most appealing feature of existing OEP approximations and takes them to a new level of accuracy.

4.3 Hierarchy of model potentials

Here we show how to construct a hierarchy of model-potential approximations for any given orbital-dependent functional. Our approach synthesizes some old [16, 49, 50] and

Table 4.1: Orbital eigenvalues and total exact-exchange energies for the N₂ molecule ($R = 2.100a_0$) obtained with the HF and effective-potential methods. For ease of comparison, all KS eigenvalues were shifted to satisfy the HOMO condition $\epsilon_{\text{HOMO}}^{\text{KS}} = \epsilon_{\text{HOMO}}^{\text{HF}}$. The HOMO and LUMO energies are highlighted in bold.

	Energies (units of E_h)		
	HF ^a	KLI ^b	OEP ^c
Occupied orbitals			
$\sigma_g 1s$	-15.6893	-14.3552	-14.3056
$\sigma_u^* 1s$	-15.6860	-14.3541	-14.3044
$\sigma_g 2s$	-1.4633	-1.2765	-1.2771
$\sigma_u^* 2s$	-0.7840	-0.7275	-0.7191
$\pi_u 2p$	-0.6082	-0.6551	-0.6318
$\sigma_g 2p$	-0.6346	-0.6082	-0.6082
Unoccupied orbitals			
$\pi_g^* 2p$	0.1252	-0.2942	-0.2668
$\sigma_u^* 2p$	0.0986	-0.1594	-0.1402
Total energies			
E	-108.9868	-108.9818	-108.9814

^a Computed using the UGBS1O basis.

^b From Ref. 41.

^c Computed by the Yang–Wu method [46, 47] using the UGBS1O basis for the orbitals and the potential. This OEP has defects near the nuclei. In the basis-set limit, the total OEP energy would be below the KLI value.

recent [51, 52] ideas, and advances them significantly. Because the exact-exchange OEP is by far the best-studied and the most important effective potential, we focus our exposition on the exact-exchange functional as the prototype of all orbital-dependent approximations.

4.3.1 Orbital-averaged effective potentials

A crude approximation to the functional derivative of an orbital-dependent functional can be obtained as follows. Consider the one-electron operator \hat{u}_{XC} defined by Eq. (1.53). In the case of exact exchange, \hat{u}_{XC} is the Fock integral operator,

$$\hat{K}\phi_i(\mathbf{r}) = \frac{\delta E_X^{\text{exact}}}{\delta \phi_i^*(\mathbf{r})} = -\frac{1}{2} \int \frac{\gamma(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \phi_i(\mathbf{r}') d\mathbf{r}', \quad (4.3)$$

where we define \hat{K} with a sign opposite to that used traditionally in the HF theory. For a τ -dependent functional of Eq. (1.47), \hat{u}_{XC} is a differential operator [37],

$$\hat{u}_{\text{XC}} = \frac{\partial f}{\partial \rho} - \nabla \cdot \frac{\partial f}{\partial \nabla \rho} - \frac{1}{2} \left(\nabla \frac{\partial f}{\partial \tau} \right) \cdot \nabla - \frac{1}{2} \frac{\partial f}{\partial \tau} \nabla^2, \quad (4.4)$$

where f is the energy density. In either case, \hat{u}_{XC} is non-multiplicative. For such operators one can generalize [38, 52] the old idea due to Slater [49] and define an average of the quantities $(\hat{u}_{\text{XC}}\phi_i)/\phi_i$ ($i = 1, 2, \dots, N$) weighted by $|\phi_i|^2/\rho$. We call the result an orbital-averaged effective potential (OAEP),

$$v_{\text{XC}}^{\text{OAEP}}(\mathbf{r}) = \frac{1}{\rho(\mathbf{r})} \sum_{i=1}^N \phi_i^*(\mathbf{r}) \hat{u}_{\text{XC}} \phi_i(\mathbf{r}), \quad (4.5)$$

a multiplicative operator that is the same for all orbitals. In particular, the OAEP corresponding to $E_{\text{X}}^{\text{exact}}$ is the original Slater potential [49],

$$v_{\text{S}}(\mathbf{r}) = \frac{1}{\rho(\mathbf{r})} \sum_{i=1}^N \phi_i^* \hat{K} \phi_i = -\frac{1}{2\rho(\mathbf{r})} \int \frac{|\gamma(\mathbf{r}, \mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'. \quad (4.6)$$

For explicit density functionals such as GGAs, the OAEP coincides with the functional derivative $v_{\text{XC}}(\mathbf{r})$ of the parent functional, but for an orbital-dependent functional the OAEP is only an approximation to $v_{\text{XC}}(\mathbf{r})$. The extent to which an OAEP is close to the true functional derivative $v_{\text{XC}}(\mathbf{r})$ depends on the functional. Here it suffices to say that the exact-exchange functional represents the most unfavorable case. For example, the exact-exchange OEP reduces in the uniform-electron-gas limit to $v_{\text{X}}^{\text{LDA}} = -k_{\text{F}}/\pi$, where $k_{\text{F}} = (3\pi^2\rho)^{1/3}$, whereas the corresponding OAEP reduces in the same limit to $(3/2)v_{\text{X}}^{\text{LDA}}$, a nominal 50% error [53]. A similar error for hybrids and meta-GGAs is expected to be much smaller.

In this work, we define the total KS effective potential in the OAEP approximation as

$$v_{\text{eff}}^{\text{OAEP}}(\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + v_{\text{H}}^{\text{KS}}(\mathbf{r}) + v_{\text{S}}^{\text{HF}}(\mathbf{r}), \quad (4.7)$$

where $v_{\text{H}}^{\text{KS}}(\mathbf{r}) \equiv v_{\text{H}}([\rho^{\text{KS}}]; \mathbf{r})$ is the Hartree potential of the self-consistent KS density, whereas $v_{\text{S}}^{\text{HF}}(\mathbf{r}) \equiv v_{\text{S}}([\rho^{\text{HF}}]; \mathbf{r})$ is the Slater potential constructed with the fixed HF orbitals. This choice is made for consistency with the definitions of $v_{\text{eff}}(\mathbf{r})$ adopted for the more accurate model potentials introduced later in this work.

Examples of atomic and molecular OAEPs are shown in Fig. 4.1. Although the OAEP is generally not a very realistic approximation to the exact-exchange OEP, total

energies obtained from such crude approximations may be reasonable [54]. Even the KS eigenvalues computed with the Slater potential are closer to the OEP eigenvalues than to HF orbital energies (see Sec. 4.5 below).

The eigenfunctions of an OAEP are of course generally different from the HF and OEP orbitals. We will now show that one can devise a better model by asking the question: what is the effective KS potential whose eigenfunctions are GKS orbitals?

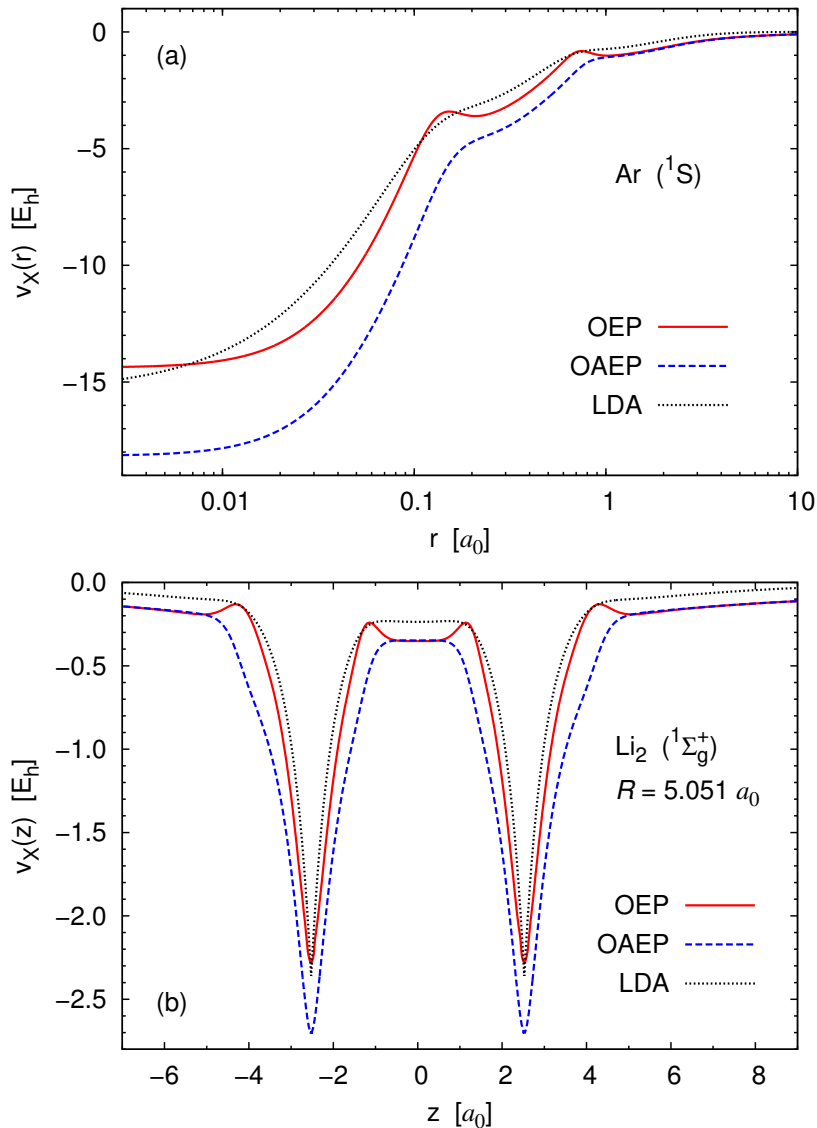


Figure 4.1: Atomic and molecular exact-exchange OEPs and their crude approximations: the OAEP (Slater) and exchange-only LDA potentials constructed with the HF/UGBS10 orbitals. The potentials for Li_2 are shown along the internuclear axis.

4.3.2 Orbital-consistent effective potentials

Della Sala and Görling [16] derived an OEP approximation called the localized HF (LHF) potential by assuming that the KS exact-exchange-only and HF Slater determinants are identical. We can derive another OEP approximation by making a more restrictive assumption that the occupied canonical KS exact-exchange-only orbitals and the occupied canonical HF orbitals are the same,

$$\phi_i^{\text{KS}} = \phi_i^{\text{HF}}, \quad (i = 1, 2, \dots, N). \quad (4.8)$$

We call the potential defined by this property an orbital-consistent effective potential (OCEP), where the ‘‘consistency’’ refers to the assumed equivalence of the KS and GKS orbitals. Although Eq. (4.8) is generally impossible to satisfy exactly, let us ignore this concern for a moment and examine the consequences of our assumption.

Consider again the exact-exchange functional of Eq. (1.44). The GKS equations corresponding to this functional are the HF equations,

$$\left[-\frac{1}{2}\nabla^2 + v_{\text{ext}}(\mathbf{r}) + v_{\text{H}}^{\text{HF}}(\mathbf{r}) + \hat{K} \right] \phi_i^{\text{HF}}(\mathbf{r}) = \epsilon_i^{\text{HF}} \phi_i^{\text{HF}}(\mathbf{r}), \quad (4.9)$$

where $v_{\text{H}}^{\text{HF}}(\mathbf{r})$ is the Hartree potential of $\rho^{\text{HF}}(\mathbf{r})$. Let us multiply Eq. (4.9) by ϕ_i^{HF} , sum over i from 1 to N , and divide through by ρ^{HF} . The result may be written as

$$\frac{\tau_L^{\text{HF}}(\mathbf{r})}{\rho^{\text{HF}}(\mathbf{r})} + v_{\text{ext}}(\mathbf{r}) + v_{\text{H}}^{\text{HF}}(\mathbf{r}) + v_{\text{S}}^{\text{HF}}(\mathbf{r}) = -\bar{I}^{\text{HF}}(\mathbf{r}), \quad (4.10)$$

where τ_L^{HF} is the Laplacian form of the HF kinetic energy density,

$$\tau_L^{\text{HF}}(\mathbf{r}) = -\frac{1}{2} \sum_{i=1}^N \phi_i^{\text{HF}*} \nabla^2 \phi_i^{\text{HF}}, \quad (4.11)$$

$v_{\text{S}}^{\text{HF}}(\mathbf{r})$ is the OAEP defined by Eq. (4.6) and built with the HF orbitals, and \bar{I}^{HF} is the HF average local ionization energy defined [55, 56] by

$$\bar{I}^{\text{HF}}(\mathbf{r}) = -\frac{1}{\rho^{\text{HF}}(\mathbf{r})} \sum_{i=1}^N \epsilon_i^{\text{HF}} |\phi_i^{\text{HF}}(\mathbf{r})|^2. \quad (4.12)$$

(Note that in Ref. 51 this quantity was defined with an opposite sign; here we revert to the original sign convention of Ref. 55). Now suppose there exists a multiplicative exchange potential whose occupied orbitals are the same as the HF orbitals. By definition, this

potential (OCEP) satisfies the exchange-only KS equations,

$$\left[-\frac{1}{2}\nabla^2 + v_{\text{ext}}(\mathbf{r}) + v_{\text{H}}^{\text{KS}}(\mathbf{r}) + v_{\text{X}}^{\text{OCEP}}(\mathbf{r}) \right] \phi_i^{\text{KS}}(\mathbf{r}) = \epsilon_i^{\text{KS}} \phi_i^{\text{KS}}(\mathbf{r}), \quad (4.13)$$

where $v_{\text{H}}^{\text{KS}}(\mathbf{r})$ is the Hartree potential of $\rho^{\text{KS}}(\mathbf{r})$ and the eigenvalues ϵ_i^{KS} are yet unknown. Performing similar manipulations on Eq. (4.13) as above we transform it into

$$\frac{\tau_L^{\text{KS}}(\mathbf{r})}{\rho^{\text{KS}}(\mathbf{r})} + v_{\text{ext}}(\mathbf{r}) + v_{\text{H}}^{\text{KS}}(\mathbf{r}) + v_{\text{X}}^{\text{OCEP}}(\mathbf{r}) = -\bar{I}^{\text{KS}}(\mathbf{r}), \quad (4.14)$$

where

$$\tau_L^{\text{KS}}(\mathbf{r}) = -\frac{1}{2} \sum_{i=1}^N \phi_i^{\text{KS}*} \nabla^2 \phi_i^{\text{KS}} \quad (4.15)$$

and

$$\bar{I}^{\text{KS}}(\mathbf{r}) = -\frac{1}{\rho^{\text{KS}}(\mathbf{r})} \sum_{i=1}^N \epsilon_i^{\text{KS}} |\phi_i^{\text{KS}}(\mathbf{r})|^2. \quad (4.16)$$

Finally, we subtract Eq. (4.10) from Eq. (4.14). Under the assumption expressed by Eq. (4.8), most terms cancel out and the remaining ones give

$$v_{\text{X}}^{\text{OCEP}}(\mathbf{r}) = v_{\text{S}}^{\text{HF}}(\mathbf{r}) + \bar{I}^{\text{HF}}(\mathbf{r}) - \bar{I}^{\text{KS}}(\mathbf{r}). \quad (4.17)$$

We define the total KS effective potential in the OCEP approximation as

$$v_{\text{eff}}^{\text{OCEP}}(\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + v_{\text{H}}^{\text{KS}}(\mathbf{r}) + v_{\text{X}}^{\text{OCEP}}(\mathbf{r}). \quad (4.18)$$

The OCEP approximation of Eq. (4.17) was anticipated by Bulat *et al.* [57] on the basis of comparison of KS and HF average local ionization energies in atoms.

To compute an OCEP, we first carry out an HF SCF calculation on the system. Then, starting with some initial guess for the unknown $\{\epsilon_i^{\text{KS}}\}$ and $\{\phi_i^{\text{KS}}\}$ we construct $v_{\text{eff}}^{\text{OCEP}}(\mathbf{r})$ by Eq. (4.18). Then we solve the KS eigenvalue problem with $v_{\text{eff}}^{\text{OCEP}}(\mathbf{r})$ and use the solutions to construct a new OCEP. The procedure is repeated until the KS orbitals *and* orbital eigenvalues are self-consistent. An alternative definition of $v_{\text{eff}}^{\text{OCEP}}(\mathbf{r})$, in which $v_{\text{H}}^{\text{KS}}(\mathbf{r})$ is replaced with $v_{\text{H}}^{\text{HF}}(\mathbf{r})$, was also tested and abandoned because of somewhat slower SCF convergence.

Since the OCEP and its orbital eigenvalues are defined up to a constant shift, we eliminate this ambiguity by shifting all eigenvalues ϵ_i^{KS} so that the energy of the highest

occupied level satisfies the condition

$$\epsilon_{\text{HOMO}}^{\text{KS}} = \epsilon_{\text{HOMO}}^{\text{HF}}. \quad (4.19)$$

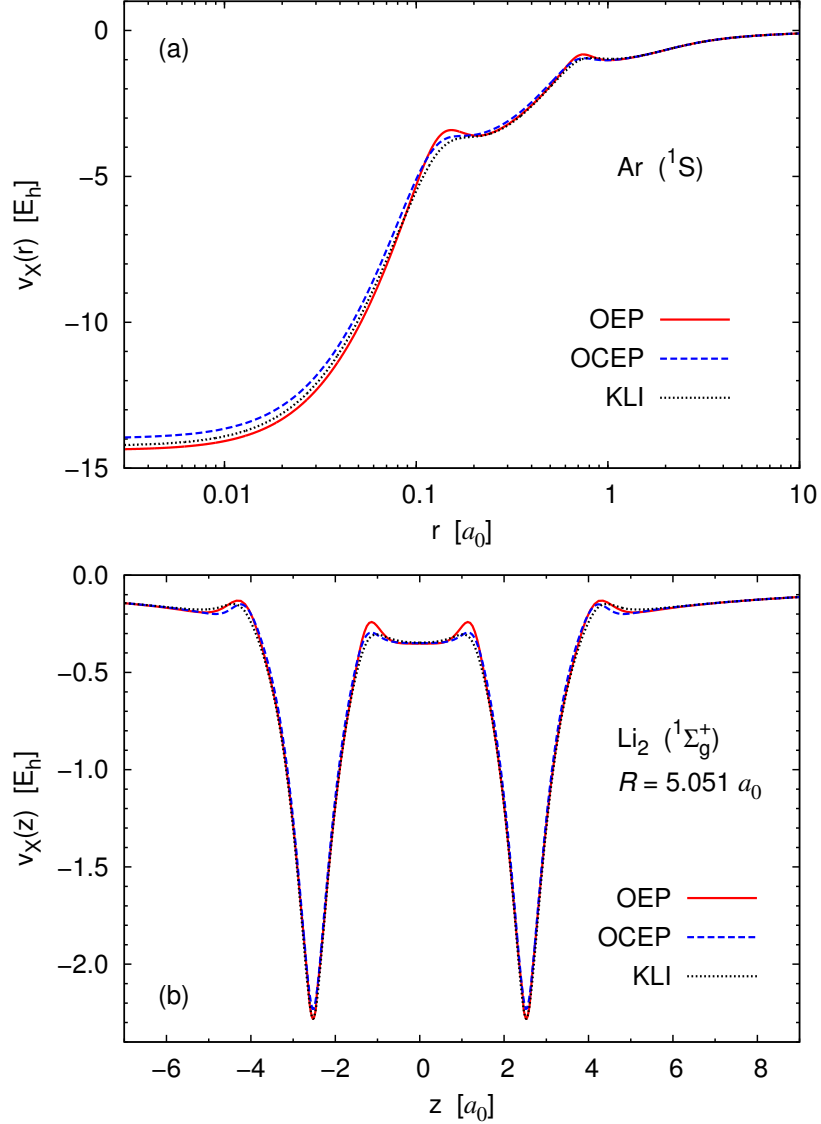


Figure 4.2: Atomic and molecular exact-exchange OEPs and their second-level approximations: OCEP (computed using the UGBS10 basis) and KLI.

It is known [58–61] that the exact exchange OEP decays asymptotically as $-1/r$ in all directions except on nodal surfaces of the HOMO, where the decay is $C - 1/r$ with C being a system-dependent constant. By analyzing the $r \rightarrow \infty$ limits of $\bar{I}^{\text{HF}}(\mathbf{r})$ and $\bar{I}^{\text{KS}}(\mathbf{r})$ and taking into account Eq. (4.19), one can show that the OCEP formally exhibits the same type of behavior as the exact OEP (and KLI/LHF potentials): namely, it decays

as the Slater potential $(-1/r)$ in all directions except on nodal surfaces of the HOMO, where it approaches $C - 1/r$ with $C = \epsilon_{\text{HOMO}-1}^{\text{KS}} - \epsilon_{\text{HOMO}-1}^{\text{HF}} \neq 0$. Thus, condition (4.19) also imparts the OCEP with correct asymptotic behavior.

The computational cost of the OCEP SCF approximation includes the cost of an HF SCF calculation but, in contrast to the KLI/LHF SCF methods, requires only one evaluation of the Slater potential. We have computed OCEPs for several atoms and molecules and found that they are very reasonable approximations to OEPs. A typical OCEP is similar to a KLI potential (Fig. 4.2).

