1-26-2017 12:00 AM

Integration of orbital-dependent exchange-correlation potentials

Hanqing Zhao, *The University of Western Ontario*

Supervisor: Viktor N. Staroverov, *The University of Western Ontario*

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

Recommended Citation
Zhao, Hanqing, "Integration of orbital-dependent exchange-correlation potentials" (2017). *Electronic Thesis and Dissertation Repository*. 4414.
https://ir.lib.uwo.ca/etd/4414

Abstract

In density-functional theory, one can approximate either the exchange-correlation energy functional or the corresponding Kohn–Sham effective potential, which is then converted into an energy functional by functional integration. A directly approximated potential may depend on the electron density explicitly or implicitly through Kohn–Sham orbitals. A potential that depends on the electron density explicitly can be converted into an energy functional by evaluating the Leeuwen–Baerends line integral along some path of electron densities. We extend this technique to orbital-dependent potentials by integrating them along the path of scaled orbitals. Using this method, we assign energy expressions to the Slater, Becke–Johnson and van Leeuwen–Baerends model Kohn–Sham potentials. We also investigate the conditions under which the zero-force test for functional derivatives holds in finite basis set. Specifically, we show that any functional derivative of an explicitly density-dependent functional satisfies the zero-force test in any finite basis set. Approximate exchange-correlation potentials constructed by the Ryabinkin–Kohut–Staroverov (RKS) method are found to pass the zero-force test only in the basis-set limit. Our results confirm that RKS potentials obtained from Hartree–Fock wave functions are practically indistinguishable from exact exchange potentials when a large basis set is employed.

Keywords: density-functional theory, exchange-correlation functional, Kohn-Sham potential, line integral, orbital-dependent functionals, functional derivative

Acknowledgements

First, I would first like to thank my supervisor, Dr. Viktor N. Staroverov, for his guidance and encouragement. The door to Prof. Staroverov's office was always open whenever I ran into a problem or had a question about my research or writing. It is a privilege and pleasure to be Dr. Staroverov's student.

I also want to thank my current and former group fellows: Sviataslau Kohut, Darya Komsa, Egor Ospadov, Rogelio Cuevas-Saavedra, Angela Murcia Ríos, Victor González Chávez, Rayner Mendes, Zitong Wang and Amin Torabi for the stimulating discussions and for all the fun we have had in the last two years.

Finally, I must express gratitude to my parents, Jiancheng Zhao and Xiuqin Li, and to my wife, Ni Zhou, for their love and support throughout all these years.

List of Abbreviations

BJ — Becke–Johnson (model potential)

C — correlation

DOS — direct orbital-scaling

DFT — density functional theory

FA — Fermi–Amaldi (potential)

GGA — generalized gradient approximation

HF — Hartree–Fock (method)

KLI — Krieger–Li–Iafrate (model potential)

KS — Kohn–Sham (method)

LB94 — van Leeuwen–Baerends (model potential of 1994)

LDA — local density approximation

MAE — mean absolute error

OEP — optimized effective potential

PBE — Perdew–Burke–Ernzerhof (approximate density functional)

RKS — Ryabinkin–Kohut–Staroverov (method)

RPP — Räsänen–Pittalis–Proetto (model potential)

SCF — self-consistent field

S — Slater (model potential)

UGBS — universal Gaussian basis set

XC — exchange-correlation

X — exchange

Atomic units are employed throughout the thesis. The energy unit is the hartree (E_h), and the unit of length is the Bohr radius (a_0): $1\,a_0 = 0.529177\,\text{Å}$.

Contents

Chapter 1

Introduction

1.1 Density functional theory and the Hohenberg–Kohn theorems

Much of the chemically relevant information about molecular structure and properties can be extracted from stationary electronic wave functions obtained as solutions to the time-independent Schrödinger equation. Unfortunately, this equation cannot be solved analytically except for a few model systems that are of limited interest in chemistry. Another challenge when dealing with the Schrödinger equation is that as the electron number N becomes large, the wave function (a function of $3N$ spatial and N spin variables) becomes extremely complicated and prohibitively expensive to compute. Density-functional theory (DFT) is a clever approach that overcomes these difficulties.

DFT treats the total energy as a functional of electron density,

$$E_{\text{total}} = E[\rho]. \tag{1.1}$$

By using the electron density as input, DFT significantly decreases the computational cost by reducing the N-electrons problem involving wave functions of $3N$ spatial coordinates to a problem involving a function of 3 spatial coordinates.