Note that the conventional definitions [57] of $\bar{I}^{\text{HF}}(\mathbf{r})$ and $\bar{I}^{\text{KS}}(\mathbf{r})$ by Eqs. (4.12) and (4.16) are meaningful only in terms of *canonical* HF and KS orbitals and their eigenvalues. It can be shown [62] that there exists a generalized definition of the average local ionization energy which is invariant under unitary transformations of the occupied orbitals. Written in terms of the generalized definition, the OCEP would be manifestly invariant, sharing this property with the LHF and Becke–Johnson potentials, and in agreement with the conclusions of Ref. 57.

4.3.3 Density-consistent effective potentials

The third and highest level of the proposed hierarchy of OEP approximations is the density-consistent effective potential (DCEP). This model is similar in spirit to the OCEP but is based on a less restrictive assumption that only the ground-state electron densities in the KS and GKS schemes are equal. For the exact-exchange functional this amounts to imposing the condition

$$\rho^{\text{KS}}(\mathbf{r}) = \rho^{\text{HF}}(\mathbf{r}). \quad (4.20)$$

The special case of the DCEP for the exact-exchange functional was recently presented in Ref. 51 under the name of Hartree–Fock exchange–correlation (HFXC) potential. Here we will use the general name DCEP for consistency with the OAEP and OCEP, and to emphasize the fact that the principle behind the HFXC model is not limited to the exact-exchange functional.

Assuming that an effective potential satisfying Eq. (4.20) exists, we can capitalize on the results of Sec. 4.3.2 to derive an expression for the DCEP in a few simple steps. First we use a basic property of the Laplacian form of the kinetic energy density to write

$$\tau_L^{\text{HF}} = \tau^{\text{HF}} - \frac{1}{4} \nabla^2 \rho^{\text{HF}}, \quad (4.21)$$

where $\tau^{\text{HF}} = (1/2) \sum_{i=1}^N |\nabla \phi_i^{\text{HF}}|^2$ is the positive-definite form of the HF kinetic energy

density. Then we substitute Eq. (4.21) into Eq. (4.10) to obtain

$$\frac{\tau^{\text{HF}}}{\rho^{\text{HF}}} - \frac{1}{4} \frac{\nabla^2 \rho^{\text{HF}}}{\rho^{\text{HF}}} + v_{\text{ext}} + v_{\text{H}}^{\text{HF}} + v_{\text{S}}^{\text{HF}} = -\bar{I}^{\text{HF}}. \quad (4.22)$$

Similarly we rewrite Eq. (4.14) as

$$\frac{\tau^{\text{KS}}}{\rho^{\text{KS}}} - \frac{1}{4} \frac{\nabla^2 \rho^{\text{KS}}}{\rho^{\text{KS}}} + v_{\text{ext}} + v_{\text{H}}^{\text{KS}} + v_{\text{X}}^{\text{DCEP}} = -\bar{I}^{\text{KS}}. \quad (4.23)$$

The assumed equality of the KS and HF densities does not imply the equality of the

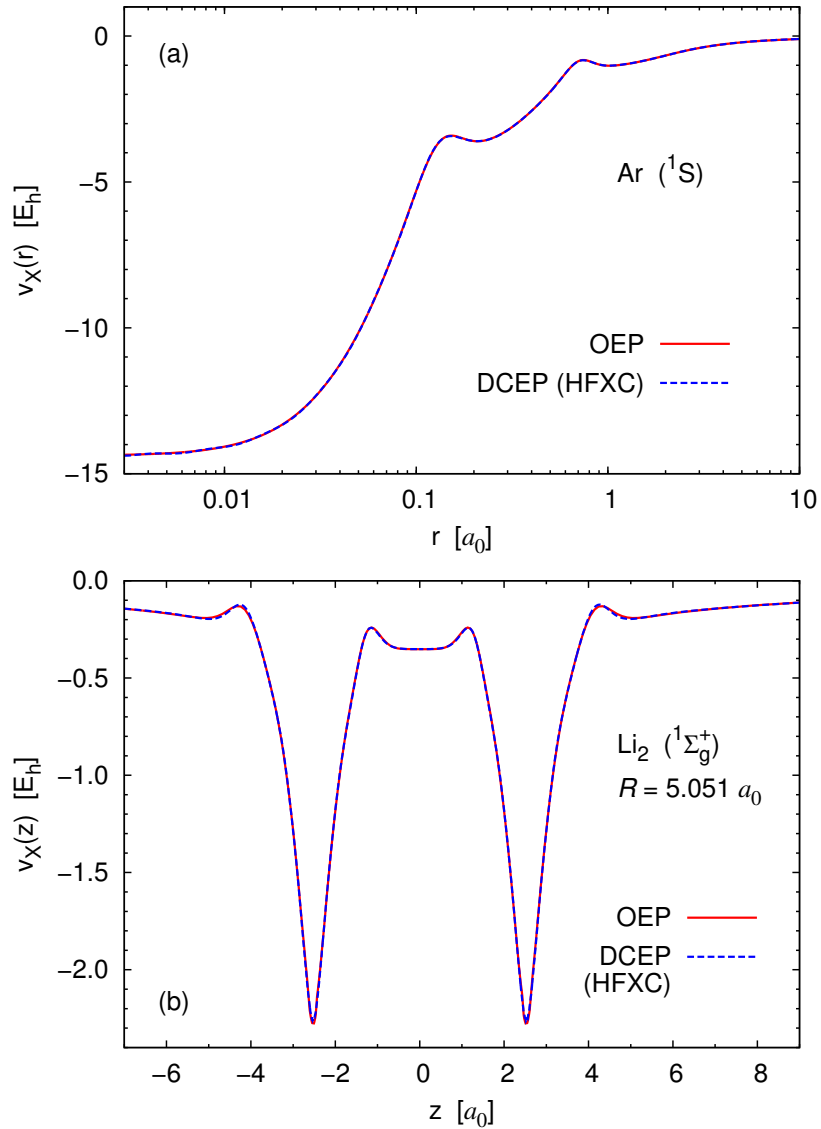


Figure 4.3: DCEPs (HFXC potentials) computed using the UGBS10 basis are virtually exact representations of benchmark exact-exchange OEPs both for atoms and molecules.

orbitals, so here $\phi_i^{\text{KS}} \neq \phi_i^{\text{HF}}$ and $\tau_L^{\text{KS}} \neq \tau_L^{\text{HF}}$. Subtracting Eq. (4.22) from (4.23) and using equality (4.20) we arrive at [51]

$$v_X^{\text{DCEP}}(\mathbf{r}) = v_X^{\text{OCEP}}(\mathbf{r}) + \frac{\tau^{\text{HF}}(\mathbf{r})}{\rho^{\text{HF}}(\mathbf{r})} - \frac{\tau^{\text{KS}}(\mathbf{r})}{\rho^{\text{KS}}(\mathbf{r})}, \quad (4.24)$$

where $v_X^{\text{OCEP}}(\mathbf{r})$ is given by Eq. (4.17).

To compute a DCEP, we combine Eq. (4.24) with the Hartree potential of $\rho^{\text{KS}}(\mathbf{r})$ to produce

$$v_{\text{eff}}^{\text{DCEP}}(\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + v_{\text{H}}^{\text{KS}}(\mathbf{r}) + v_X^{\text{DCEP}}(\mathbf{r}). \quad (4.25)$$

The KS density, orbitals and eigenvalues in the DCEP formula are then determined by solving the KS equations iteratively until self-consistency is reached, exactly as in the relaxed-orbital OCEP of Sec. 4.3.2. DCEPs are expected to have the same type of asymptotic behavior and orbital-rotation invariance as OCEPs.

We experimented with a minor modification of the DCEP method which consists in replacing the variable $v_{\text{H}}^{\text{KS}}(\mathbf{r})$ with the fixed $v_{\text{H}}^{\text{HF}}(\mathbf{r})$. It turned out that our original choice [51] of $v_{\text{H}}^{\text{KS}}(\mathbf{r})$ in Eq. (4.25) leads to better SCF convergence and gives more accurate results than the use of $v_{\text{H}}^{\text{HF}}(\mathbf{r})$. We also caution against replacing $\rho^{\text{KS}}(\mathbf{r})$ with $\rho^{\text{HF}}(\mathbf{r})$ in Eq. (4.24) because the resulting mismatch between τ^{KS} and ρ^{HF} will cause the ratio $\tau^{\text{KS}}/\rho^{\text{HF}}$ to behave erratically in the asymptotic region.

As shown in Ref. 51 and in Fig. 4.3 of this work, the DCEP is an extraordinarily accurate representation of the OEP, even when compared to the best existing models. The reason for this is the non-obvious fact that the OEP and DCEP equations are nearly equivalent. To show this we follow Miao [63] and treat the HF method as a perturbation of the KS scheme by writing the canonical HF orbitals as

$$\phi_i^{\text{HF}}(\mathbf{r}) = \phi_i^{\text{KS}}(\mathbf{r}) + \lambda\psi_i(\mathbf{r}) + O(\lambda^2), \quad (4.26)$$

where λ is a perturbation parameter and $\psi_i(\mathbf{r})$ is the first-order correction. The perturbation is the difference between the Fock and KS operators, and the first-order correction ψ_i is known as the ‘‘orbital shift’’ [60, 61]. Now let us multiply Eq. (4.26) by its complex conjugate and sum the products from $i = 1$ to N . The result is

$$\rho^{\text{HF}}(\mathbf{r}) = \rho^{\text{KS}}(\mathbf{r}) + \lambda \left[\sum_{i=1}^N \psi_i^*(\mathbf{r})\phi_i^{\text{KS}}(\mathbf{r}) + \text{c.c.} \right] + O(\lambda^2), \quad (4.27)$$

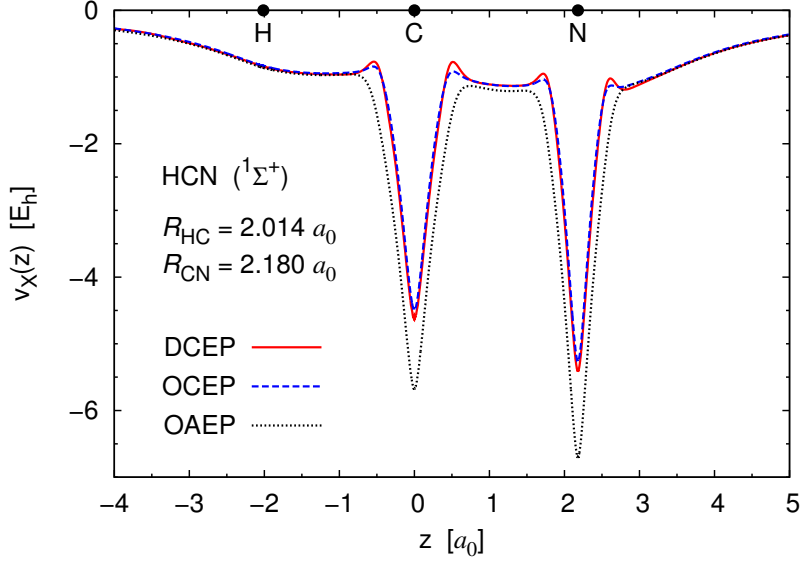


Figure 4.4: Three model potentials of the proposed hierarchy computed using the UGBS10 basis and shown along the internuclear axis of the ground-state H–C≡N molecule. Note the absence of any defects near the nuclei. The exact OEP is not available, but we presume it to be almost indistinguishable from the DCEP curve.

where c.c. stands for “complex conjugate”. But if ϕ_i^{KS} are the OEP eigenfunctions, then [60, 64, 65]

$$\sum_{i=1}^N \psi_i^*(\mathbf{r}) \phi_i^{\text{KS}}(\mathbf{r}) + \text{c.c.} = 0, \quad (4.28)$$

which is one of several forms of the OEP equation, so Eq. (4.27) becomes

$$\rho^{\text{HF}}(\mathbf{r}) = \rho^{\text{KS}}(\mathbf{r}) + O(\lambda^2). \quad (4.29)$$

This means that the HF and OEP densities are equal to first order in λ . It follows that a multiplicative potential that reproduces the HF ground-state density must be very close to the OEP. Furthermore, if we operate on both sides of the equality $\rho^{\text{HF}} = \rho^{\text{KS}}$ with $-(1/2)\nabla^2$ and use the KS and HF equations to simplify the result, we obtain the DCEP Eq. (4.24). Thus, the DCEP and OEP equations are intimately related.

The OAEP, OCEP, and DCEP approximations to the OEP can be readily computed for molecules (see, for instance, Fig. 4.4). But before we proceed to comparing the OAEP, OCEP, and DCEP models in practical calculations, let us elaborate on the basic assumptions underlying the OCEP and DCEP approximations.

4.4 The effect of freezing the Kohn–Sham orbitals and densities

In deriving the OCEP approximation of Eq. (4.17) we assumed that HF orbitals and the KS orbitals generated by an OCEP are exactly the same. However, a multiplicative potential whose eigenfunctions are identical with the HF orbitals cannot exist in the basis-set limit except for one- and closed-shell two-electron systems. If it did exist, then the exact-exchange energy computed with the OCEP orbitals would be equal to the HF energy. That would be a contradiction because the multiplicative potential which delivers the lowest possible total energy is the OEP and, in the basis-set limit, the OEP energy is strictly above the HF energy except for systems with a single occupied spatial KS orbital [66]. (The equality $E_{\text{OEP}} = E_{\text{HF}}$ is possible in *finite* basis sets [4], but that is irrelevant here.) Equation (4.8) is also not expected to hold exactly in finite-basis-set calculations because of discretization errors. This is why it makes sense to relax the KS orbitals in the OCEP SCF scheme.

It is nevertheless instructive to explore what happens to the OCEP approximation if the strict equality of the KS and HF orbitals is enforced. This can be done by building $\bar{I}^{\text{KS}}(\mathbf{r})$ in each SCF iteration with the HF orbitals instead of the current KS orbitals generated by the OCEP. Using Eq. (4.8) once again we can rewrite the OCEP constructed with the HF orbitals (OCEP-HF) as

$$v_{\text{X}}^{\text{OCEP-HF}}(\mathbf{r}) = v_{\text{S}}^{\text{HF}}(\mathbf{r}) + \frac{1}{\rho^{\text{HF}}(\mathbf{r})} \sum_{i=1}^N (\epsilon_i^{\text{KS}} - \epsilon_i^{\text{HF}}) |\phi_i^{\text{HF}}(\mathbf{r})|^2. \quad (4.30)$$

The eigenvalues $\{\epsilon_i^{\text{KS}}\}$ in Eq. (4.30) are still unknown but can be determined by iteration as in the OCEP SCF method. As in the OCEP and DCEP methods, the total effective KS potential in the OCEP-HF scheme is obtained by combining the exchange potential with $v_{\text{H}}^{\text{KS}}(\mathbf{r})$. The OCEP-HF method is identical with the model potential discussed by us briefly in Ref. 52.

The OCEP-HF model assumes that the i th HF orbital correlates with the i th KS orbital of the OCEP-HF Hamiltonian, which is not always the case (Table 4.1). Thus, if Eq. (4.30) is implemented naïvely, then for molecules such as N_2 the OCEP-HF will not be axially symmetric and will break the degeneracy of the $\pi_u 2p$ orbitals. In order to avoid unphysical symmetry breaking, one has to keep track of which HF orbital corresponds to which eigenfunction of the OCEP-HF. An additional complication arises when the HOMO in the HF scheme becomes the LUMO in the KS method. By contrast, the

Table 4.2: Various definitions of the factors Q_{ij} in Eq. (4.31)

Model	Q_{ij}
KLI	$\langle \phi_i v_X - \hat{K} \phi_i \rangle \delta_{ij}$
ELP, LHF, CEDA	$\langle \phi_i v_X - \hat{K} \phi_j \rangle$
GLLB ^a	$K[\rho] \sqrt{\epsilon_{\text{HOMO}} - \epsilon_i}$
OCEP-HF	$(\epsilon_i^{\text{KS}} - \epsilon_i^{\text{HF}}) \delta_{ij}$

^a $K[\rho]$ is a numerical coefficient defined in Ref. 25.

OCEP approximation does not require pairing up HF and KS orbitals and does not break spatial symmetry.

The OCEP-HF can be also thought of as the KS potential operator (v_X) whose eigenfunctions are as close as possible to the eigenfunctions of the corresponding GKS operator (\hat{K}). The OCEP-HF should therefore be close to the “effective local potential” [19] (ELP) defined as the multiplicative operator that provides the best fit to the Fock exchange operator \hat{K} in a least-squares sense. The ELP is itself numerically equivalent [20] to the “transformed LHF” potential [16] and to the common energy denominator approximation [17] (CEDA). Our calculations indicate that the OCEP-HF, KLI, and ELP potentials are virtually interchangeable, but at the same time distinct from the relaxed-orbital OCEP (cf. Fig. 4.2).

A model exchange potential similar to the OCEP-HF, but with ϕ_i^{KS} in place of ϕ_i^{HF} , was also obtained by Nagy [50] in the process of an “alternative derivation” of the KLI potential. Nagy’s method for computing her potential was restricted to few-electron atoms, so numerical results for only one atom (Be) were ever published [50].

Thus, the OCEP-HF belongs to the same class of model potentials as KLI, ELP, LHF, CEDA, and the model of Gritsenko, van Lenthe, van Leeuwen, and Baerends (GLLB) [25]. All these potentials have the form

$$v_X(\mathbf{r}) = v_X^{\text{S}}(\mathbf{r}) + \frac{1}{\rho(\mathbf{r})} \sum_{i,j=1}^N Q_{ij} \phi_i^*(\mathbf{r}) \phi_j(\mathbf{r}), \quad (4.31)$$

where the quantities Q_{ij} are defined in Table 4.2. As emphasized by Nagy [50], the relationship between Eq. (4.30) and the KLI approximation is particularly close because

$$\langle \phi_i^{\text{HF}} | v_X - \hat{K} | \phi_i^{\text{HF}} \rangle = \langle \phi_i^{\text{HF}} | \hat{h} - \hat{F} | \phi_i^{\text{HF}} \rangle \approx \epsilon_i^{\text{KS}} - \epsilon_i^{\text{HF}}, \quad (4.32)$$

where \hat{h} is the exchange-only KS Hamiltonian and \hat{F} is the one-electron Fock operator.

As with the OCEP method, there is no guarantee that the KS ground-state density generated by a DCEP is exactly equal to the HF density in finite-basis-set calculations. But unlike the OCEP scheme, the DCEP can satisfy its underlying assumption [Eq. (4.20)] exactly in the basis-set limit, provided the particular $\rho^{\text{HF}}(\mathbf{r})$ is non-interacting v -representable.

4.5 Total energies and orbital eigenvalues

Now we put the proposed hierarchy of model exchange potentials to test in Gaussian-basis-set calculations on atoms and molecules. All results of this section were obtained using density-functional integration grids containing at least 300 radial points and enough angular points to ensure that the total energies are converged to all digits reported.

The total electronic energy was computed as

$$E = T_s + \int \rho(\mathbf{r})v_{\text{ext}}(\mathbf{r}) d\mathbf{r} + E_{\text{H}} + E_{\text{X}}, \quad (4.33)$$

where $T_s = -(1/2) \sum_{i=1}^N \langle \phi_i | \nabla^2 | \phi_i \rangle$ is the KS kinetic energy, $E_{\text{H}} = (1/2) \int \rho(\mathbf{r})v_{\text{H}}(\mathbf{r}) d\mathbf{r}$ is the Hartree energy and E_{X} is the exchange energy. The first three terms on the right-hand side of Eq. (4.33) were always computed analytically for a given set of orbitals. The exchange contribution was obtained in two different ways: analytically by Eq. (1.44) and by numerical integration using the Levy–Perdew virial relation [67–69],

$$E_{\text{X}}^{\text{vir}} = \int v_{\text{X}}(\mathbf{r}) [3\rho(\mathbf{r}) + \mathbf{r} \cdot \nabla\rho(\mathbf{r})] d\mathbf{r}. \quad (4.34)$$

The total electronic energies obtained through Eqs. (1.44) and (4.34) are denoted E_{conv} and E_{vir} , respectively. For the exact OEP, $E_{\text{conv}} = E_{\text{vir}}$ [70, 71].

The quantity

$$\Delta E_{\text{conv}} = E_{\text{conv}} - E_{\text{OEP}}, \quad (4.35)$$

where E_{OEP} is the benchmark OEP energy, is often used as a measure of the accuracy of a model exchange potential. Another useful measure is the virial energy discrepancy [39, 72],

$$\Delta E_{\text{vir}} = E_{\text{vir}} - E_{\text{conv}}. \quad (4.36)$$

The difference ΔE_{vir} can be either positive or negative and is more sensitive to the quality of exchange potentials than ΔE_{conv} [54].

The values of ΔE_{conv} and ΔE_{vir} obtained with various OEP approximations for 20 atoms (half of which have open shells) are given in Table 4.3. The H and He atoms are not included because all OEP approximations of Table 4.3 are exact for any system with a single occupied spatial KS orbital. Judging by the magnitudes of ΔE_{conv} and ΔE_{vir} , the OCEP, ELP, and KLI are roughly two orders of magnitude more accurate than the OAEP model, and the DCEP is roughly two orders of magnitude better than the OCEP, ELP, and KLI. Observe that the conventional exact-exchange energies obtained from the OCEP-HF model are slightly lower than the energies from the KLI and ELP approximations.

For any model exchange potential the value of ΔE_{conv} should be non-negative in the basis-set limit because E_{conv} is bounded below by the true OEP energy. The DCEP/UGBS values of ΔE_{conv} , however, are slightly negative for some atoms in Table 4.3. We interpret this result as a manifestation of the finiteness of the UGBS because, in finite basis sets, the matrix of a multiplicative operator can be identical with the matrix of some non-multiplicative operator [73], and so the exact-exchange KS scheme can yield E_{conv} values below the basis-set-limit OEP energy (cf. Ref. 4).

Exchange-only KS energies should also satisfy [67] the conventional virial theorem,

$$T_s + E_{\text{conv}} = 0, \quad (4.37)$$

which can be used as another test of OEP approximations [39]. Let us rewrite Eq. (4.37) as

$$(T_s + E_{\text{vir}}) - \Delta E_{\text{vir}} = 0, \quad (4.38)$$

where ΔE_{vir} is defined by Eq. (4.36), and note that both terms on the left-hand side of Eq. (4.38) should vanish separately. In an atom, the sum $T_s + E_{\text{conv}}$ may be nonzero for two different reasons: because of finiteness of the basis set and because the potential v_X is not the functional derivative of the exchange functional. By contrast, ΔE_{vir} vanishes in any basis set as long the exchange potential is the functional derivative (one can verify this property of ΔE_{vir} numerically for any approximate exchange functional). Therefore, if we interpret $-\Delta E_{\text{vir}}$ as the functional-derivative error, then $T_s + E_{\text{vir}}$ may be interpreted as the basis-set error. We found that $T_s + E_{\text{conv}}$ has more or less the same values as $-\Delta E_{\text{vir}}$ in Table 4.3 (much greater for OCEPs than for DCEPs), while the magnitudes of $T_s + E_{\text{vir}}$ are small (mostly between 0.01 and 1 mE_h) and are roughly the same for OCEPs and DCEPs. This suggests that ΔE_{vir} indeed reflects deviations of the corresponding potentials from the true OEPs.

Table 4.4 summarizes results of exact-exchange KS calculations on many-electron molecules for which benchmark-quality numerical OEP energies are available [42]. The DCEP/UGBS1O energies for Li_2 and BH are slightly lower than the numerical OEP values of Makmal *et al.* [42]. In the case of LiH, the DCEP/UGBS1O energy is $11 \mu E_h$ above the OEP energy reported by Makmal *et al.*, but our DCEP estimate can be lowered by $18 \mu E_h$ by using the larger UGBS2O basis. At the same time, a switch from UGBS1O to UGBS2O increases the DCEP energy of BH by $27 \mu E_h$, underscoring the fact that the DCEP energy is not variational.

Finally, Table 4.5 compares typical KS eigenvalue spectra obtained with standard OEP approximations and the model potentials of this work. The agreement between the OEP and DCEP (HFXC) eigenvalues is excellent, just as the agreement between total energies. Note the close agreement between the KLI and OCEP-HF eigenvalues, which once again suggests that these two approximations are very similar.

4.6 Conclusion

The proposed hierarchy of approximations to the exact-exchange OEP can be summarized as the following list ordered by increasing accuracy:

$$\text{OAEP} < \text{OCEP} \approx \text{OCEP-HF} < \text{DCEP} \approx \text{OEP}$$

The first-level approximation, OAEP, is equivalent to Slater’s statistical average of the Fock operator. The second-level approximation, OCEP, is numerically similar to the KLI, LHF, ELP, and related models. The frozen-orbital modification of the OCEP, called OCEP-HF, is slightly more accurate than the OCEP, but its advantage is offset by the inconvenience of having to keep track of the correspondence between the HF and KS orbitals. Finally, the third-level approximation, DCEP, is practically identical to the true functional derivative of the exact-exchange functional, OEP. One way to understand the superiority of DCEPs is to note that the OCEP and LHF models assume that the KS orbitals are unitary transformations of the HF orbitals, whereas the DCEP model does not make that restrictive assumption.

The relationship between the analytic expressions of the three models is that of Chinese boxes: the OAEP is built into OCEP, while the OCEP is subsumed by the DCEP. Despite vast differences in accuracy, all three levels of this nested hierarchy have the same computational cost and are easily affordable for atoms and molecules.

Hierarchies of model potentials similar to the above can be constructed for any functional of occupied orbitals. Starting with $v_{\text{XC}}^{\text{OAEP}}(\mathbf{r})$ constructed with the self-consistent GKS orbitals, we would have

$$v_{\text{XC}}^{\text{OCEP}}(\mathbf{r}) = v_{\text{XC}}^{\text{OAEP}}(\mathbf{r}) + \bar{I}^{\text{GKS}}(\mathbf{r}) - \bar{I}^{\text{KS}}(\mathbf{r}) \quad (4.39)$$

and

$$v_{\text{XC}}^{\text{DCEP}}(\mathbf{r}) = v_{\text{XC}}^{\text{OCEP}}(\mathbf{r}) + \frac{\tau^{\text{GKS}}(\mathbf{r})}{\rho^{\text{GKS}}(\mathbf{r})} - \frac{\tau^{\text{KS}}(\mathbf{r})}{\rho^{\text{KS}}(\mathbf{r})}, \quad (4.40)$$

in obvious notation. As with exact exchange, the method requires solving the GKS equations and constructing the corresponding OAEP. The latter task can be simplified using the techniques developed by our group recently [52, 74].

The most important message of this work is that instead of tackling the complicated OEP integral equation one can obtain its solution almost exactly by constructing a model potential (DCEP). The DCEP approach works so well because the DCEP and OEP equations are formally identical to the first order of perturbation of the KS Hamiltonian. As a numerically excellent approximation to the functional derivative $\delta E_{\text{XC}}/\delta\rho$ of an orbital-dependent functional, the DCEP model can serve as an uncompromising alternative to the OEP procedure in atomic and molecular calculations with finite basis sets.

Table 4.3: Total ground-state energies of spherical atoms computed with various effective potentials for exact exchange. The OEP and KLI values are from Refs. 39–41; the others were computed in this work using the UGBS.

Atom	E_{OEP}											$\Delta E_{\text{conv}} = E_{\text{conv}} - E_{\text{OEP}}$ (units of mE_h)				$\Delta E_{\text{vir}} = E_{\text{vir}} - E_{\text{conv}}$ (units of mE_h)			
	(units of E_h)	OAEP	KLI	ELP	OCEP-HF	OCEP	DCEP	OAEP	KLI	OCEP-HF	OCEP	DCEP	OAEP	KLI	OCEP-HF	OCEP	DCEP		
Li	-7.43250	5.81	0.06	0.08	0.05	0.09	0.00	-114.3	-5.3	-2.5	9.9	-0.04							
Be	-14.57243	11.23	0.15	0.15	0.12	0.20	-0.01	-351.1	-21.2	-10.4	31.0	-0.10							
N	-54.40340	26.19	0.36	0.34	0.32	0.47	0.00	-1345.7	24.7	29.2	131.0	-0.21							
Ne	-128.54541	43.05	0.58	0.57	0.54	0.73	0.01	-3058.8	155.6	145.9	291.6	-0.13							
Na	-161.85664	62.78	0.73	0.73	0.66	0.86	0.00	-3776.1	183.1	177.6	337.8	-0.28							
Mg	-199.61158	78.24	0.87	0.88	0.77	1.02	0.00	-4680.2	182.3	196.2	386.4	-0.26							
P	-340.71500	88.83	1.28	1.28	1.03	1.41	-0.03	-6993.3	144.9	237.0	530.5	-1.84							
Ar	-526.81222	104.83	1.74	1.83	1.41	1.87	-0.07	-9789.9	124.7	283.5	692.8	-4.08							
K	-599.15912	126.38	1.99	1.91	1.62	2.00	-0.05	-10920.5	85.5	284.6	747.6	-5.34							
Ca	-676.75193	143.31	2.23	1.99	1.75	2.07	-0.13	-12195.0	14.9	275.2	799.5	-5.87							
Cr	-1043.34575	182.90	3.51	3.42	2.28	2.35	-0.15	-17366.7	303.3	456.0	1039.9	-6.25							
Zn	-1777.83436	251.06	3.65	3.05	2.97	2.85	-0.07	-27120.2	1047.9	976.7	1396.9	-5.93							
As	-2234.22812	260.66	2.97	2.85	2.70	2.98	-0.16	-31761.6	1344.9	1255.9	1564.7	-9.51							
Kr	-2752.04295	277.24	3.18	3.44	2.90	3.36	-0.07	-36992.2	1468.1	1502.1	1739.8	-7.43							
Mo	-3975.53711	340.78	5.11	4.71	4.03	4.26	-0.04	-48594.9	1476.9	1802.7	2088.1	-19.48							
Ag	-5197.68151	384.70	5.72	5.58	4.76	5.12	-0.18	-59295.2	1850.6	2163.2	2377.9	-0.27							
Cd	-5465.11441	406.80	6.04	5.58	5.06	5.12	-0.26	-61735.4	1883.9	2187.5	2450.1	-6.99							
Sb	-6313.46970	418.57	5.78	6.63	5.24	5.23	-0.02	-68194.9	1959.8	2408.5	2633.2	-37.50							
Xe	-7232.12107	435.78	6.06	6.20	5.22	5.15	-0.44	-75176.8	1834.7	2590.6	2808.8	-26.75							
Cs	-7553.91654	457.93	6.27	6.54	5.60	5.52	-0.21	-77660.5	1732.6	2638.7	2872.4	-7.64							
m.a.v. ^a		205.35	2.91	2.89	2.45	2.63	0.09	27856.2	792.2	981.2	1246.5	7.30							

^a Mean absolute value.

Table 4.4: Conventional total energies (in units of E_h) of many-electron molecules obtained by numerical solution of the KLI and OEP equations and by the effective-potential methods of this work. The bond lengths are given in Ref. 42.

Molecule	Grabo <i>et al.</i> [65]				Makmal <i>et al.</i> [42]				This work				
	KLI	KLI ^a	OEP ^a	OAE ^a	OEP	OCEP	OCEP	DCEP	DCEP	DCEP	DCEP	DCEP	DCEP
LiH (¹ Σ ⁺)	-7.9868	-7.98680(8)	-7.98691(9)	-7.981017	-7.986787	-7.986908	-7.986908	-7.986908	-7.986908	-7.986908	-7.986908	-7.986908	-7.986926
Li ₂ (¹ Σ _g ⁺)	-14.8706	-14.87058(0)	-14.87076(5)	-14.852016	-14.870542	-14.870772	-14.870772	-14.870772	-14.870772	-14.870772	-14.870772	-14.870772	-14.870775
BH (¹ Σ ⁺)	-24.1290	-25.12903(0)	-25.12963(6)	-25.107737	-25.129026	-25.129690	-25.129690	-25.129690	-25.129690	-25.129690	-25.129690	-25.129690	-25.129663

^a The digits shown in parentheses are not converged.

Table 4.5: Orbital eigenvalues for the Ar atom computed with HF and various effective-potential methods. The OEP and KLI values are from Refs. 39–41 (see also Ref. 60); the others were computed in this work using the UGBS10 basis. All orbital eigenvalues were shifted to satisfy the HOMO condition of Eq. (4.19).

Orbital	Energies (units of E_h)									
	HF	OEP ^a	OAE ^a	KLI ^a	ELP ^a	OCEP-HF	OCEP	DCEP	OCEP	DCEP
Occupied orbitals										
1s	-118.6103	-114.4524	-117.0285	-114.4296	-114.3471	-114.4013	-114.1616	-114.4565	-114.1616	-114.4565
2s	-12.3221	-11.1535	-11.7670	-11.1838	-11.1171	-11.1598	-11.0690	-11.1563	-11.0690	-11.1563
2p	-9.5714	-8.7340	-9.4131	-8.7928	-8.7246	-8.7678	-8.6778	-8.7367	-8.6778	-8.7367
3s	-1.2773	-1.0995	-1.1019	-1.0959	-1.0962	-1.0957	-1.0974	-1.0994	-1.0974	-1.0994
3p	-0.5910	-0.5910	-0.5910	-0.5910	-0.5910	-0.5910	-0.5910	-0.5910	-0.5910	-0.5910
Unoccupied orbitals										
4s	0.3033		-0.0179			-0.0409		-0.0392		-0.0392
4p	0.1730		-0.0280			-0.0639		-0.0604		-0.0604
3d	0.2035		-0.0095			-0.0447		-0.0418		-0.0418

^a Eigenvalues of the OEP, KLI, and ELP virtual orbitals are not available.

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Chapter 5

Exchange-correlation potentials from many-electron wavefunctions

5.1 Introduction

Most existing methods for generating exact exchange-correlation potentials fit the function $v_{\text{XC}}(\mathbf{r})$ to a given ground-state density, $\rho(\mathbf{r})$, via the Kohn–Sham (KS) equations either by iterative updates [1–4] or through some constrained optimization [5–7]. The target densities are usually obtained from *ab initio* wavefunctions which are themselves discarded. Because small changes in $\rho(\mathbf{r})$ can induce large changes in $v_{\text{XC}}(\mathbf{r})$ [8], potential-reconstruction methods that use only $\rho(\mathbf{r})$ as input suffer from numerical instabilities. Moreover, electron densities generated using ubiquitous Gaussian basis sets correspond to exchange-correlation potentials that wildly oscillate and diverge [9–12], a result that is formally correct but unwanted. Kohn–Sham potentials can be also constructed by many-body methods [13–17], but these techniques are quite elaborate and often require solving an integral equation for $v_{\text{XC}}(\mathbf{r})$, which is a challenge by itself.

Here, we propose a radically different method for computing the exchange-correlation potential of a given many-electron system, which avoids the above difficulties. In this method, the functional derivative of the exact $E_{\text{XC}}[\rho]$ is obtained directly from the system’s electronic wavefunction. The approach represents a nontrivial generalization of our

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technique for constructing Kohn–Sham potentials corresponding to Hartree–Fock (HF) electron densities [18, 19] devised in Chapter 4 (the density-consistent effective potential) and is conceptually related to the wavefunction-based analysis of Kohn–Sham potentials developed by Baerends and co-workers [20–24].

5.2 Derivation of the method

The basic idea of our approach is to derive two expressions for the local electron energy balance, one of which originates from the Kohn–Sham equations, the other from the Schrödinger equation. When one expression is subtracted from the other under the assumption that the Kohn–Sham and wavefunction-based densities are equal, the system’s electrostatic potentials cancel out and the difference gives an explicit formula for $v_{\text{XC}}(\mathbf{r})$. For simplicity, the treatment presented in this chapter is restricted to electronic singlet ground states described with closed-shell Kohn–Sham determinants, and assumes that all basis functions and orbitals are real (although the notation for complex conjugate is retained).

Accomplishing the first part of this plan is easy. In the Kohn–Sham scheme, the ground-state density of a singlet N -electron system is obtained as $\rho^{\text{KS}}(\mathbf{r}) = \sum_i n_i |\phi_i(\mathbf{r})|^2$, where $n_i = 0$ or 2 are occupation numbers of the corresponding Kohn–Sham orbitals ($N = \sum_i n_i$). The orbitals are obtained by solving the equation

$$\left[-\frac{1}{2}\nabla^2 + v_{\text{ext}}(\mathbf{r}) + v_{\text{H}}^{\text{KS}}(\mathbf{r}) + v_{\text{XC}}(\mathbf{r}) \right] \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r}), \quad (5.1)$$

where $v_{\text{ext}}(\mathbf{r})$ is the electrostatic potential of the nuclei and $v_{\text{H}}^{\text{KS}}(\mathbf{r})$ is the electrostatic potential of $\rho^{\text{KS}}(\mathbf{r})$. If we multiply Eq. (5.1) by $n_i \phi_i^*(\mathbf{r})$, sum over i , and divide through by $\rho^{\text{KS}}(\mathbf{r})$, we obtain

$$\frac{\tau_L^{\text{KS}}(\mathbf{r})}{\rho^{\text{KS}}(\mathbf{r})} + v_{\text{ext}}(\mathbf{r}) + v_{\text{H}}^{\text{KS}}(\mathbf{r}) + v_{\text{XC}}(\mathbf{r}) = \bar{\epsilon}^{\text{KS}}(\mathbf{r}), \quad (5.2)$$

where $\tau_L^{\text{KS}}(\mathbf{r}) = -(1/2) \sum_i n_i \phi_i^*(\mathbf{r}) \nabla^2 \phi_i(\mathbf{r})$ is the Kohn–Sham kinetic energy density and

$$\bar{\epsilon}^{\text{KS}}(\mathbf{r}) = \frac{1}{\rho^{\text{KS}}(\mathbf{r})} \sum_i n_i \epsilon_i |\phi_i(\mathbf{r})|^2 \quad (5.3)$$

is the average local Kohn–Sham orbital energy [25].

The second part of the plan is to reduce the N -electron Schrödinger equation to a local energy balance expression analogous to Eq. (5.2). There is more than one way to do this. Holas and March [26] had considered a contracted Schrödinger equation for this purpose, but their proposal led to a complicated integral equation for $v_{\text{XC}}(\mathbf{r})$ involving the three-electron reduced density matrix (3-RDM). The Baerends group [20–24] used an expression involving $(N - 1)$ -electron conditional amplitudes. The method we propose here is motivated by Löwdin’s approach [27] to the problem of finding the optimal finite one-electron basis set for a configuration interaction (CI) expansion.

Suppose we have an N -electron ground-state wavefunction Ψ expressed in terms of orthonormal orbitals $\{\psi_i\}$. Then the total electronic energy may be written as

$$E = \sum_{ij} \gamma_{ij} \langle \psi_j | \hat{h} | \psi_i \rangle + \sum_{ikjl} \Gamma_{ikjl} \langle \psi_j \psi_l | r_{12}^{-1} | \psi_i \psi_k \rangle, \quad (5.4)$$

where $\hat{h}(\mathbf{r}) = -(1/2)\nabla^2 + v_{\text{ext}}(\mathbf{r})$ is the one-electron core Hamiltonian, $\gamma_{ij} = \sum_{\sigma} \langle \Psi | \hat{a}_{j\sigma}^{\dagger} \hat{a}_{i\sigma} | \Psi \rangle$ ($\sigma = \alpha, \beta$ is the spin index) are matrix elements of the spin-free 1-RDM, and $\Gamma_{ikjl} = (1/2) \sum_{\sigma\sigma'} \langle \Psi | \hat{a}_{j\sigma}^{\dagger} \hat{a}_{l\sigma'}^{\dagger} \hat{a}_{k\sigma'} \hat{a}_{i\sigma} | \Psi \rangle$ are matrix elements of the spin-free 2-RDM.

Our objective is to turn Eq. (5.4) into a local energy balance equation. We start by minimizing E with respect to the functions $\{\psi_i\}$, subject to the constraint $\langle \psi_j | \psi_i \rangle = \delta_{ji}$, while keeping γ_{ij} and Γ_{ikjl} fixed. The corresponding Euler–Lagrange equation is

$$\frac{\delta E}{\delta \psi_j^*(\mathbf{r})} = \sum_i \lambda_{ij} \psi_i(\mathbf{r}), \quad (5.5)$$

where λ_{ij} are yet undetermined Lagrange multipliers. We evaluate the functional derivative in Eq. (5.5), multiply the result by $\psi_j^*(\mathbf{r}')$, sum over j , and obtain

$$\hat{h}(\mathbf{r})\gamma(\mathbf{r}, \mathbf{r}') + 2 \int \frac{\Gamma(\mathbf{r}, \mathbf{r}_2; \mathbf{r}', \mathbf{r}_2)}{|\mathbf{r} - \mathbf{r}_2|} d\mathbf{r}_2 = \sum_{ij} \lambda_{ij} \psi_i(\mathbf{r}) \psi_j^*(\mathbf{r}'). \quad (5.6)$$

where

$$\gamma(\mathbf{r}, \mathbf{r}') = \sum_{ij} \gamma_{ij} \psi_i(\mathbf{r}) \psi_j^*(\mathbf{r}') \quad (5.7)$$

and

$$\Gamma(\mathbf{r}, \mathbf{r}_2; \mathbf{r}', \mathbf{r}'_2) = \sum_{ikjl} \Gamma_{ikjl} \psi_i(\mathbf{r}) \psi_k(\mathbf{r}_2) \psi_j^*(\mathbf{r}') \psi_l^*(\mathbf{r}'_2) \quad (5.8)$$

are the coordinate representations of the spin-free 1-RDM and 2-RDM, respectively.

We denote the left-hand side of Eq. (5.6) by $G(\mathbf{r}, \mathbf{r}')$ and treat it as the kernel of an integral operator defined by

$$\hat{G}\psi_j(\mathbf{r}) = \int G(\mathbf{r}, \mathbf{r}')\psi_j(\mathbf{r}') d\mathbf{r}'. \quad (5.9)$$

Then λ_{ij} can be determined from Eqs. (5.6) and (5.9) as

$$\lambda_{ij} = \langle \psi_i | \hat{G} | \psi_j \rangle. \quad (5.10)$$

The operator \hat{G} , known as the generalized Fock operator or orbital Lagrangian, arises in various problems of quantum chemistry [27–31].