DFT is based on two theorems due to Hohenberg and Kohn [1]. The first Hohenberg–Kohn theorem states that the ground-state electron density uniquely determines the external potential, hence the Hamiltonian and all other information about the system that can be derived from it. For the total electronic energy, this fact can be expressed as

$$E[\rho] = \int v_{\text{ext}}(\mathbf{r})\rho(\mathbf{r})\, d\mathbf{r} + F[\rho], \tag{1.2}$$

where $v_{\text{ext}}(\mathbf{r})$ is the external potential (usually the electrostatic potential of the nuclei) and $F[\rho]$ is the so-called universal (i.e., system-independent) density functional. The second Hohenberg–Kohn theorem states that the exact ground-state energy and density of the system can be found by minimizing $E[\rho]$ over all acceptable densities [1,2].

1.2 Kohn–Sham scheme

The functional $F[\rho]$ in Eq. (1.2) can be separated into two terms

$$F[\rho] = T[\rho] + V_{\text{ee}}[\rho], \tag{1.3}$$

where $T[\rho]$ is the kinetic energy of the electrons and V_{ee} is the electron-electron interaction. The electron-electron interaction can be partitioned into classical and quantum-mechanical parts

$$V_{\text{ee}} = J + E_{\text{xc}}^{(\text{c})}, \tag{1.4}$$

where J is the classical Coulomb repulsion energy

$$J = \frac{1}{2}\int d\mathbf{r}_1 \int d\mathbf{r}_2 \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}, \tag{1.5}$$

and $E_{\text{xc}}^{(\text{c})}$ is the conventional (in wave function-based methods) non-classical exchange-correlation energy. Thus, $F[\rho]$ becomes

$$F[\rho] = T[\rho] + J[\rho] + E_{\text{xc}}^{(\text{c})}[\rho]. \tag{1.6}$$

The remaining problems are how to approximate $T[\rho]$ and the non-classical part of V_{ee}. Kohn and Sham proposed a method for handling the kinetic energy term [3], which turned DFT into a practical tool. The Kohn–Sham method is based on the assumption that for any real (interacting) system with the ground-state density $\rho(\mathbf{r})$ there exists a corresponding non-interacting system which has the same ground-state $\rho(\mathbf{r})$. Thus, the difficult many-body problem of interacting electrons in a static external potential is reduced to a simpler problem of non-interacting electrons moving in an effective potential $v_{\mathrm{eff}}(\mathbf{r})$. Non-interacting systems are relatively easy to solve as their wave functions are just Slater determinants. The non-interacting single-particle Schrödinger equations,

$$\left[-\frac{1}{2}\nabla^2 + v_{\mathrm{eff}}(\mathbf{r})\right]\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r}), \tag{1.7}$$

can also be readily solved. The universal functional for the non-interacting system $F_0[\rho]$ becomes

$$F_0[\rho] = T_{\mathrm{s}}[\rho] = -\frac{1}{2}\sum_{i=1}^{\mathrm{N}}\langle\phi_i|\nabla^2|\phi_i\rangle, \tag{1.8}$$

where the density is

$$\rho(\mathbf{r}) = \sum_{i=1}^{N}|\phi_i(\mathbf{r})|^2. \tag{1.9}$$

Since Kohn and Sham assumed $\rho^{\mathrm{KS}} = \rho^{\mathrm{real}}$, Eq. (1.6) can be rewritten as

$$F[\rho] = T_{\mathrm{s}}[\rho] + J[\rho] + E_{\mathrm{xc}}[\rho], \tag{1.10}$$

where $T_{\mathrm{s}}[\rho]$ is the kinetic energy of the non-interacting electrons and $E_{\mathrm{xc}}[\rho]$ is the exchange-correlation energy defined as

$$E_{\mathrm{xc}}[\rho] = T[\rho] - T_{\mathrm{s}}[\rho] + E_{\mathrm{xc}}^{(\mathrm{c})}. \tag{1.11}$$

The total energy functional from Kohn and Sham is written as

$$E[\rho] = \int v(\mathbf{r})\, d\mathbf{r} + T_{\mathrm{s}}[\rho] + J[\rho] + E_{\mathrm{xc}}[\rho]. \tag{1.12}$$