For our purposes, we need only the $\mathbf{r} = \mathbf{r}'$ part of Eq. (5.6) which after division by $\rho^{\text{WF}}(\mathbf{r}) = \gamma(\mathbf{r}, \mathbf{r})$ becomes

$$\frac{\tau_L^{\text{WF}}(\mathbf{r})}{\rho^{\text{WF}}(\mathbf{r})} + v_{\text{ext}}(\mathbf{r}) + \frac{2}{\rho^{\text{WF}}(\mathbf{r})} \int \frac{P(\mathbf{r}, \mathbf{r}_2)}{|\mathbf{r} - \mathbf{r}_2|} d\mathbf{r}_2 = \bar{\epsilon}^{\text{WF}}(\mathbf{r}), \quad (5.11)$$

where $\tau_L^{\text{WF}}(\mathbf{r}) = -(1/2) [\nabla^2 \gamma(\mathbf{r}, \mathbf{r}')]_{\mathbf{r}'=\mathbf{r}}$ is the interacting kinetic energy density, $P(\mathbf{r}, \mathbf{r}_2) = \Gamma(\mathbf{r}, \mathbf{r}_2; \mathbf{r}, \mathbf{r}_2)$ is the pair function, and

$$\bar{\epsilon}^{\text{WF}}(\mathbf{r}) = \frac{1}{\rho^{\text{WF}}(\mathbf{r})} \sum_{ij} \lambda_{ij} \psi_i(\mathbf{r}) \psi_j^*(\mathbf{r}). \quad (5.12)$$

One can always write the pair function as

$$P(\mathbf{r}, \mathbf{r}_2) = \frac{1}{2} \rho^{\text{WF}}(\mathbf{r}) [\rho^{\text{WF}}(\mathbf{r}_2) + \rho_{\text{XC}}^{\text{WF}}(\mathbf{r}, \mathbf{r}_2)], \quad (5.13)$$

which defines $\rho_{\text{XC}}^{\text{WF}}(\mathbf{r}, \mathbf{r}_2)$, the exchange-correlation hole density. Substituting Eq. (5.13) into Eq. (5.11) we obtain

$$\frac{\tau_L^{\text{WF}}(\mathbf{r})}{\rho^{\text{WF}}(\mathbf{r})} + v_{\text{ext}}(\mathbf{r}) + v_{\text{H}}^{\text{WF}}(\mathbf{r}) + v_{\text{S}}^{\text{WF}}(\mathbf{r}) = \bar{\epsilon}^{\text{WF}}(\mathbf{r}), \quad (5.14)$$

where $v_{\text{H}}^{\text{WF}}(\mathbf{r})$ is the electrostatic potential of $\rho^{\text{WF}}(\mathbf{r})$ and

$$v_{\text{S}}^{\text{WF}}(\mathbf{r}) = \int \frac{\rho_{\text{XC}}^{\text{WF}}(\mathbf{r}, \mathbf{r}_2)}{|\mathbf{r} - \mathbf{r}_2|} d\mathbf{r}_2 \quad (5.15)$$

is the Slater exchange-correlation-charge potential [32]. The above quantity is also

known in the literature [22, 23, 33] as the exchange-correlation hole potential, $v_{\text{XC}}^{\text{hole}}$. Equation (5.14) is the wavefunction counterpart of Eq. (5.2).

Observe that the sum in Eq. (5.12) does not change if we replace every λ_{ij} with λ_{ji}^* . This means that $\bar{\epsilon}^{\text{WF}}(\mathbf{r})$ is determined by the Hermitian (symmetric) part of \hat{G} . If desired, one can define the self-adjoint operator $\hat{F} = (\hat{G} + \hat{G}^\dagger)/2$ and solve the Hermitian eigenvalue problem $\hat{F}f_i(\mathbf{r}) = \lambda_i f_i(\mathbf{r})$. This optional step allows one to cast Eq. (5.12) as

$$\bar{\epsilon}^{\text{WF}}(\mathbf{r}) = \frac{1}{\rho^{\text{WF}}(\mathbf{r})} \sum_i \lambda_i |f_i(\mathbf{r})|^2, \quad (5.16)$$

which is formally analogous to Eq. (5.3). The quantity $\bar{\epsilon}^{\text{WF}}(\mathbf{r})$ as given by Eq. (5.16) was introduced by our group earlier under the name of ‘‘average local electron energy’’ [34].

Now let us subtract Eq. (5.14) from Eq. (5.2), substitute the identity $\tau_L = \tau - \nabla^2 \rho/4$ for τ_L^{KS} and for τ_L^{WF} with $\tau^{\text{KS}} = (1/2) \sum_i n_i |\nabla \phi_i|^2$ and $\tau^{\text{WF}}(\mathbf{r}) = (1/2) [\nabla_{\mathbf{r}'} \nabla_{\mathbf{r}} \gamma(\mathbf{r}, \mathbf{r}')]_{\mathbf{r}'=\mathbf{r}}$, and apply the condition $\rho^{\text{KS}}(\mathbf{r}) = \rho^{\text{WF}}(\mathbf{r})$. This yields the central equation of this work:

$$v_{\text{XC}}(\mathbf{r}) = v_{\text{S}}^{\text{WF}}(\mathbf{r}) + \bar{\epsilon}^{\text{KS}}(\mathbf{r}) - \bar{\epsilon}^{\text{WF}}(\mathbf{r}) + \frac{\tau^{\text{WF}}(\mathbf{r})}{\rho^{\text{WF}}(\mathbf{r})} - \frac{\tau^{\text{KS}}(\mathbf{r})}{\rho^{\text{KS}}(\mathbf{r})}. \quad (5.17)$$

Since τ^{KS} and $\bar{\epsilon}^{\text{KS}}$ are initially unknown, Eq. (5.17) must be solved iteratively in conjunction with the Kohn–Sham equations. The transition from τ_L to τ is not strictly necessary but beneficial for numerical calculations because τ does not diverge at the nuclei as does τ_L .

It may seem like nothing beyond the inverted Kohn–Sham equation [Eq. (5.2)] can be achieved if one adds to it the local energy balance equation for the wavefunction quantities [Eq. (5.14)]. Of course, if the symbol $\bar{\epsilon}^{\text{WF}}$ is taken to mean the left-hand side of Eq. (5.14) (that is, $\bar{\epsilon}^{\text{WF}}$ is computed as the sum of four ingredients), then Eq. (5.17) is trivially the same as Eq. (5.2) for $\rho^{\text{KS}} = \rho^{\text{WF}}$. We wish to emphasize that in our approach $\bar{\epsilon}^{\text{WF}}$ is defined according to Eq. (5.16). The left-hand side of Eq. (5.14) and the right-hand side of Eq. (5.16) are *not* equal in finite basis sets (Fig. 5.1), a fact that plays a crucial role. When $\bar{\epsilon}^{\text{WF}}$ is properly understood as the right-hand side of Eq. (5.16), Eq. (5.17) becomes a nontrivial relation between v_{XC} and wavefunction quantities. It is both legitimate and profitable to regard Eq. (5.17) as an equation for v_{XC} in terms of v_{S}^{WF} , $\bar{\epsilon}^{\text{WF}}$ of Eq. (5.16), and $\tau^{\text{WF}}/\rho^{\text{WF}}$. By computing these wavefunction quantities from a 2-RDM and then solving Eq. (5.17) for v_{XC} , one *can* obtain accurate approximations to v_{XC} and the associated KS determinant, as we will demonstrate in the next section.

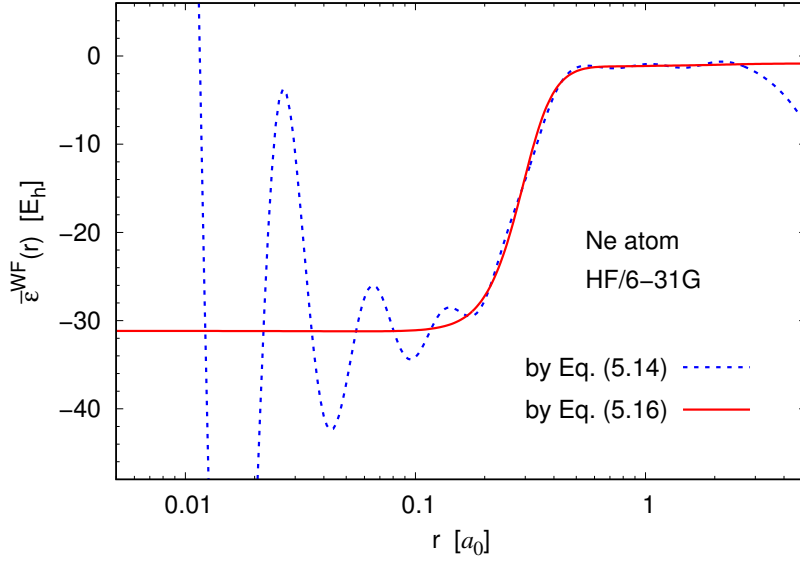


Figure 5.1: Quantity $\bar{\epsilon}^{\text{WF}}$ computed from the HF/6-31G wavefunction by Eqs. (5.14) and (5.16).

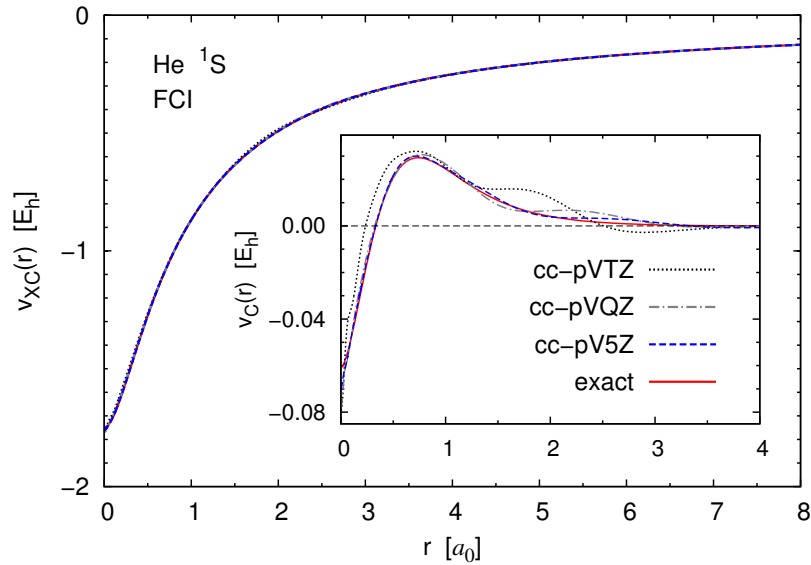


Figure 5.2: Exchange-correlation and correlation (inset) potentials for the He atom calculated from FCI wavefunctions using various basis sets.

5.3 Numerical tests

Note that as $r \rightarrow \infty$, the term v_S^{WF} vanishes, but the other ingredients remain nonzero: $\bar{\epsilon}^{\text{KS}}$, $\tau_L^{\text{KS}}/\rho^{\text{KS}}$, and $-\tau^{\text{KS}}/\rho^{\text{KS}}$ approach ϵ_{HOMO} [35], while $\bar{\epsilon}^{\text{WF}}$, $\tau_L^{\text{WF}}/\rho^{\text{WF}}$, and $-\tau^{\text{WF}}/\rho^{\text{WF}}$ approach $-I_{\text{min}}$ [34], where I_{min} is the first ionization energy of the system as determined by the extended Koopmans theorem [36]. To ensure that $v_{\text{XC}}(\mathbf{r})$ as given by Eq. (5.17)

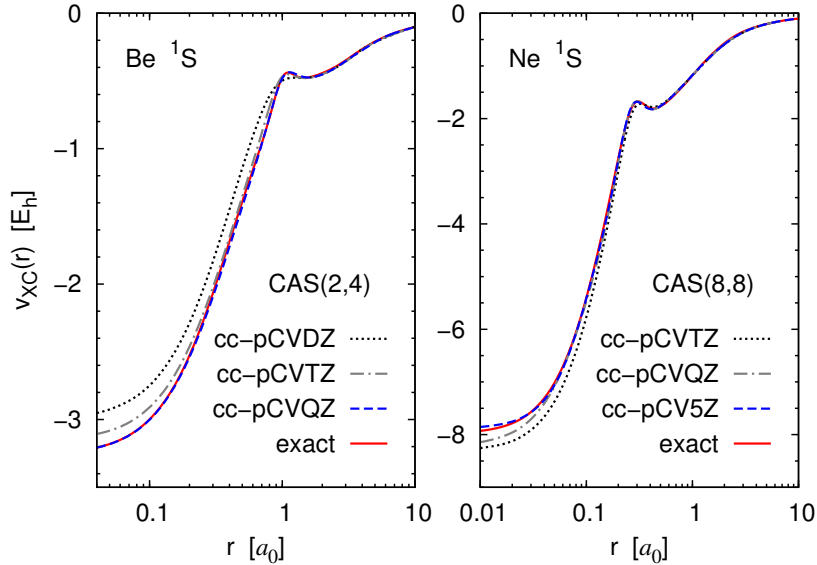


Figure 5.3: Exchange-correlation potentials for the Ne and Be atoms calculated from compact CASSCF wavefunctions using various basis sets.

properly vanishes at infinity, we shift all current values of ϵ_i in each Kohn–Sham iteration to satisfy the condition

$$\epsilon_{\text{HOMO}} = -I_{\text{min}}, \quad (5.18)$$

which also imparts $\rho^{\text{KS}}(\mathbf{r})$ with proper asymptotic decay.

The proposed algorithm is as follows.

1. Obtain a wavefunction for the system of interest. Calculate ρ^{WF} , τ^{WF} , v_{S}^{WF} , $\bar{\epsilon}^{\text{WF}}$, and I_{min} .
2. Generate an initial guess for the occupied Kohn–Sham orbitals $\{\phi_i\}$ and their eigenvalues $\{\epsilon_i\}$.
3. Using the current guess for $\{\phi_i\}$ and shifted $\{\epsilon_i\}$, construct the potential v_{XC} by Eq. (5.17).
4. Solve the Kohn–Sham equations using the current v_{XC} and the same basis as in step 1. This gives new sets $\{\phi_i\}$ and $\{\epsilon_i\}$.
5. Return to step 3 and iterate until the potential v_{XC} is self-consistent.

The method was implemented in the GAUSSIAN 09 suite of programs [37], which already contains subroutines for constructing the generalized Fock matrix as part of the multiconfigurational self-consistent-field (MCSCF) module. The values of I_{min} were computed as in Ref. 30, while ρ^{WF} and τ^{WF} were assembled from natural orbitals. Any reasonable density-functional approximation may be used to generate an initial guess for

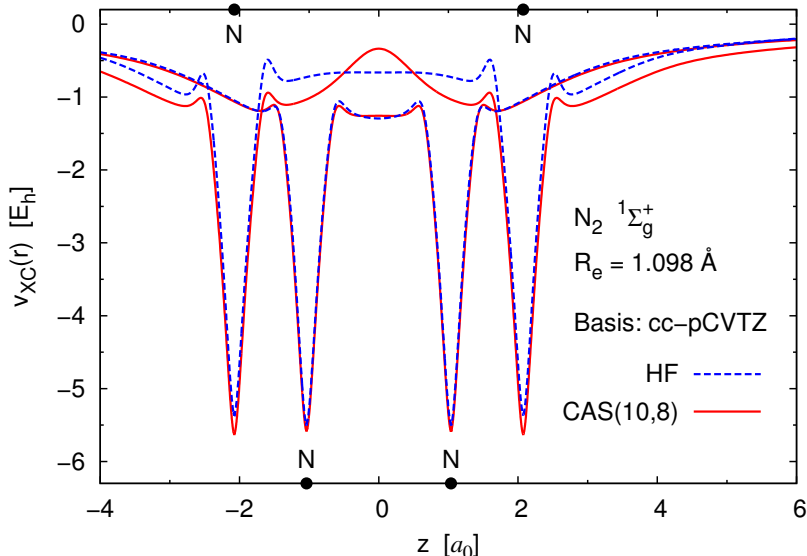


Figure 5.4: Exchange-correlation potentials for the N_2 molecule obtained from HF and valence CASSCF wavefunctions at the experimental equilibrium bond length and at $2R_e$.

$\{\phi_i\}$ and $\{\epsilon_i\}$. The potential was considered converged when all Kohn–Sham density matrix elements from consecutive iterations differed by less than 10^{-10} in the root-mean-square sense. The method works best with basis sets that are not heavily contracted in the core region.

An added benefit of generating $v_{XC}(\mathbf{r})$ from a wavefunction is that one can readily obtain the corresponding exchange-correlation energy, E_{XC}^{KS} , which is inaccessible when only the electron density is known. We computed this energy as $E_{XC}^{KS} = E_{XC}^{WF} + T_c$, where E_{XC}^{WF} is the *ab initio* exchange-correlation energy defined as $E_{XC}^{WF} = (1/2) \int \rho^{WF}(\mathbf{r}) v_S^{WF}(\mathbf{r}) d\mathbf{r}$ and $T_c = T - T_s$ is the difference between the *ab initio* and Kohn–Sham total kinetic energies, evaluated analytically. Also of interest is the integrated density difference, $\Delta\rho = \int |\rho^{KS}(\mathbf{r}) - \rho^{WF}(\mathbf{r})| d\mathbf{r}$, evaluated for the self-consistent $v_{XC}(\mathbf{r})$. Because the condition $\rho^{KS}(\mathbf{r}) = \rho^{WF}(\mathbf{r})$ is imposed in our approach only in the derivation of Eq. (5.17), $\Delta\rho$ strictly vanishes only in the basis-set limit. Insistence on reproducing $\rho^{WF}(\mathbf{r})$ *exactly* in Gaussian basis sets would be misplaced because (i) it brings out unwanted oscillations and divergences of $v_{XC}(\mathbf{r})$ and (ii) the potential that yields a given density in a finite basis is not unique anyway [38, 39].

To test the method, we computed exchange-correlation potentials for the three atoms (He, Be, and Ne) for which exact potentials are available in the literature [40, 41] using full CI (FCI) and complete active space (CAS) SCF wavefunctions and standard Gaussian basis sets [42]. For He, already the potential extracted from the FCI wavefunction in the cc-pVTZ basis set is very close to the exact $v_{XC}(\mathbf{r})$, and the cc-pVQZ and cc-pV5Z

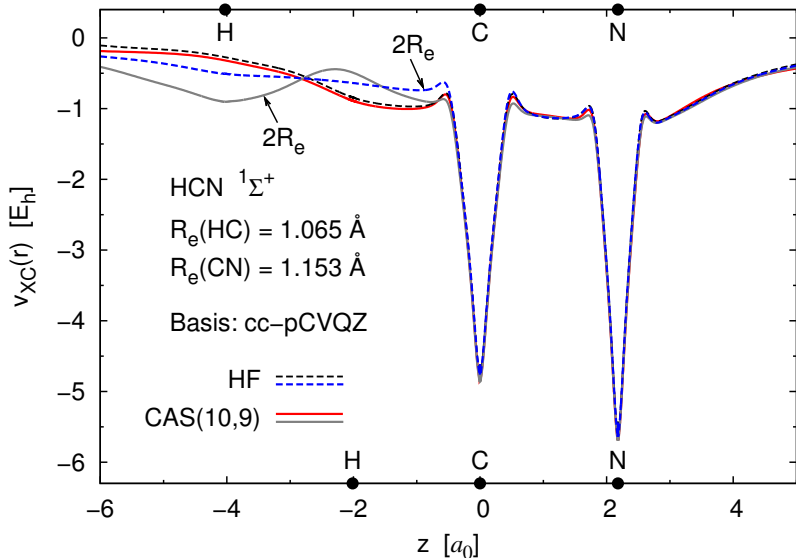


Figure 5.5: Exchange-correlation potentials for HCN obtained from HF and valence CASSCF wavefunctions at the experimental equilibrium geometry and with $R(\text{HC}) = 2R_e(\text{HC})$.

FCI exchange-correlation potentials are visually indistinguishable from the benchmark (Fig. 5.2 and Table 5.1). Even the correlation potential for He, $v_c(\mathbf{r}) = v_{\text{XC}}(\mathbf{r}) - v_{\text{H}}(\mathbf{r})/2$, which is almost two orders of magnitude smaller than $v_{\text{XC}}(\mathbf{r})$, is very accurate at the FCI/cc-pV5Z level (Fig. 5.2). For Be, the sequence of potentials from CAS(2,4) wavefunctions quickly approaches the exact $v_{\text{XC}}(\mathbf{r})$ with increasing basis set size (Fig. 5.3), as do the corresponding T_s values (Table 5.1). By contrast, T_c and $E_{\text{XC}}^{\text{KS}}$ converge slowly because they depend not only on $v_{\text{XC}}(\mathbf{r})$ but also on the accuracy of the wavefunction through the value of T . Potentials for the Ne atom constructed from CAS(8,8) wavefunctions also improve rapidly with the size of the basis set (Fig. 5.3). Thus, even compact correlated wavefunctions can produce accurate Kohn–Sham potentials, provided that the basis set is of good quality.

The method works equally well for molecules. It is known that, in molecules, the onset of strong correlation induced by bond stretching manifests itself in characteristic mid-bond peaks of $v_{\text{XC}}(\mathbf{r})$ [23, 43–45]. Using our method, we readily reproduced these peaks in a number of stretched diatomics exemplified by N_2 (Fig. 5.4). Exchange-correlation potentials for polyatomic molecules can also be generated by our method (Fig. 5.5).

It is remarkable that Kohn–Sham potentials computed from wavefunctions are always well-defined and free from spurious features. Conventional methods for extracting $v_{\text{XC}}(\mathbf{r})$ from densities, when implemented in matrix form, would not deliver such unambiguous results because there is no one-to-one correspondence between densities and potentials

in finite basis sets [38]. Furthermore, when density-to-potential mapping techniques are rigorously applied to electron densities generated in Gaussian basis sets, one obtains unphysical potentials [9–12]. Neither of these complications affects our approach.

5.4 Conclusion

In conclusion, we have developed a practical method for folding a many-electron wavefunction into the corresponding exchange-correlation potential. The key ingredient of our approach is the generalized Fock matrix which is commonly available in *ab initio* codes as a by-product of computing MCSCF wavefunctions, nuclear gradients, and first-order properties. The method possesses several advantages over existing techniques for constructing exchange-correlation potentials: it delivers $v_{\text{XC}}(\mathbf{r})$ in a simple analytic form, avoids the ambiguity of associating a given electron density with a Kohn–Sham potential in a finite basis set, is stable with respect to changes in basis sets, convergence thresholds and other details of the calculation, and produces potentials without oscillations and divergences when using Gaussian basis sets.

Table 5.1: Characteristics of selected wavefunctions and the corresponding Kohn–Sham effective potentials (in atomic units).

System	Wavefunction	E_{tot}	I_{min}	T_s	$T_c = T - T_s$	$E_{\text{XC}}^{\text{KS}}$	$\Delta\rho$
He	FCI/cc-pVTZ	-2.900232	0.9013	2.8571	0.0435	-1.0550	0.00251
	FCI/cc-pVQZ	-2.902411	0.9026	2.8652	0.0370	-1.0645	0.00065
	FCI/cc-pV5Z	-2.903152	0.9032	2.8668	0.0364	-1.0662	0.00013
	Exact ^a	-2.903724	0.9037	2.8671	0.0366	-1.0667	
Be	CAS(2,4)/cc-pCVDZ	-14.61545	0.3485	14.4901	0.1333	-2.6146	0.01729
	CAS(2,4)/cc-pCVTZ	-14.61653	0.3489	14.5538	0.0619	-2.6866	0.00493
	CAS(2,4)/cc-pCVQZ	-14.61677	0.3490	14.5910	0.0258	-2.7232	0.00547
	FCI/u-cc-pCVTZ	-14.66370	0.3421	14.5956	0.0654	-2.7715	0.00215
	Exact ^a	-14.66736	0.3426	14.5942	0.0732	-2.7701	

^a Accurate estimates from Ref. 40 (He) and Ref. 41 (Be).

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Chapter 6

Origin of the step structure of molecular exchange-correlation potentials

6.1 Introduction

Consider the dissociation of a heteronuclear diatomic molecule AB into neutral atoms A and B. The isolated atoms A and B have different external potentials and hence different Kohn–Sham highest-occupied molecular orbital (HOMO) energies, $\epsilon_{\text{HOMO}}^{\text{A}}$ and $\epsilon_{\text{HOMO}}^{\text{B}}$. In the exact Kohn–Sham scheme, these energies are such that $\epsilon_{\text{HOMO}}^{\text{A}} = -I_{\text{A}}$ and $\epsilon_{\text{HOMO}}^{\text{B}} = -I_{\text{B}}$, where I_{A} and I_{B} are the first ionization energies of A and B, respectively [1–4].

Suppose for the sake of definiteness that $I_{\text{A}} < I_{\text{B}}$. Then for the isolated atoms $\epsilon_{\text{HOMO}}^{\text{A}} > \epsilon_{\text{HOMO}}^{\text{B}}$. On the other hand, if A and B are viewed as constituent parts of a dissociated AB molecule, then the variational principle for the total energy implies [4] that the HOMO levels of A and B must be equal, $\epsilon_{\text{HOMO}}^{\text{A}} = \epsilon_{\text{HOMO}}^{\text{B}}$. In approximate DFT, the equalization in the dissociated molecule is attained by transferring a fractional electron charge from A to B, which is physically incorrect. In the exact DFT, the equilibration is accomplished via the elevation of a region of $v_{\text{XC}}(\mathbf{r})$ around nucleus B by a constant equal to [4, 5]

$$\epsilon_{\text{HOMO}}^{\text{A}} - \epsilon_{\text{HOMO}}^{\text{B}} = I_{\text{B}} - I_{\text{A}}. \quad (6.1)$$

In other words, the exchange-correlation potential well of the atom B with the higher

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ionization energy becomes upshifted by $I_B - I_A$ relative to the well of atom A in the separated AB system. This upshift creates a characteristic step structure of the exact $v_{\text{XC}}(\mathbf{r})$, also known as the “counterionic field”, which prevents the electron density from flowing toward the atom with the higher ionization energy. Moreover, when A and B are not bonded, the step is enhanced by a peak separating the potential wells of the two atoms [4]. In commonly used density-functional approximations for $v_{\text{XC}}(\mathbf{r})$, these features are absent, which is why one often finds that atoms in stretched molecules carry fractional charges [6].

The steps and barriers of molecular exchange-correlation potentials have been extensively studied both analytically and numerically by Baerends, Gritsenko, and co-workers [7–11] and later by other groups [12–17]. The approach of Baerends, Gritsenko and co-workers is based on an exact partitioning of $v_{\text{XC}}(\mathbf{r})$ derived from first principles [18–21],

$$v_{\text{XC}}(\mathbf{r}) = v_{\text{XC}}^{\text{hole}}(\mathbf{r}) + v_{c,\text{kin}}(\mathbf{r}) + v_{\text{resp}}(\mathbf{r}). \quad (6.2)$$

Here $v_{\text{XC}}^{\text{hole}}(\mathbf{r})$ is the exchange-correlation hole potential of the interacting system, $v_{c,\text{kin}}(\mathbf{r})$ is the kinetic correlation potential (the difference of interacting and noninteracting kinetic energies per electron), and $v_{\text{resp}}(\mathbf{r})$ is the “response potential”

$$v_{\text{resp}}(\mathbf{r}) = v^{N-1}(\mathbf{r}) - v_s^{N-1}(\mathbf{r}), \quad (6.3)$$

where $v_s^{N-1}(\mathbf{r})$ is defined in terms of the system’s Kohn–Sham orbitals and orbital energies [19], and $v^{N-1}(\mathbf{r})$ is defined in terms of wavefunction quantities [19, 21].

By examining the analytic properties of each component of $v_{\text{XC}}(\mathbf{r})$, Gritsenko and Baerends identified [8] $v_{\text{resp}}(\mathbf{r})$ as the term responsible for the localized upshift of the potential around the atom with the higher ionization energy in a molecule. They also illustrated their conclusions numerically using the following method [7–10]: (i) obtain an accurate ground-state electron density from a high-quality correlated wave function; (ii) construct the corresponding $v_{\text{XC}}(\mathbf{r})$ by fitting it to the density using an iterative local update procedure, which also gives the Kohn–Sham orbitals and orbital energies associated with $v_{\text{XC}}(\mathbf{r})$; (iii) calculate $v_{\text{XC}}^{\text{hole}}(\mathbf{r})$ and $v_{c,\text{kin}}(\mathbf{r})$ from the wavefunction and the Kohn–Sham orbitals; (iv) finally, obtain the response term as the difference

$$v_{\text{resp}}(\mathbf{r}) = v_{\text{XC}}(\mathbf{r}) - v_{\text{XC}}^{\text{hole}}(\mathbf{r}) - v_{c,\text{kin}}(\mathbf{r}). \quad (6.4)$$

This indirect path to $v_{\text{resp}}(\mathbf{r})$ has to deal with various numerical and basis-set artifacts [7, 8, 21, 22] associated with fitting exchange-correlation potentials to target electron

densities. These artifacts then show up in plots of the response potential as spurious or exaggerated wiggles, dips near the nuclei, and other distortions [7–10].

In Chapter 5, we derived a new analytic expression [Eq. (5.16)] for the wavefunction component of $v_{\text{resp}}(\mathbf{r})$ in terms of eigenfunctions of the generalized Fock operator for the interacting wavefunction of the system. This expression allows one to generate $v_{\text{resp}}(\mathbf{r})$ without fitting $v_{\text{XC}}(\mathbf{r})$ to a target density. In this chapter, we use our expression for $v_{\text{resp}}(\mathbf{r})$ to compute and plot this quantity with previously unavailable accuracy and detail. Our results provide the clearest and most direct illustration to date that the localized upshifts of $v_{\text{XC}}(\mathbf{r})$ are encoded in the wavefunction component of the response term.

6.2 Calculation of the response potential

In Ref. 23, Cuevas-Saavedra and Staroverov showed that the response potential may be obtained as

$$v_{\text{resp}}(\mathbf{r}) = \bar{\epsilon}^{\text{KS}}(\mathbf{r}) - \bar{\epsilon}^{\text{WF}}(\mathbf{r}), \quad (6.5)$$

where $\bar{\epsilon}^{\text{KS}}(\mathbf{r})$ and $\bar{\epsilon}^{\text{WF}}(\mathbf{r})$ are the Kohn–Sham average local electron energy (ALEE) and the wavefunction ALEE defined in Chapter 5 by Eqs. (5.3) and (5.16), respectively. These quantities are referred to as ALEEs because each of them may be written as the sum of a local kinetic energy per electron and an effective potential [24].

The quantities $\bar{\epsilon}^{\text{WF}}(\mathbf{r})$ and $\bar{\epsilon}^{\text{KS}}(\mathbf{r})$ are formally related to the components of Eq. (6.3) by the formulas [23]

$$v^{N-1}(\mathbf{r}) = -\bar{\epsilon}^{\text{WF}}(\mathbf{r}) - I, \quad (6.6)$$

where I is the first vertical ionization energy of the interacting system, and

$$v_s^{N-1}(\mathbf{r}) = -\bar{\epsilon}^{\text{KS}}(\mathbf{r}) + \epsilon_{\text{HOMO}}, \quad (6.7)$$

where ϵ_{HOMO} is the exact Kohn–Sham HOMO eigenvalue. These relations hold exactly for exact wavefunctions, when $\epsilon_{\text{HOMO}} = -I$.

The wavefunction part of the response term, $\bar{\epsilon}^{\text{WF}}(\mathbf{r})$, can be constructed in several different ways [23]: (i) from the Dyson orbitals and ionization energies of the system [21], (ii) as the sum of a local kinetic energy per electron and $v(\mathbf{r}) + v_{\text{H}}(\mathbf{r}) + v_{\text{XC}}^{\text{hole}}(\mathbf{r})$ [24] (which follows from the expression [19] for $v^{N-1}(\mathbf{r})$ in terms of conditional probability amplitudes), and (iii) from the eigenfunctions and eigenvalues of the generalized Fock

operator [24] by Eq. (5.16). Of these expressions, the first one is clearly impractical; the second requires at most the diagonal part of the two-electron reduced density matrix (2-RDM) but produces plots that are distorted by Gaussian basis-set artifacts (unphysical oscillations and divergences similar to those reported for the inverted Kohn–Sham equation [25, 26]); the third expression requires no more than the 2-RDM and is numerically robust. It is this last representation of $\bar{\epsilon}^{\text{WF}}(\mathbf{r})$ that we will employ in this work.

Thus, to construct $v_{\text{resp}}(\mathbf{r})$ by our method we need to evaluate its two components: $\bar{\epsilon}^{\text{KS}}(\mathbf{r})$ by Eq. (5.3) and $\bar{\epsilon}^{\text{WF}}(\mathbf{r})$ by Eq. (5.16). The component $\bar{\epsilon}^{\text{WF}}(\mathbf{r})$ involves only wavefunction quantities and can be directly computed from a 2-RDM. The component $\bar{\epsilon}^{\text{KS}}(\mathbf{r})$, however, involves the Kohn–Sham orbitals and orbital energies of the system, which are determined by $v_{\text{XC}}(\mathbf{r})$ and are initially unknown (note that construction of v_{resp} by Eq. (6.4) also required Kohn–Sham orbitals for the term $v_{c,\text{kin}}$). In Chapter 5, we showed that these unknowns can be numerically extracted from the 2-RDM through iterative solution of a nonlinear equation relating $v_{\text{XC}}(\mathbf{r})$, $\phi_i(\mathbf{r})$, and ϵ_i to certain wavefunction-based quantities. This equation has the general form of Eq. (6.2) with special representations for the kinetic correlation and response terms. Explicitly,

$$v_{\text{XC}}(\mathbf{r}) = v_{\text{XC}}^{\text{hole}}(\mathbf{r}) + \frac{\tau^{\text{WF}}(\mathbf{r})}{\rho^{\text{WF}}(\mathbf{r})} - \frac{\tau^{\text{KS}}(\mathbf{r})}{\rho^{\text{KS}}(\mathbf{r})} + \bar{\epsilon}^{\text{KS}}(\mathbf{r}) - \bar{\epsilon}^{\text{WF}}(\mathbf{r}), \quad (6.8)$$

where $v_{\text{XC}}^{\text{hole}}(\mathbf{r})$ is the same ingredient as $v_{\text{S}}^{\text{WF}}(\mathbf{r})$ of Eq. (5.15) and $\bar{\epsilon}^{\text{WF}}(\mathbf{r})$ is given specifically by Eq. (5.16). Comparing this expression to Eq. (6.2), one can write the kinetic correlation potential as

$$v_{c,\text{kin}}(\mathbf{r}) = \frac{\tau^{\text{WF}}(\mathbf{r})}{\rho^{\text{WF}}(\mathbf{r})} - \frac{\tau^{\text{KS}}(\mathbf{r})}{\rho^{\text{KS}}(\mathbf{r})}, \quad (6.9)$$

where the quantities $\tau_{\text{WF}}(\mathbf{r})$, $\tau_{\text{KS}}(\mathbf{r})$, $\rho_{\text{WF}}(\mathbf{r})$, and $\rho_{\text{KS}}(\mathbf{r})$ are defined in Sec. 5.2 of Chapter 5. We will refer to our iterative technique as RKS (Ryabinkin, Kohut, and Staroverov). A similar technique was described by Cuevas-Saavedra, Ayers, and Staroverov in Ref. 27; it differs from the RKS procedure in details of the calculation of $\bar{\epsilon}^{\text{WF}}(\mathbf{r})$, but otherwise is equivalent.

The RKS procedure involves the following steps. First, we run an *ab initio* calculation on the system of interest and compute the wavefunction ingredients $\rho^{\text{WF}}(\mathbf{r})$, $\tau^{\text{WF}}(\mathbf{r})$, $v_{\text{XC}}^{\text{hole}}(\mathbf{r})$, and $\bar{\epsilon}^{\text{WF}}(\mathbf{r})$ of Eq. (5.16) from the resulting 2-RDM. Then we generate a reasonable initial guess for $\phi_i(\mathbf{r})$ and ϵ_i using any standard density-functional approximation, substitute this guess into Eq. (6.8), solve the Kohn–Sham eigenvalue problem [Eq. (1.18)] in the same one-electron basis that was used to generate the wavefunction quantities, and repeat the cycle until the potential $v_{\text{XC}}(\mathbf{r})$ is converged. Our convergence criterion is that

the Kohn–Sham density matrices from two consecutive iterations differ by less than 10^{-10} in the root-mean-square sense. Matrix elements of all ingredients of $v_{\text{XC}}(\mathbf{r})$ are computed by standard numerical integration techniques used in density-functional methods. The Coulomb potential, $v_{\text{H}}(\mathbf{r})$, appearing in Eq. (1.19) is constructed using the current Kohn–Sham density $\rho^{\text{KS}}(\mathbf{r})$; the matrix elements of $v_{\text{H}}(\mathbf{r})$ are computed analytically in terms of integrals involving one-electron basis functions. Other details of the RKS method may be found in Sec. 5.3 of Chapter 5.

A special note should be made on the meaning of potentials obtained by the RKS method in finite basis sets. The exchange-correlation potential obtained by the RKS method for a given 2-RDM is the true $v_{\text{XC}}(\mathbf{r})$ corresponding to $\rho^{\text{WF}}(\mathbf{r})$ only when all the ingredients of Eq. (6.8) are generated and handled in a complete basis set. In a finite basis set, the RKS method produces a well-defined, smooth, oscillation-free approximation to the basis-set-limit $v_{\text{XC}}(\mathbf{r})$ at the level of that finite basis. The density $\rho^{\text{KS}}(\mathbf{r})$ arising as a byproduct of the RKS method is not exactly equal to $\rho^{\text{WF}}(\mathbf{r})$ in a finite basis set, but it tends to $\rho^{\text{WF}}(\mathbf{r})$ in the basis-set limit [27, 28]. For wavefunctions computed in large Gaussian basis sets, exchange-correlation potentials obtained by the RKS method are visually indistinguishable from the corresponding exact potentials, and $\rho^{\text{KS}}(\mathbf{r})$ is practically identical to $\rho^{\text{WF}}(\mathbf{r})$ [27–30].

6.3 Results and discussion

We chose to revisit the LiH molecule ($R_e = 1.5949 \text{ \AA}$) whose exchange-correlation potentials were studied earlier by Gritsenko *et al.* [7, 8, 20]. Although the steps and barriers of the exact $v_{\text{XC}}(\mathbf{r})$ are qualitatively reproduced by the RKS method even for relatively crude correlated wavefunctions and modest basis sets [27, 28], in this work we decided to aim for higher accuracy. To this end, we employed full configuration interaction (FCI) wavefunctions for LiH generated in the fully uncontracted version of Jensen’s pc-2 basis set, referred to as u-pc-2: (10s,4p,1d) for Li and (6s,2p,1d) for H [31, 32], with pure d functions. We uncontracted the basis set to make it sufficiently flexible in atomic core regions [27].

Figure 6.1 shows that, in agreement with previous studies [7, 8, 20], the step structure of the exact $v_{\text{XC}}(\mathbf{r})$ for a stretched LiH molecule ($R = 3R_e$) originates in the response term, and that the barrier separating the exchange-correlation potential wells for Li and H arises mostly from the kinetic-correlation contribution.

Let us now examine each of the two components of the response potential, $\bar{\epsilon}^{\text{KS}}(\mathbf{r})$ and $\bar{\epsilon}^{\text{WF}}(\mathbf{r})$. One can show [24] that, for an exact wavefunction, both $\bar{\epsilon}^{\text{KS}}(\mathbf{r})$ and $\bar{\epsilon}^{\text{WF}}(\mathbf{r})$

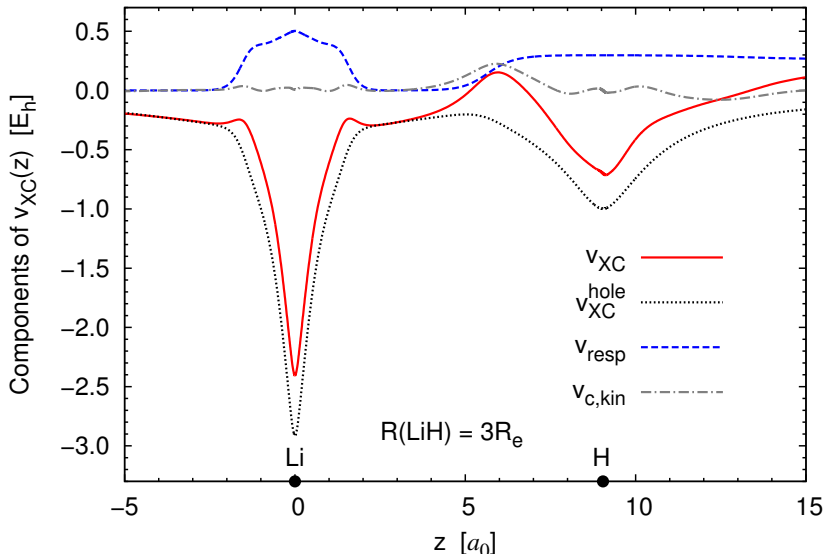


Figure 6.1: Exchange-correlation potential and its components obtained for LiH from the FCI/u-pc-2 wavefunction. The exchange-correlation potential well of the H atom is elevated by $I_{\text{H}} - I_{\text{Li}}$ relative to the well of Li.

asymptotically approach the negative of the first vertical ionization energy of the system,

$$\lim_{r \rightarrow \infty} \bar{\epsilon}^{\text{KS}}(\mathbf{r}) = \lim_{r \rightarrow \infty} \bar{\epsilon}^{\text{WF}}(\mathbf{r}) = -I. \quad (6.10)$$

Moreover, for any one-electron system, both $\bar{\epsilon}^{\text{KS}}(\mathbf{r})$ and $\bar{\epsilon}^{\text{WF}}(\mathbf{r})$ are constants everywhere.

For an approximate wavefunction, $\bar{\epsilon}^{\text{KS}}(\mathbf{r})$ approaches ϵ_{HOMO} , whereas $\bar{\epsilon}^{\text{WF}}(\mathbf{r})$ approaches [27] the negative of the first vertical ionization energy computed by the extended Koopmans theorem [33–40] (EKT), $-I^{\text{EKT}}$. The EKT ionization potentials computed from the FCI/u-pc-2 wavefunction are very good approximations to the exact I_{H} and I_{Li} values (Table 6.1).

Because $I_{\text{Li}} < I_{\text{H}}$, the first ionization energy of the separated LiH is $I_{\text{LiH}} = I_{\text{Li}}$. Therefore, both the Kohn–Sham and wavefunction ALEEs in separated LiH must approach

Table 6.1: Ionization energies of the isolated Li and H atoms computed by the EKT from the FCI/u-pc-2 wavefunction and the corresponding exact values from Ref. 41.