Applying the variational principle to the Kohn–Sham functional, we obtain the one-electron equation

$$\left[-\frac{1}{2}\nabla^2 + v(\mathbf{r}) + v_{\mathrm{H}}(\mathbf{r}) + v_{\mathrm{xc}}(\mathbf{r})\right]\phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r}), \tag{1.13}$$

where v_{H} is the Hartree potential, the functional derivative of the electrostatic repulsion functional,

$$v_{\mathrm{H}} = \frac{\delta J[\rho]}{\delta \rho(\mathbf{r})} = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}', \tag{1.14}$$

and v_{xc} is the exchange-correlation potential, defined as the functional derivative of E_{xc} with respect to the density,

$$v_{\mathrm{xc}} = \frac{\delta E_{\mathrm{xc}}[\rho]}{\delta \rho(\mathbf{r})}. \tag{1.15}$$

Eqs. (1.9) and (1.13) are known as the Kohn–Sham equations. In a way, the Kohn–Sham method packs the complexity of the interacting wave function into the exchange-correlation functional $E_{\mathrm{xc}}[\rho]$. The principal task of DFT is to design accurate approximations to the unknown exact exchange-correlation energy functional. Usually, the $E_{\mathrm{xc}}[\rho]$ can be separated into two parts, exchange and correlation functionals:

$$E_{\mathrm{xc}}[\rho] = E_{\mathrm{x}}[\rho] + E_{\mathrm{c}}[\rho]. \tag{1.16}$$

The exchange part is defined exactly by

$$E_{\mathrm{x}}^{\mathrm{exact}}[\rho] = -\sum_{k,l=1}^{N/2} \int d\mathbf{r}_1 \int d\mathbf{r}_2 \frac{\phi_k(\mathbf{r}_1)\phi_k^*(\mathbf{r}_2)\phi_l^*(\mathbf{r}_1)\phi_l(\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|}. \tag{1.17}$$

The above expression is the same as in the Hartree–Fork (HF) theory [4, 5] but uses the Kohn–Sham orbitals instead of HF orbitals. Since the exact exchange functional combined with standard correlation functionals gives poor accuracy in most cases [6], approximate exchange energy functionals are commonly employed, even though the exact one is available. The exact exchange energy functional itself is used as a guide for developing new exchange energy functionals [7, 8].

1.3 Explicit and implicit energy functionals

The simplest functional in DFT is the local density approximation (LDA) to the exchange and correlation energy

$$E_{\mathrm{xc}}[\rho] = \int \rho(\mathbf{r})\epsilon_{\mathrm{xc}}(\rho)d\mathbf{r}, \tag{1.18}$$

where $\epsilon_{\mathrm{xc}}(\rho)$ is the exchange-correlation energy per particle of a uniform electron gas. The uniform electron gas is a useful model of metallic systems.

The $\epsilon_{\mathrm{xc}}(\rho)$ can be partitioned into exchange and correlation parts

$$\epsilon_{\mathrm{xc}}(\rho) = \epsilon_{\mathrm{x}}(\rho) + \epsilon_{\mathrm{c}}(\rho). \tag{1.19}$$

The $\epsilon_{\mathrm{x}}(\rho)$ is given by

$$\epsilon_{\mathrm{x}}(\rho) = -C_{\mathrm{x}}\rho^{1/3}(\mathbf{r}), \tag{1.20}$$

where $C_{\mathrm{x}} = (3/4)(3/\pi)^{1/3}$. The correlation part can be calculated by the quantum Monte Carlo method [9].

LDA gives reasonably accurate predictions for solids [10] but produces poor results for atoms and molecules because the electron densities of atoms and molecules are far from uniform. For this reason, LDA is rarely useful for chemical systems.

Many failures of the LDA are corrected by introducing the gradient of density into $\epsilon_{\text{xc}}(\rho)$,

$$E_{\text{xc}}[\rho] = \int \rho(\mathbf{r})\epsilon_{\text{xc}}(\rho, \nabla\rho)d\mathbf{r}. \tag{1.21}$$

Density functionals of this type are known as generalized gradient approximations (GGA). GGAs give much better results than LDA [11–18]. LDA and GGAs are said to be explicit or density-dependent, since all variables in the Eq. (1.18) and (1.21) depend on ρ explicitly. In general, a functional E_{xc} of the form

$$E_{\text{xc}}[\rho] = \int e_{\text{xc}}(\rho, \nabla\rho, \nabla^2\rho)d\mathbf{r} \tag{1.22}$$

is said to be explicit or density-dependent. The $\nabla^2\rho$ in the above equation is the Laplacian of the electron density.