Atom	I, E_{h}	
	EKT	Exact
H	0.4999	0.5000
Li	0.1979	0.1981

$-I_{\text{Li}}$ in every direction. That is precisely what $\bar{\epsilon}^{\text{KS}}(\mathbf{r})$ does in the HOMO-dominated regions $\Omega_{\text{HOMO}}^{\text{LiH}}$ of a stretched LiH molecule (Fig. 6.2),

$$\bar{\epsilon}^{\text{KS}}(\mathbf{r} \in \Omega_{\text{HOMO}}^{\text{LiH}}) = -I_{\text{Li}}. \quad (6.11)$$

The wavefunction ALEE behaves quite differently (Fig. 6.2): it agrees with $\bar{\epsilon}^{\text{KS}}(\mathbf{r})$ in the region dominated by the HOMO of the Li atom,

$$\bar{\epsilon}^{\text{WF}}(\mathbf{r} \in \Omega_{\text{HOMO}}^{\text{Li}}) = -I_{\text{Li}}, \quad (6.12)$$

but dips to $-I_{\text{H}}$ in the region dominated by the HOMO of the H atom,

$$\bar{\epsilon}^{\text{WF}}(\mathbf{r} \in \Omega_{\text{HOMO}}^{\text{H}}) = -I_{\text{H}}, \quad (6.13)$$

before returning to the $-I_{\text{Li}}$ asymptote (not shown). This occurs because the Li and H atoms in a stretched LiH molecule are almost isolated, so physically the ALEE should be $-I_{\text{Li}}$ and $-I_{\text{H}}$ in the HOMO-dominated regions of the Li and H atoms, respectively. Around the H atom, the difference between $\bar{\epsilon}^{\text{KS}}(\mathbf{r})$ and $\bar{\epsilon}^{\text{WF}}(\mathbf{r})$ attains a constant value of $(I_{\text{H}} - I_{\text{Li}})$, which is precisely the height of the step exhibited by $v_{\text{resp}}(\mathbf{r})$. Thus, the localized upshift of the exact $v_{\text{XC}}(\mathbf{r})$ in a stretched diatomic is due to the step behavior of the quantity $\bar{\epsilon}^{\text{WF}}(\mathbf{r})$ which assumes values equal to the negative ionization energies

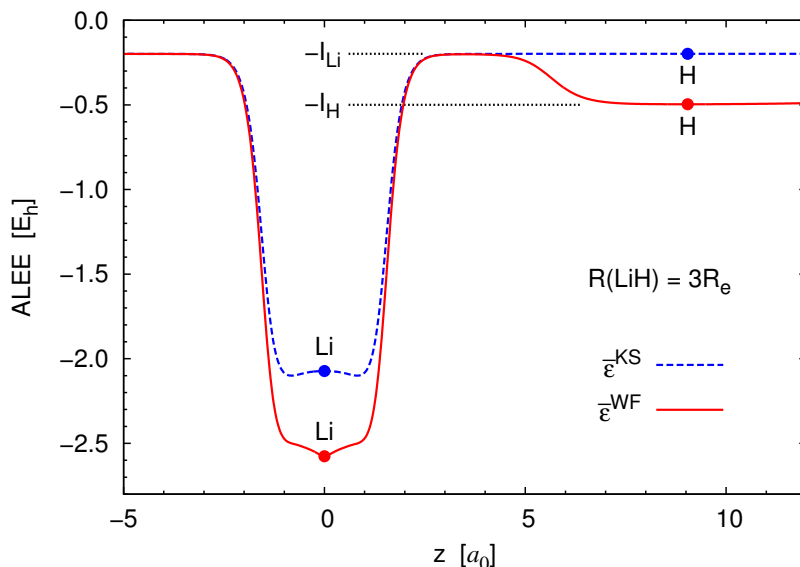


Figure 6.2: The Kohn–Sham ALEE of Eq. (5.3) and wavefunction ALEE of Eq. (5.16) obtained from the FCI/u-pc-2 wavefunction for a stretched LiH molecule. I_{Li} and I_{H} are the EKT ionization energies from Table 6.1.

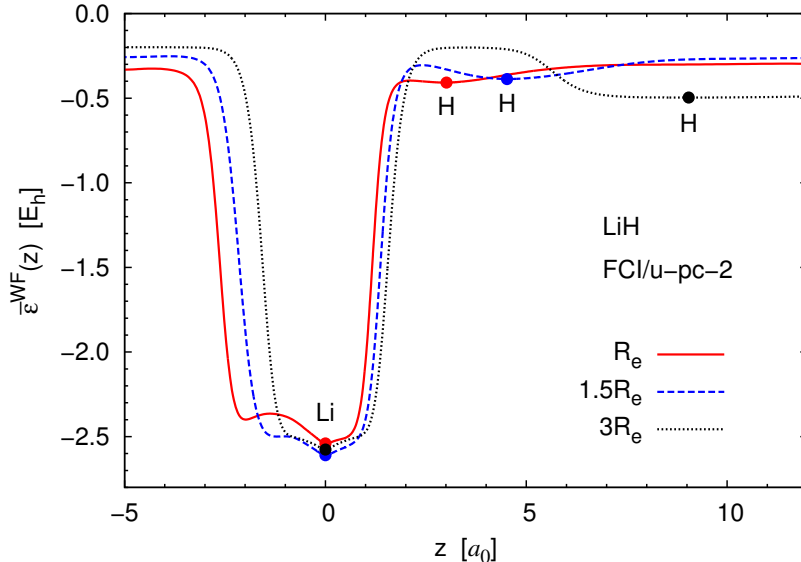


Figure 6.3: The wavefunction ALEE computed by Eq. (5.16) from the FCI/u-pc-2 wavefunction of LiH for various internuclear distances.

of the constituent atoms in the HOMO-dominated regions of these atoms. A parallel theoretical explanation of the step in terms of quantities $v^{N-1}(\mathbf{r})$ and $v_s^{N-1}(\mathbf{r})$ may be found in Ref. 8.

The step structure of $\bar{\epsilon}^{\text{WF}}(\mathbf{r})$ is not developed at short internuclear distances when the two atoms strongly overlap, but becomes more and more pronounced with increasing bond length, tending to a well-defined step when the atoms are completely separated (Fig. 6.3).

The step structure of $\bar{\epsilon}^{\text{WF}}(\mathbf{r})$ is a manifestation of long-range correlation effects, so it would be absent in the Hartree–Fock (HF) theory. This is illustrated with plots of $\bar{\epsilon}^{\text{WF}}(\mathbf{r})$ obtained from the HF/u-pc-2 wavefunctions of LiH (Fig. 6.4). Similar to the Kohn–Sham ALEE, the HF ALEE exhibits no steps at any internuclear distance.

Finally, Fig. 6.5 shows the entire response term as a function of internuclear distance in the dissociating LiH molecule. Observe that the response potentials in Fig. 6.5 do not have any wiggles or dips commonly seen when the Kohn–Sham potentials are fitted to Gaussian-basis electron densities.[22] This is because our expression for $v_{\text{resp}}(\mathbf{r})$ is a difference of two well-behaved terms given by Eqs. (5.3) and (5.16), neither of which oscillates or diverges even when the orbitals $\phi_i(\mathbf{r})$ and $f_j(\mathbf{r})$ are represented in terms of Gaussian basis functions.

It is also instructive to verify that the atomic charges on Li and H in a separated LiH are actually zero when the density of the system is generated by a Kohn–Sham potential with a proper step structure. To this end, we computed $\rho^{\text{KS}}(\mathbf{r})$ corresponding

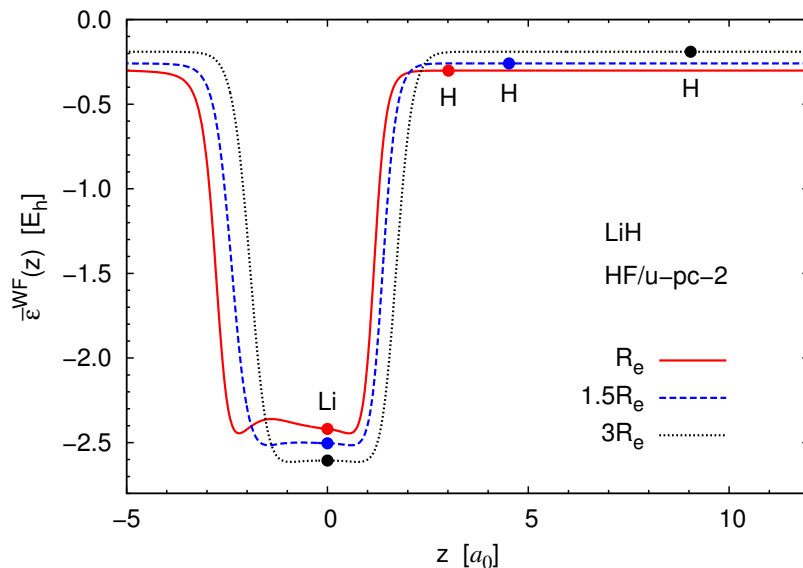


Figure 6.4: The wavefunction ALEE computed by Eq. (5.16) from the HF/u-pc-2 wavefunction of LiH for various internuclear distances.

to various exchange-correlation potentials of dissociating LiH and then extracted the atomic charges on Li and H by fitting them to reproduce the dipole moment of the molecule. Calculations using the exchange-correlation potentials generated from FCI/u-pc-2 wavefunctions correctly predict that the atomic charges on Li and H tend to zero with increasing bond length (Table 6.2). This is to be contrasted with large spurious

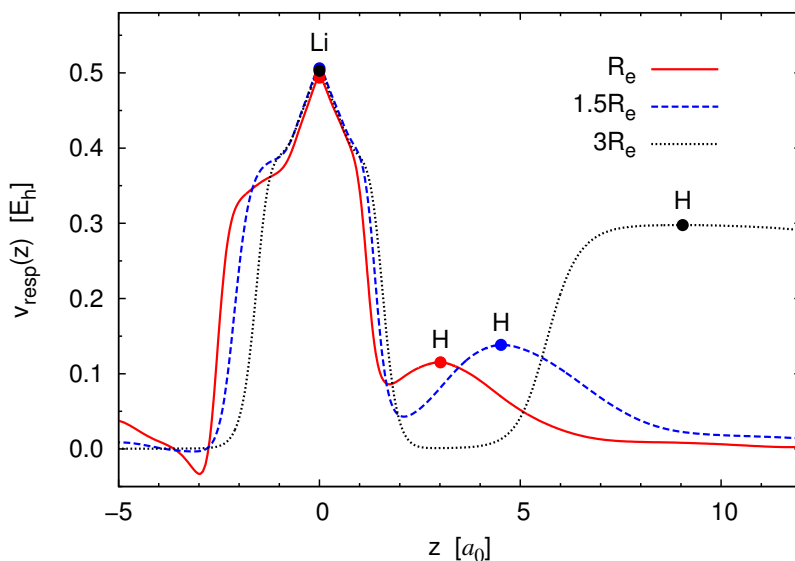


Figure 6.5: The response potential constructed by Eq. (6.5) from the FCI/u-pc-2 wavefunction of LiH for various internuclear distances.

Table 6.2: Atomic charges in LiH for various internuclear distances (R) obtained from the exchange-correlation potentials generated by the RKS method using the FCI and HF wavefunctions in the u-pc-2 basis set. BLYP and B3LYP charges computed with the same basis set are included for comparison. All calculations are spin-restricted.

R/R_e	Atomic charges $q_{\text{Li}} = -q_{\text{H}}$, a.u.			
	FCI ^a	HF ^a	BLYP	B3LYP
1.0	0.754	0.782	0.722	0.741
1.5	0.620	0.710	0.591	0.629
2.0	0.388	0.695	0.496	0.550
2.5	0.109	0.677	0.422	0.479
3.0	0.020	0.646	0.373	0.426
3.5	0.005	0.613	0.343	0.390
∞	0.000	0.432	0.234	0.263

^a Direct calculations from wavefunction-based densities give nearly the same values.

charges obtained from the exchange-correlation potentials corresponding to the HF/u-pc-2 wavefunction or from standard density-functional approximations.

Although we focused on a small molecule (LiH) described at the FCI level, similar results are obtained for any heteronuclear diatomic using any approximate wavefunction that includes static correlation effects. Consider, for instance, $\bar{\epsilon}^{\text{WF}}(\mathbf{r})$ computed for the NaCl molecule from the 8-electron, 8-orbital complete active space self-consistent field (CASSCF) wavefunction in the 6-31G* basis set (Fig. 6.6). Even at this modest level of theory, the correlated-wavefunction ALEE has a fully developed step structure at $3R_e$ ($R_e = 2.3609 \text{ \AA}$), complete with tell-tale step between the Na and Cl atoms.

We have also observed that it is particularly easy to see the step structure of $\bar{\epsilon}^{\text{WF}}(\mathbf{r})$ for a stretched molecule when the correlated wavefunction is computed in a very compact basis set such as STO-3G. This is because the HOMO-dominated region of the atom with the higher ionization energy described with a compact basis set is more localized and has better-defined boundaries than when the same atom is described with a high-quality basis.

6.4 Conclusion

The exact exchange-correlation potential of a dissociating heteronuclear diatomic molecule AB builds up a counterionic field that prevents the formation of spurious fractional

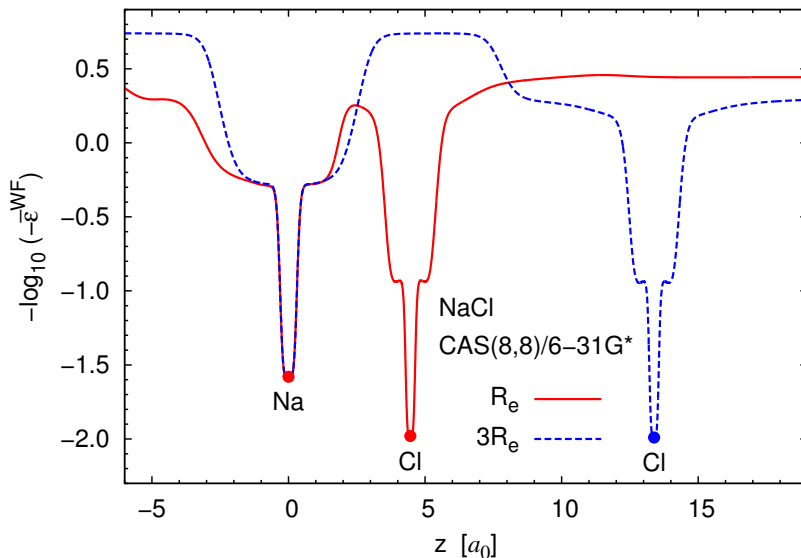


Figure 6.6: The wavefunction ALEE computed by Eq. (5.16) from the (8,8)CASSCF/6-31G* wavefunction of NaCl at R_e and $3R_e$. Note the logarithmic scale on the vertical axis.

charges on the separated atoms. Gritsenko and Baerends [8] traced the origin of this field to the response term of $v_{XC}(\mathbf{r})$ by showing that the two components of $v_{\text{resp}}(\mathbf{r})$ assume different constant values (related to the ionization energies of the isolated atoms) in the HOMO-dominated regions of the atoms in a stretched molecule. In this work, we illustrated this mechanism in detail by computing the two components of $v_{\text{resp}}(\mathbf{r})$ and displaying their behavior as functions of internuclear distance. Our analysis most directly demonstrates that the step structure of $v_{XC}(\mathbf{r})$ is linked to the step-like drop of $\bar{\epsilon}^{\text{WF}}(\mathbf{r})$, the wavefunction component of $v_{\text{resp}}(\mathbf{r})$, in the HOMO-dominated region of the atom with the higher ionization energy.

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Chapter 7

Step structure in molecular exchange-correlation potentials obtained from restricted Hartree–Fock wavefunctions

7.1 Introduction

The step structure is a feature of the exact exchange-correlation potential of Kohn–Sham (KS) density-functional theory (DFT). This feature manifests itself in stretched heteronuclear diatomic molecules as a localized upshift of the potential well of the atom with the higher ionization energy. Steps of the exchange-correlation potential, v_{XC} , and their implications have been extensively studied by several groups [1–10]. The role of the step structure is to ensure that molecules properly dissociate into neutral atoms. Because standard semilocal density-functional approximations fail to reproduce the step structure of the exact v_{XC} , unphysical fractional charges are often observed on molecular fragments at separation [3, 11–14]. In particular, Ruzsinszky and coworkers [13] showed that, in the spin-unrestricted local density approximation for exchange, fractional-charge dissociation occurs in 174 out of all possible 276 distinct pairs XY ($X \neq Y$) obtained by combining the first 24 open sp -shell atoms. Perdew, Ruzsinszky, and coworkers [13] also established a simple test that allows one to predict fractional dissociation in diatomics by comparing orbital energies of isolated atomic fragments. The problem of fractional charges is also known in the literature as the density delocalization error [15] of semilocal functionals.

In Chapter 6, we applied the RKS method presented in Chapter 5 to study the origin of the step structure of the exact v_{XC} . Our numerical examples were based on nearly exact exchange-correlation potentials generated from full configuration interaction (FCI) wavefunctions of LiH. Here, we show that the step structure also arises in approximate exchange-correlation potentials obtained from restricted Hartree–Fock (RHF) wavefunctions of some stretched heteronuclear diatomic molecules, such as CO, and illustrate the relation between the step structure and the density delocalization error. These potentials have another unanticipated feature—exaggerated bumps in v_{XC} near one of the atoms, which will be referred to as *horns* in the following discussion. We demonstrate that these horns can be explained by analyzing the difference between the RHF and KS densities.

7.2 Molecular dissociation in the restricted Hartree–Fock description

Perdew, Ruzsinszky, and coworkers [13] analyzed the role of atomic orbital energies in the dissociation of heteronuclear diatomic molecules. Let us recapitulate their results. Consider a pair of separated atomic fragments X and Y ($X \neq Y$) in one-determinantal description. Let q' be any non-negative fractional charge ($0 \leq q' < 1$) on X. Next, suppose that a fraction of electron $\delta q > 0$ is transferred from $X^{+q'}$ to $Y^{-q'}$. The charge transfer raises the energy of the system if

$$\epsilon^{\text{LU}}(Y^{-q'}) > \epsilon^{\text{HO}}(X^{+q'}), \quad (7.1)$$

where $\epsilon^{\text{LU}}(Y^{-q'})$ is the lowest-unoccupied molecular orbital (LUMO) of $Y^{-q'}$ and $\epsilon^{\text{HO}}(X^{+q'})$ is the highest-occupied molecular orbital (HOMO) of $X^{+q'}$. If the condition of Eq. (7.1) is not satisfied, the charge transfer is energetically favorable and will continue until the eigenvalues on both sides of Eq. (7.1) equalize at some charge $q' = q$. Perdew and coworkers used Eq. (7.1) in the context of KS DFT, but the same equation is applicable to the Hartree–Fock theory. This is because Eq. (7.1) was derived using Janak’s theorem [16], which is valid for any one-determinantal method.

Orbital energies of neutral atoms ($q' = 0$) within the unrestricted Hartree–Fock theory (UHF) generally satisfy the above condition. This is why fractional charges on separated atoms are generally *not* observed [3, 12, 13, 17] in the UHF method. On the other hand, the condition of Eq. (7.1) is usually violated [3, 11–14] in restricted and unrestricted calculations with semilocal density-functional approximations (DFAs). One can show that the fractional-charge dissociation problem is intrinsically linked to the many-electron

Table 7.1: RHF/cc-pcVTZ NPA atomic charges (q) in stretched heteronuclear diatomic molecules XY made up of atoms X and Y possessing an *even* number of electrons each and orbital energy differences of these atoms in the singlet state at the same theory level. All values are in atomic units.

XY	R_e^c	$q(X)^d$	$\epsilon^{\text{LU}}(^1\text{Y}^0) - \epsilon^{\text{HO}}(^1\text{X}^0)$
BeO	2.515	0.000	+0.3032
BeS	3.291	0.000	+0.2405
CO	2.132	0.000	+0.3497
CS	2.904	0.000	+0.2870
SiO	2.853	0.000	+0.2365
CaO	3.443	0.000	+0.1895
CaS	4.380	0.000	+0.1268
MgO	3.305	0.000	+0.2470
MgS	4.050	0.000	+0.1843

^a Natural population analysis of Reed and coworkers [24].

^b All the molecules are stretched to $5R_e$.

^c From Ref. [25], three decimal places are retained.

^d X is the less electronegative atom.

self-interaction error [13, 18]. A functional is said to be many-electron self-interaction free if it is able to describe the piecewise linear behavior [19, 20] of the exact energy functional as a function of the number of electrons. Semilocal density functionals cannot realistically reproduce this linear variation of the total energy with respect to the number of electrons. Not only does this lead to spurious fractional charges in stretched molecules, but also to incorrectly shaped potential energy surfaces [17, 21] and unbound anions [22, 23].

Equation (7.1) can also be used to rationalize molecular dissociation in the *restricted* Hartree–Fock (RHF) description. We computed RHF atomic charges for eighteen common heteronuclear diatomic molecules. Table 7.1 demonstrates that the RHF method properly dissociates nine of them into neutral atoms. For BeO and CO, this has been pointed out earlier by Yoshimine [26] and Green [27], respectively. Importantly, these nine molecules share one characteristic: they consist of atoms with an *even* number of electrons.

Recall that the RHF theory can only be applied to closed-shell systems because it constraints all spatial orbitals to be doubly occupied. Thus, one can obtain physically correct RHF atomic charges in a stretched heteronuclear diatomic molecule if separated atoms in such a molecule can be represented as closed-shell singlets. This is clearly

Table 7.2: Same as in Table 7.1 but for molecules XY consisting of atoms X and Y with an *odd* number of electrons. Orbital energy differences are now calculated for the *singlet ions* ${}^1X^+$ and ${}^1Y^-$.

XY	R_e	$q(X)$	$\epsilon^{\text{LU}}({}^1Y^-) - \epsilon^{\text{HO}}({}^1X^+)$
LiF	2.955	0.992	-0.0659
BH	2.329	0.381	-0.2719
BN	2.421	0.465	-0.2583
BF	2.386	0.809	-0.1453
HCl	2.409	0.229	-0.3675 ^a
NF	2.489	0.376	-0.3146
NaCl	4.461	0.979	-0.0496
AlH	3.115	0.528	-0.1908
AlCl	4.025	0.948	-0.0623

$${}^a \epsilon^{\text{LU}}(\text{H}^+) = \epsilon^{\text{HO}}(\text{H}^0).$$

possible for molecules that include atoms with an even number of electrons. Additionally, the condition of Eq. (7.1) evaluated for singlet atoms is satisfied for all the molecules XY of Table 7.1, which means that a fraction of charge transferred from X to Y does not lower the energy of the system. These two reasons explain zero charges of Table 7.1.

By contrast, the remaining nine molecules dissociate into fractionally charged atoms (Table 7.2). These molecules consist of atoms with an *odd* number of electrons. Owing to the requirement that all spatial orbitals must be doubly occupied, the RHF theory cannot separate such molecules into neutral atoms but will instead produce a pair of singlet ions. The energy of this ionic system can be further lowered via charge transfer, which is why one observes spurious fractional charges in Table 7.2. This is predicted by Eq. (7.1) when it is applied to the HOMO and LUMO orbital energies of singlet ions. (The corresponding eigenvalue differences are negative for all the molecules of Table 7.2). The observation that the RHF theory dissociates some heteronuclear diatomic molecules to fractionally charged species instead of singly charged ions was first made by King and Stanton [28] in 1969.

The extent of the charge transfer is proportional to the orbital energy difference: the higher the difference, the more electron charge is needed to equalize the orbital energies. This is illustrated in Fig. 7.1. For example, the atomic charges in stretched NaCl ($q_{\text{Na}} = 0.979$ a.u.) are very close to a purely ionic bond. This is a consequence of the very low HOMO-LUMO energy difference of the corresponding ions—very small amount of electron charge transferred from Cl^- to Na^+ is sufficient to close the gap.

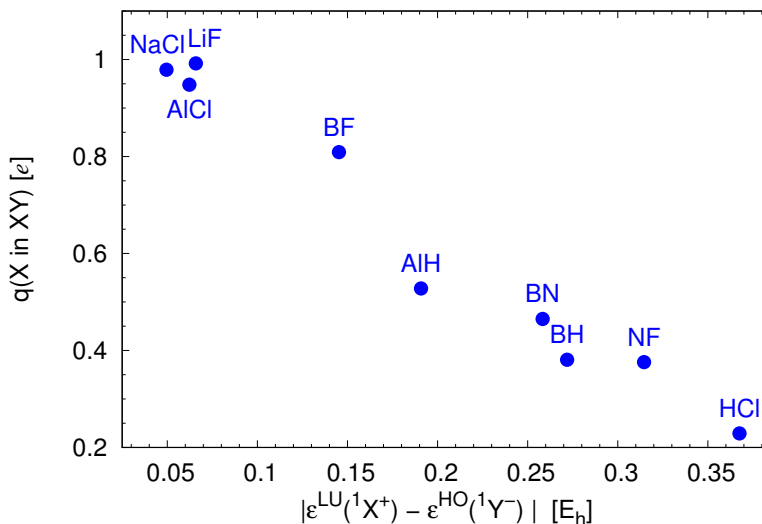


Figure 7.1: Atomic charges of Table 7.2 plotted against the corresponding orbital energy differences.

To summarize, we have seen that, in the RHF picture, two dissociation scenarios are observed for a representative set of heteronuclear diatomic molecules. The dissociation outcome depends on the composition of their constituent atoms. For diatomics that are composed of atoms with an odd number of electrons, one obtains spurious fractional atomic charges. For diatomics that include atoms with an even number of electrons, neutral atoms are predicted. Our next step is to analyze the shape of exchange-correlation potentials generated from molecular RHF wavefunctions corresponding to each of these scenarios.

7.3 Observations

We generated exchange-correlation potentials for two isoelectronic molecules, CO and BF. While the RHF theory predicts neutral atoms in the dissociation limit for CO, unphysical fractional charges are found in stretched BF. We used a modification [29] of the RKS algorithm of Chapter 5 to fold molecular RHF wavefunctions into exchange-correlation potentials. This modified version (referred to as mRKS later) uses a special representation for the kinetic term and is otherwise identical to the original RKS procedure [Eq. (5.17)]. Other relevant computational details are given in Sec. 7.7.

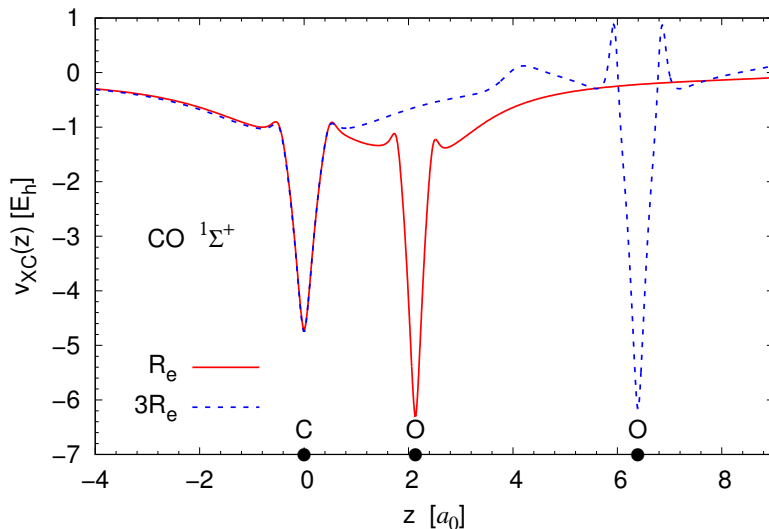


Figure 7.2: Exchange-correlation potentials obtained from the RHF/cc-pCVTZ wavefunction of CO at the experimental equilibrium geometry and at $3R_e$. The exchange-correlation potential becomes upshifted and develops exaggerated bumps around the O atom when the internuclear distance is increased.

The mRKS equation [Eq. (7.6)] has the same form as a v_{XC} partitioning equation of Baerends, Gritsenko, and coworkers [30–33]. For convenience, we rewrite v_{XC}^{mRKS} in this form and adhere to the terminology of Baerends and coworkers,

$$v_{XC}^{\text{mRKS}}(\mathbf{r}) = v_{XC}^{\text{hole}}(\mathbf{r}) + v_{\text{resp}}(\mathbf{r}) + v_{c,\text{kin}}(\mathbf{r}). \quad (7.2)$$

Here,

$$v_{\text{resp}}(\mathbf{r}) = \bar{\epsilon}^{\text{KS}}(\mathbf{r}) - \bar{\epsilon}^{\text{WF}}(\mathbf{r}) \quad (7.3)$$

is the response potential and

$$v_{c,\text{kin}}(\mathbf{r}) = \frac{\tau_P^{\text{WF}}(\mathbf{r})}{\rho^{\text{WF}}(\mathbf{r})} - \frac{\tau_P^{\text{KS}}(\mathbf{r})}{\rho^{\text{KS}}(\mathbf{r})} \quad (7.4)$$

is the kinetic correlation potential. The quantity v_{XC}^{hole} and the components of v_{resp} and $v_{c,\text{kin}}$ are defined in Sec. 7.7.

Figure 7.2 shows that the exchange-correlation potential generated from the RHF/cc-pCVTZ wavefunction of a CO molecule ($R_e = 2.132a_0$) develops a localized upshift (step) around the O atom upon the increase of the internuclear distance. The step is emphasized by a peak near the bond midpoint and accompanied by pronounced exaggerated bumps (horns) near the O atom. These horns arise due to the kinetic correlation potential.

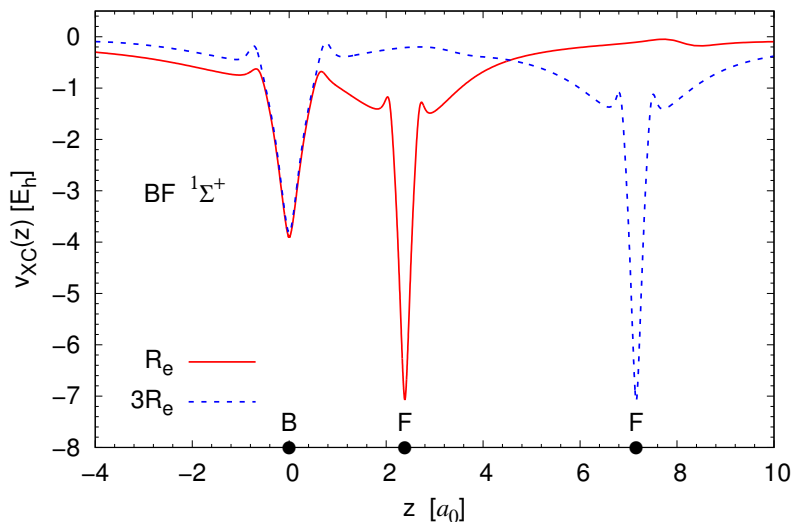


Figure 7.3: Same as in Fig. 7.2 but for BF. No peculiar steps, peaks, or bumps are present in the v_{XC} of a stretched BF molecule.

We have verified numerically that the steps and horns appear in other basis sets and therefore do not represent basis-set artifacts. Moreover, these features are also seen in other molecules of Table 7.1, such as BeO and SiO (not shown).

In striking contrast with Fig. 7.2 is Fig. 7.3 that shows the exchange-correlation potential generated from the same wavefunction but for a stretched BF molecule ($R_e = 2.386a_0$). As one can see, no peculiar steps, peaks, or bumps are present in the v_{XC} of BF. Thus, the exchange-correlation potentials of stretched CO and BF are qualitatively different despite the apparent similarity between the molecules.

7.4 Decomposition of the exchange-correlation potential and explanation of the steps

Figures 7.4 and 7.5 compare individual components [Eq. (7.2)] of the mRKS exchange-correlation potential for stretched CO and BF molecules, respectively. These components include: (i) the exchange-correlation hole potential, (ii) the response potential, and (iii) the kinetic correlation potential.

In Chapter 6, we demonstrated that the step structure originates from the step behavior of the response potential. Figure 7.4 confirms that this is the case for stretched CO whose v_{resp} develops a step near the O atom. On the other hand, the response potential of stretched BF is not elevated in the vicinity of the F atom (Fig. 7.5).

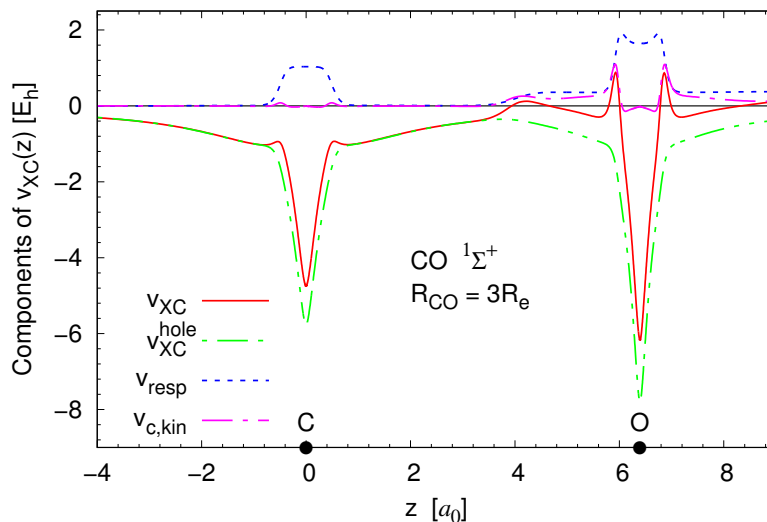


Figure 7.4: Exchange-correlation potential and its components obtained from the RHF/cc-pCVTZ wavefunction of a stretched CO molecule. The solid black line $v_{XC}(z) = 0$ is displayed to emphasize the step in v_{resp} .

Let us take a closer look at the role played by the step structure in the dissociation of CO. Recall that the condition of Eq. (7.1) is satisfied by the RHF frontier eigenvalues of the singlet C and O atoms because the RHF theory predicts zero atomic charges in stretched CO. For the same reason, this condition must also be satisfied by the mRKS frontier eigenvalues in the KS description. However, we have observed that the mRKS HOMO and LUMO energies of *isolated* singlet C and O atoms violate the condition of Eq. (7.1). The mRKS potential of stretched CO remedies this situation by developing a step structure that elevates the potential well of O and, in effect, changes the LUMO so that Eq. (7.1) is satisfied. Because for isolated C and O $\epsilon_{\text{mRKS}}^{\text{HO}}(^1\text{C}) = \epsilon_{\text{mRKS}}^{\text{LU}}(^1\text{C})$ and $\epsilon_{\text{mRKS}}^{\text{HO}}(^1\text{O}) = \epsilon_{\text{mRKS}}^{\text{LU}}(^1\text{O})$, orbital energies of O in a stretched CO molecule must be upshifted by $\epsilon_{\text{mRKS}}^{\text{HO}}(^1\text{C}) - \epsilon_{\text{mRKS}}^{\text{HO}}(^1\text{O})$ to “undo” the relation $\epsilon_{\text{mRKS}}^{\text{HO}}(^1\text{C}) > \epsilon_{\text{mRKS}}^{\text{LU}}(^1\text{O})$ that would otherwise cause the fractional-charge dissociation. Such a mechanism is not needed for BF since Eq. (7.1) is violated both for the RHF and mRKS atomic orbital energies in this case.

The step structure of v_{resp} of CO is also developed when this quantity is computed from correlated wavefunctions. This is illustrated in Fig. 7.6 in which we compare v_{resp} for the RHF and the full-valence CASSCF wavefunction of a CO molecule at $3R_e$. Both wavefunctions correctly predict neutral atoms in the dissociation limit of CO. Thus, the step structure can arise at any level of theory free from the density delocalization error and cannot be attributed to electron correlation effects.

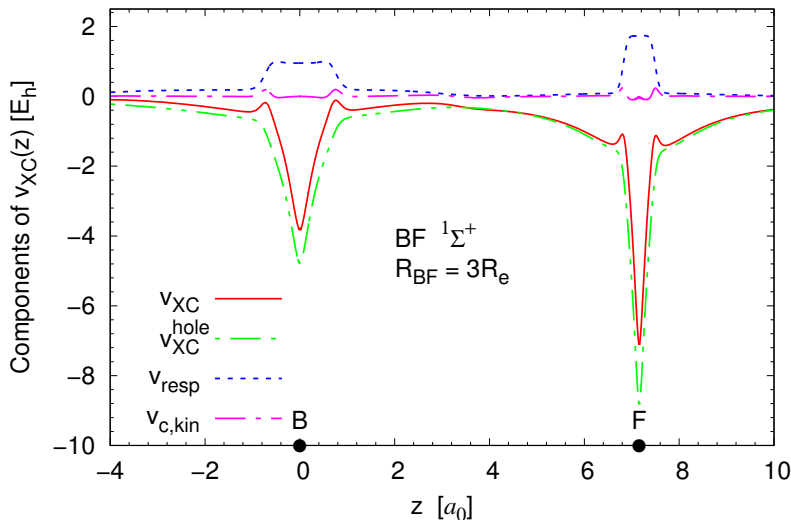


Figure 7.5: Same as in Fig. 7.4 but for BF.

7.5 Analysis of the densities and explanation of the horns

We now turn to the analysis of the horns in the v_{XC} generated from the RHF wavefunction of a stretched CO molecule (Fig. 7.1). Because the exchange-correlation potential is determined by the electron density, our approach here is to compare the RHF density of CO and BF to densities predicted by typical DFAs. Specifically, we will look at the density obtained in the spin-restricted fashion (R) using the Becke-Lee-Yang-Parr (BLYP) functional [34, 35] for exchange and correlation.

To this end, we computed and analyzed density difference profiles for CO and BF (Figs. 7.7 and 7.8). This quantity is defined as

$$\delta\rho(\mathbf{r}) = \rho_{\text{RBLYP}}(\mathbf{r}) - \rho_{\text{RHF}}(\mathbf{r}). \quad (7.5)$$

Recall that the RHF theory predicts zero atomic charges in stretched CO. Unlike the RHF method, the RBLYP approximation dissociates a CO molecule into fractionally charged C cation and O anion. As a consequence, the RBLYP density has a greater magnitude and is more diffuse around the O atomic site. This is reflected by peaks around the O atom in Fig. 7.7. In order to reproduce the shape of the RHF electron density of stretched CO, the corresponding exchange-potential potential develops pronounced positive regions (horns) to push the KS density away from the O atom. This device is not needed for a BF molecule because its RHF and RBLYP densities qualitatively agree at any internuclear

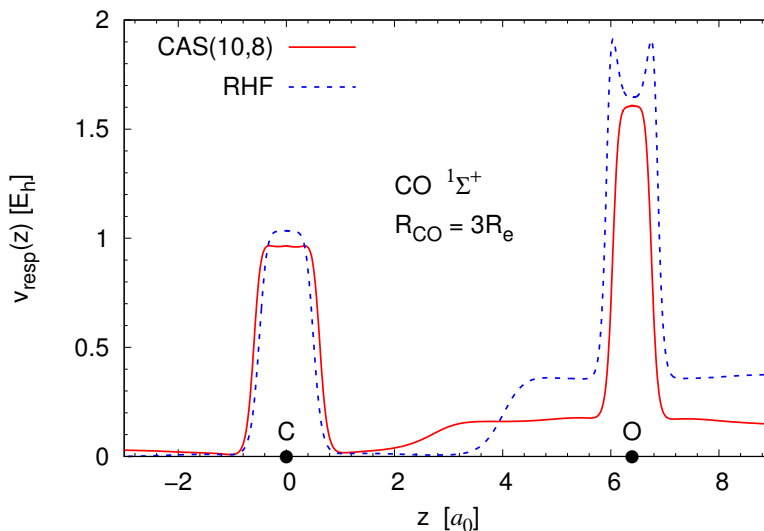


Figure 7.6: Response potentials [Eq. (7.3)] obtained from the RHF and the full-valence CASSCF wavefunction of a stretched CO molecule using the cc-pCVTZ basis set. Both quantities have a step around the O atom.

separation (Fig. 7.8). As a general remark, HF electron densities are often more accurate than their self-consistent KS analogues. The quality of approximate density functionals can be improved by evaluating DFA energies using HF densities, a method known as density-corrected DFT. This method yields accurate potential energy surfaces [17, 21, 36] and electron affinities [23].

7.6 Conclusion

The exact exchange-correlation potential of a stretched heteronuclear diatomic molecule displays a localized upshift in the domain of the atom with the higher ionization energy. The purpose of this upshift and the resulting characteristic step structure is to suppress formation of unphysical fractional charges on separated atoms. We have showed that, for certain molecules such as CO, the RHF method correctly predicts dissociation into neutral atoms and that, in such cases, the corresponding KS effective potential has a qualitatively correct step structure and exaggerated bumps (horns) in atomic core regions of a stretched molecule. We have analyzed both features and explained their origin. Our results suggest that the step structure of a KS potential is not an electron correlation effect and that it can arise at any level of theory capable of describing the system without a density delocalization error.

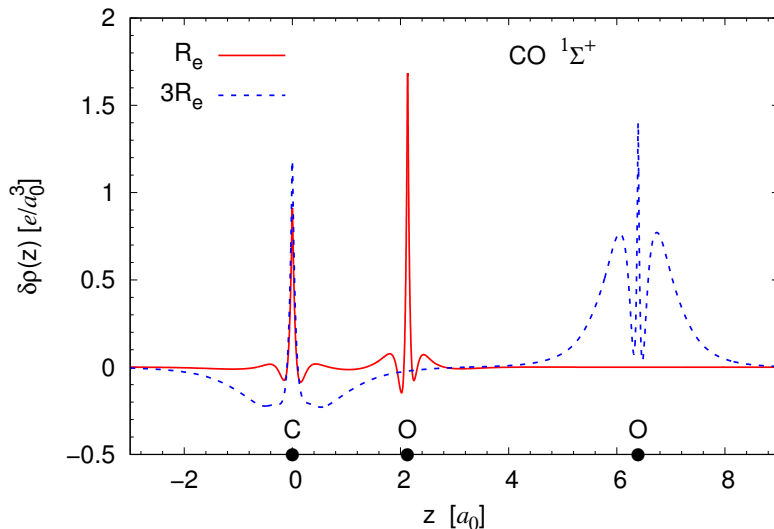


Figure 7.7: Density difference profiles [Eq. (7.5)] for CO at the experimental equilibrium geometry and at $3R_e$. The cc-pCVTZ basis set was used to generate the profiles.

Spurious fractional charges are often avoided by means of DFAs that use the exact exchange as an ingredient, for example, global hybrid functionals such as the hybrid Perdew–Burke–Ernzerhof (PBE0) functional [37] and range-separated hybrid functionals such as the long-range corrected PBE (LC- ω PBE) [38, 39]. The findings of the present work suggest that functional derivatives of these approximate density-functionals may also exhibit the step structure. This in turn raises the question about the effect of the fraction of the exact exchange on the height and position of the step in the exchange-correlation potential. We plan to address this question in our future work.

7.7 Computational details

The mRKS method is based on the following equation:

$$v_{\text{XC}}^{\text{mRKS}}(\mathbf{r}) = v_{\text{XC}}^{\text{hole}}(\mathbf{r}) + \bar{\epsilon}^{\text{KS}}(\mathbf{r}) - \bar{\epsilon}^{\text{WF}}(\mathbf{r}) + \frac{\tau_P^{\text{WF}}(\mathbf{r})}{\rho^{\text{WF}}(\mathbf{r})} - \frac{\tau_P^{\text{KS}}(\mathbf{r})}{\rho^{\text{KS}}(\mathbf{r})}, \quad (7.6)$$

where $v_{\text{XC}}^{\text{hole}}(\mathbf{r})$ is the exchange-correlation hole potential defined in Chapter 5 under the name “the Slater exchange-correlation potential” [Eq. (5.15)], $\bar{\epsilon}^{\text{KS}}(\mathbf{r})$ is the KS average local electron energy given by Eq. (5.3), $\bar{\epsilon}^{\text{WF}}(\mathbf{r})$ is the wavefunction (WF) ALEE of Eq. (5.16), $\rho^{\text{KS}}(\mathbf{r})$ is the KS electron density, and $\rho^{\text{WF}}(\mathbf{r})$ is its wavefunction counterpart. The remaining quantities, $\tau_P^{\text{KS}}(\mathbf{r})$ and $\tau_P^{\text{WF}}(\mathbf{r})$, were termed the Pauli kinetic energy densities in Ref. 29. These quantities are related [29] to the positive-definite kinetic energy

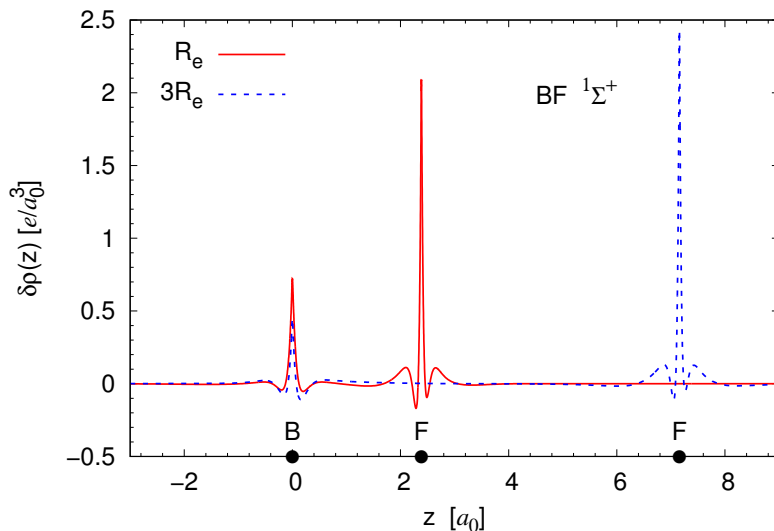


Figure 7.8: Same as in Fig. 7.7 but for BF.

densities $\tau^{\text{KS}}(\mathbf{r})$ and $\tau^{\text{WF}}(\mathbf{r})$ used in the original RKS equation [Eq. (5.17)]:

$$\tau_P^{\text{KS}}(\mathbf{r}) = \tau^{\text{KS}}(\mathbf{r}) - \tau_W^{\text{KS}}(\mathbf{r}) \quad (7.7)$$

and

$$\tau_P^{\text{WF}}(\mathbf{r}) = \tau^{\text{WF}}(\mathbf{r}) - \tau_W^{\text{WF}}(\mathbf{r}), \quad (7.8)$$

where $\tau_W^{\text{KS}} = |\nabla\rho^{\text{KS}}|^2/8\rho^{\text{KS}}$ and $\tau_W^{\text{WF}} = |\nabla\rho^{\text{WF}}|^2/8\rho^{\text{WF}}$ are the respective von Weizsäcker kinetic energy densities. We used the cc-pCVTZ basis set of Dunning and coworkers [40] for both parts of the mRKS algorithm: (i) to compute molecular RHF wavefunctions and (ii) to solve the KS equations with the v_{XC} of Eq. (7.6). All calculations were spin-restricted.

We stress that our Eq. (7.6) is not identical to the partitioning equation of Baerends' group because we construct the v_{resp} and $v_{\text{c,kin}}$ terms differently. Another important point is that the mRKS approach is not designed for solving the KS inversion problem, that is, matching ρ^{KS} to ρ^{WF} . The converged mRKS potential reproduces a given ρ^{WF} only in a complete basis set. In finite-basis-set calculations, ρ^{KS} and ρ^{WF} are very close but not equal. See Ref. [29] for a comprehensive discussion on the meaning of mRKS potentials calculated in finite basis sets.

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Chapter 8

Summary and outlook

“Were I to await perfection, my book
would never be finished.”

— TAI T’UNG, taken from GAUSSIAN 09

Practical implementation of Kohn–Sham density-functional theory employs approximations to the unknown exchange-correlation potential. This fundamental quantity is usually obtained indirectly by modelling the exchange-correlation functional. While this indirect route works well for many applications, for example, geometry optimization and calculation of total energies, it fails whenever properties of interest are susceptible to the shape of the exchange-correlation potential, which is the case for molecular response properties such as electronic excitation energies and molecular polarizabilities. The easiest way to fix this is to approximate the potential directly [1–5] and constrain it to reproduce a set of analytic properties [6–8]. This approach is beset by methodological difficulties, but many of them have been eliminated in recent years [9–12].

Among all the properties of the exact exchange-correlation potential, Coulombic asymptotic decay is the most important. Functional derivatives of common approximate functionals built from the density ingredients fall off much faster because of the exponential decay of the electron density. In this light, the electrostatic approach to modelling the exchange-correlation potential becomes very attractive. In this approach, the potential is approximated using a model exchange-correlation charge distribution, $q_{XC}(\mathbf{r})$ whose normalization guarantees the $-1/r$ decay of the underlying $v_{XC}(\mathbf{r})$ [13–15]. We presented an important caveat for attempts to devise asymptotically correct exchange-correlation potential by modeling $q_{XC}(\mathbf{r})$. We also derived integrability conditions that a model $q_{XC}(\mathbf{r})$ must satisfy in order for the corresponding $v_{XC}(\mathbf{r})$ to be a functional derivative of

some energy expression. These findings provide the basis for future potential development in the framework of the electrostatic approach.

Orbital-dependent functionals, such as hybrids and meta-GGAs, are the most accurate density-functional approximations to date. The challenge associated with these functionals is the evaluation of their functional derivatives with respect to the electron density. This can only be done indirectly by solving the OEP equation [16, 17], a path that leads to numerical instabilities in finite basis sets. We proposed a method for constructing a hierarchy of model potentials for approximating the functional derivative of a given orbital-dependent exchange-correlation functional. Overall, our method can be regarded as a robust substitute for the OEP equation in finite-basis-set calculations.

The highest-level approximation in our hierarchy is derived assuming the equality of the KS and GKS electron densities. In the case of the exact-exchange functional, this is equivalent to the assumption that the KS density and HF *wavefunction* density are equal. Following this line of thought, we generalized our method to wavefunctions of arbitrary type and devised a technique for calculating the exchange-correlation potential from a given electronic wavefunction. Our technique, which we call the Ryabinkin–Kohut–Staroverov (RKS) method, is free from numerical limitations and basis-set artifacts of conventional density-fitting schemes [1, 18, 19] and is simpler than procedures based on many-body perturbation theory [20–22]. The RKS method and its improved version (mRKS) [23] that uses a special representation for the kinetic term open practically unlimited opportunities for the analysis of the exchange-correlation potential in systems that present challenges for standard density-functional approximations, for example, dissociating molecules, weakly bound dimers, and transition-metal complexes. In this work, we focused on molecular dissociation and studied the mechanism of formation of the step structure [24, 25] of the exact exchange-correlation potential in stretched heteronuclear diatomic molecules. We also demonstrated that this feature of $v_{\text{XC}}(\mathbf{r})$ is not an electron correlation effect because it can arise in the case of non-correlated Hartree–Fock wavefunctions. We will now outline other possible applications and extensions of the RKS method.

Our pilot implementation of the RKS technique employs the HF and CASSCF wavefunctions. While the HF theory does not include electron correlation and is only important conceptually (for example, it provides an exact expression for the exchange energy in terms of the orbitals [Eq. (1.44)]), the CASSCF method has been used in a number of chemical problems [26] such as photochemistry and excitation spectra, to mention a few. As good as it is, the CASSCF theory requires the active space specification from the user. There are many ways to choose orbitals for the active space, and the optimal

choice may not be evident *a priori*. The CASSCF model that uses a moderate active space also lacks [27] dynamic correlation; this is why CASSCF calculations are often followed by a perturbation theory calculation [28, 29] that adds the dynamic component of electron correlation. Therefore, it is crucial to implement the RKS method for the “gold standard” [30] of quantum chemistry—the coupled cluster theory using single and double substitutions from the HF determinant plus triple excitations non-iteratively [CCSD(T)] [31, 32]. This theory is free from the artifacts of the CASSCF model and has become the method of choice for accurate calculations of bond energies and molecular properties. It is also beneficial to extend the RKS algorithm to a simple low-cost correlated method, for example, the Møller–Plesset second-order (MP2) perturbation theory [33], because this will allow one to study correlation effects in large systems such as biomolecules.

Very little is known about the behavior of the exact correlation potential. Benchmarks are only available for a few spherical atoms [34, 35], and more benchmark data for a broader range of systems would be of great value. This is where the RKS method could be helpful; one can use it to generate high-quality molecular correlation potentials, $v_C(\mathbf{r})$, according to the equation:

$$v_C(\mathbf{r}) = v_{XC}(\mathbf{r}) - v_X(\mathbf{r}), \quad (8.1)$$

where $v_{XC}(\mathbf{r})$ is the exchange-correlation potential obtained from a correlated *ab initio* wavefunction and $v_X(\mathbf{r})$ is the same quantity but constructed for a HF wavefunction. In Chapter 4, we showed that, for an adequate theory level, the above equation converges to the exact correlation potential upon the increase of the basis set. It would be interesting to compare isosurface plots for RKS correlation potentials with those for electronic structure ingredients used in DFT (electron density and its derivatives, kinetic energy density, etc.) to identify any possible similarity in their behavior. An open question is also the influence of the wavefunction’s quality on the correlation potential. This research avenue will provide important insights for the development of density-functional approximations for correlation.

The KS theory does not provide direct physical interpretation for the KS orbitals and the corresponding orbital energies, except for the energy of the highest-occupied KS orbital [6, 8, 36]. However, one often finds [37, 38] that the occupied KS orbital energies, $\{\epsilon_i^{\text{KS}}\}$, computed with an accurate exchange-correlation potential are in good agreement with experimental vertical ionization potentials, $\{I_i\}$,

$$\epsilon_i^{\text{KS}} \approx -I_i. \quad (8.2)$$

This empirical observation is supported by theoretical analysis in terms of an exact v_{XC} partitioning equation that involves the Dyson orbitals and the corresponding single-electron removal energies [37]. As for the *unoccupied* KS orbitals, their energies, $\{\epsilon_a^{\text{KS}}\}$, are also meaningful in that they can be used to estimate [39–41] the excitation energies, $\{\omega_{ia}\}$:

$$\epsilon_a^{\text{KS}} - \epsilon_i^{\text{KS}} \approx \omega_{ia}. \quad (8.3)$$

The above relationship between the exact (very accurate) KS orbital energy differences and excitation spectra of atoms and molecules can be deduced [42] from the coupled-perturbed equations of TDDFT combined with the KS analogue of the Koopmans theorem derived in Ref. 37. It should be possible to satisfy (to a large extent) Eqs. (8.2) and (8.3) using the eigenvalues of accurate exchange-correlation potentials obtained from high-quality *ab initio* correlated wavefunctions by the RKS method, but the degree of agreement remains a mystery and needs to be systematically studied.

In Chapter 7, we used the RKS method to show that the step structure [24, 25] of the exact exchange-correlation potential can be observed in approximate exchange-correlation potentials reconstructed from restricted HF wavefunctions. Our preliminary results demonstrate that the step structure is also exhibited by functional derivatives of hybrid density-functional approximations [Eq. (1.46)]. The effect of the fraction of the exact exchange on the height and position of these steps is unclear and constitutes an interesting research question.

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Appendix A

Properties of the Dirac delta function

The Dirac delta function or simply delta function naturally arises in the context of quantities that (i) are zero everywhere except for a single point at which they become infinite and (ii) integrate to a finite value. In order to deal with such quantities, which include, for example, the density of a point mass and the probability density of a discrete distribution, it is convenient to introduce the delta function.

The one-dimensional Dirac delta function, $\delta(x)$, is defined by the following properties:

$$\begin{aligned} \delta(x - x_0) &= 0 \quad x \neq x_0 \\ \int_b^a f(x)\delta(x - x_0)dx &= \begin{cases} f(x_0), & a < x_0 < b \\ 0, & \text{otherwise} \end{cases} \end{aligned} \quad (\text{A.1})$$

for any function $f(x)$ that is continuous at $x = x_0$. If one takes $f(x) = 1$, it is easy to see that the integral of $\delta(x)$ over a point is unity:

$$\int_b^a \delta(x - x_0)dx = 1. \quad (\text{A.2})$$

Strictly speaking, the delta function is not an ordinary function, but rather belongs to a broader class of generalized functions, or distributions [1]. It is only meaningful as part of the integral $\int \dots \delta(x - x_0)dx$ “acting” on some function $f(x)$. This permits to interpret this integral as an operator that associates $f(x)$ with its value at a particular point x_0 .

Basic properties of the delta function include:

- **Scaling**

The behavior of the delta function upon scaling by a non-zero real number a is as follows:

$$\delta(ax) = \frac{1}{|a|}\delta(x). \quad (\text{A.3})$$

More generally, the delta function of a function of x is given by

$$\delta[f(x)] = \sum_i \frac{\delta(x - x_i)}{|df/dx|_{x_i}}, \quad (\text{A.4})$$

where $\{x_i\}$ are the roots of $f(x)$.

- **Symmetry**

The delta function is an even function,

$$\delta(x - x_0) = \delta(x_0 - x), \quad (\text{A.5})$$

which follows from the scaling property of Eq. (A.3).

- **Product with ordinary functions**

$$f(x)\delta(x - x_0) = f(x_0)\delta(x - x_0) \quad (\text{A.6})$$

Properties of derivatives of the delta function are extensively used in our work. These quantities are defined by the following fundamental equation:

$$\int_a^b f(x) \frac{d^n}{dx^n} \delta(x - x_0) dx = - \int_a^b \frac{d}{dx} f(x) \frac{d^{n-1}}{dx^{n-1}} \delta(x - x_0) dx. \quad (\text{A.7})$$

By applying integration by parts and using the property of Eq. (A.6) one further obtains:

$$\begin{aligned} - \int_a^b \frac{d}{dx} f(x) \frac{d^{n-1}}{dx^{n-1}} \delta(x - x_0) dx &= \int_a^b \frac{d^2}{dx^2} f(x) \frac{d^{n-2}}{dx^{n-2}} \delta(x - x_0) dx \\ &= \dots \\ &= (-1)^n \int_a^b \frac{d^n}{dx^n} f(x) \delta(x - x_0) dx \\ &= (-1)^n \frac{d^n f}{dx^n} [x_0]. \end{aligned} \quad (\text{A.8})$$

In our notation, $\frac{d^n f}{dx^n}[x_0]$ signifies the n th-order derivative of $f(x)$ evaluated at a point x_0 . From this follows that

$$\int_a^b f(x) \frac{d}{dx} \delta(x - x_0) dx = -\frac{df}{dx}[x_0] \quad (\text{A.9})$$

and

$$\int_a^b f(x) \frac{d^2}{dx^2} \delta(x - x_0) dx = \frac{d^2 f}{dx^2}[x_0]. \quad (\text{A.10})$$

The first derivative of the delta function is an odd function which means that

$$\frac{d\delta}{dx}[x_0] = -\frac{d\delta}{dx}[-x_0]. \quad (\text{A.11})$$

This property is not to be confused with what is implied by Eq. (A.5):

$$\frac{d}{dx}[\delta(x - x_0)] = \frac{d}{dx}[\delta(x_0 - x)]. \quad (\text{A.12})$$

In the first equation, differentiation is followed by evaluating the derivative at a point x_0 while in the second one the functions are differentiated *after* replacing the variable. Another useful property of the first derivative of the delta function is that its sign changes if one switches to differentiation with respect to x_0 :

$$\frac{d}{dx}[\delta(x - x_0)] = -\frac{d}{dx_0}[\delta(x - x_0)]. \quad (\text{A.13})$$

The three-dimensional delta function in Cartesian coordinate space is defined similarly to Eq. (A.1). One can verify that it can be written as a product of one-dimensional delta functions in each direction:

$$\delta(\mathbf{r} - \mathbf{r}') \equiv \delta(x - x_0)\delta(y - y_0)\delta(z - z_0). \quad (\text{A.14})$$

This representation is used for generalizing all properties of the one-dimensional delta function to three dimensions. The properties relevant to this work can be rewritten as follows:

$$\delta(a\mathbf{r}) = \frac{\delta(\mathbf{r})}{|a|^3}, \quad (\text{A.15})$$

$$\delta(\mathbf{r} - \mathbf{r}') = \delta(\mathbf{r}' - \mathbf{r}), \quad (\text{A.16})$$

$$\int f(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}')d\mathbf{r} = f(\mathbf{r}'), \quad (\text{A.17})$$

$$\int f(\mathbf{r})\nabla_{\mathbf{r}}\delta(\mathbf{r} - \mathbf{r}')d\mathbf{r} = -\nabla_{\mathbf{r}}f[\mathbf{r}'], \quad (\text{A.18})$$

$$\int f(\mathbf{r}) \nabla_{\mathbf{r}}^2 \delta(\mathbf{r} - \mathbf{r}') d\mathbf{r} = \nabla_{\mathbf{r}}^2 f[\mathbf{r}'], \quad (\text{A.19})$$

$$\nabla_{\mathbf{r}} \delta[\mathbf{r} - \mathbf{r}'] = -\nabla_{\mathbf{r}} \delta[\mathbf{r}' - \mathbf{r}], \quad (\text{A.20})$$

$$\nabla_{\mathbf{r}}[\delta(\mathbf{r} - \mathbf{r}')] = \nabla_{\mathbf{r}}[\delta(\mathbf{r}' - \mathbf{r})], \quad (\text{A.21})$$

and

$$\nabla_{\mathbf{r}}[\delta(\mathbf{r} - \mathbf{r}')] = -\nabla_{\mathbf{r}'}[\delta(\mathbf{r} - \mathbf{r}')], \quad (\text{A.22})$$

where we retain the same notation as before.

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Appendix B

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14. **S. V. Kohut**, V. N. Staroverov, “Step structure in molecular exchange-correlation potentials obtained from restricted Hartree–Fock wavefunctions”, *in preparation*.
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4. “Toward approximating the exchange-correlation potential by explicit modeling of the exchange-correlation charge distribution”, Applied Mathematics, Modeling and Computational Science Conference, Wilfrid Laurier University, Waterloo, Ontario, Canada, August 26–30, 2013.
3. “Theoretical investigation of thermodynamic properties of 1-butyl-3-methyltrifluoromethanesulfonate and butyltrimethylammonium bis(triflyl)amide ionic liquids in the gaseous state”, 18th International Lomonosov Conference of Student Researchers and Young Scientists, Moscow State University, Moscow, Russia, April 11–15, 2011.
2. “Vapor pressure, thermal stability and thermodynamic properties in the ideal-gas state of 1-butyl-3-methylimidazolium triflate ionic liquid”, First Belarusian National Scientific Conference “Scientific Intentions 2010”, The National Academy of Sciences of Belarus, Minsk, Belarus, November 1–3, 2010.
1. “Thermodynamics of 1-butyl-3-methylimidazolium triflate and trends in total entropy change when going from crystal to liquid for 1-alkyl-3-methylimidazolium derivatives”, 17th International Lomonosov Conference of Student Researchers and Young Scientists, Moscow State University, Moscow, Russia, April 12–15, 2010.

Poster presentations

6. “Origin of the step structure of the exact exchange-correlation potential”, 2015 Symposium on Chemical Physics, Waterloo, Ontario, Canada, November 6–8, 2015.
5. “Exchange-correlation potentials from many-electron wavefunctions”, 55th Sanibel Symposium, St. Simons Island, Georgia, USA, February 15–20, 2015.
4. “Average local ionization energy as a generalization of the electrostatic potential”, 25th Canadian Symposium on Theoretical and Computational Chemistry, Concordia University, Montréal, Québec, Canada, July 6–11, 2014.

3. “Apparent violation of the sum rule for exchange-correlation charges by generalized gradient approximations”, 96th Canadian Chemistry Conference and Exhibition, Québec City, Québec, Canada, May 26–30, 2013.
2. “Comprehensive study of thermodynamic properties for some 1-alkyl-4-nitro-1,2,3-triazole derivatives”, 14th JCF-Frühjahrssymposium, Universität Rostock, Rostock, Germany, March 18–21, 2012.
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