Although GGAs produce better overall predictions than LDA, both of those approximations suffer from two deficiencies. First, there is a self-interaction error in LDA and GGAs. In Eq. (1.4), the electron-electron interaction energy is artificially partitioned into the Hartree part and the exchange-correlation part. The Hartree potential in Eq. (1.13) is inherently in error because it includes the spurious self-interaction energy of electrons. In exact DFT, the self-interaction error is canceled out by the exchange-correlation term. Unfortunately, only part of this error is canceled in LDA and GGAs. Another drawback of LDA and GGAs is that they lack derivative discontinuities in the exchange-correlation energies.

The above-mentioned errors in LDA and GGAs can be reduced by employing orbital-dependent functionals which use Kohn–Sham orbitals directly in the construction of exchange-correlation functionals.

A functional of the type

$$E_{\mathrm{xc}}[\rho] = \int e_{\mathrm{xc}}(\rho, \nabla\rho, \nabla^2, \tau) d\mathbf{r}, \tag{1.23}$$

where τ is Kohn–Sham (non-interacting) kinetic energy density

$$\tau = \frac{1}{2}\sum_{k}^{occ.} |\nabla\phi_k|^2, \tag{1.24}$$

is said to be implicit or orbital-dependent, because τ cannot be written explicitly in terms of ρ, even though it is determined by the density. An orbital-dependent functional given by Eq. (1.23) is also known as the meta-GGA for exchange and correlation energy. Meta-GGAs give more accurate results than GGAs in the prediction of atomization energies, metal surface energies and lattice constants of solids [19–24]. There is also more flexibility in the construction of density functionals afforded by using orbitals directly. Therefore, orbital-dependent functionals are the most practically important types of density-functional approximations.

1.4 Functionals and functional derivatives

In this section, we present a brief mathematical discussion of functionals and functional derivatives. "A *function* is a rule for going from a variable to a number. A *functional* is a rule for going from a function to a number" [25]. A function uses a number as input and gives a number as output, whereas a functional takes an entire function as input and gives a number:

$$f(\mathbf{r}) \xrightarrow{\text{rule}} F[f]. \tag{1.25}$$

Most functionals used in DFT have the form of integrals over some well-behaved function $f(x)$. For example, if

$$F[f] = \int_{-1}^{1} f(x)dx, \tag{1.26}$$

and we take $f(x) = x^2$, then

$$F[f] = \int_{-1}^{1} x^2 dx = \frac{2}{3}. \tag{1.27}$$

One of the simplest functionals in DFT, as discussed in Section 1.3, is the LDA for exchange energy

$$E_{\mathrm{x}}^{\mathrm{LDA}}[\rho] = -C_{\mathrm{x}} \int \rho^{4/3}(\mathbf{r})d\mathbf{r}, \tag{1.28}$$

where $C_{\mathrm{x}} = (3/4)(3/\pi)^{1/3}$. The integration in the above equation is over the entire three-dimensional space.

Let us consider functional derivatives. A variation of any function $f(\mathbf{r})$ in the direction $h(\mathbf{r})$ may be described as

$$\delta_h f = th(\mathbf{r}), \tag{1.29}$$

where t is a real number and $h(\mathbf{r})$ is an arbitrary integrable function. Suppose that $F[\rho]$ satisfies the following formula

$$\begin{aligned} DF[\rho, h] &= \lim_{t\to 0} \frac{F[\rho + th] - F[\rho]}{t} && (1.30) \\ &= \left\{ \frac{d}{dt} F[\rho + th] \right\}_{t=0}. && (1.31) \end{aligned}$$

If the above limit exists for all h, we say that $F[\rho]$ is Gâteaux-differentiable.

The Gâteaux derivative $DF[\rho, h]$ can be written as an integral

$$DF[\rho, h] = \int v([\rho]; \mathbf{r}) h(\mathbf{r})\, d\mathbf{r}, \tag{1.32}$$

where $v([\rho]; \mathbf{r})$ is defined as the functional derivative of $F[\rho]$

$$v([\rho]; \mathbf{r}) \equiv \frac{\delta F[\rho]}{\delta \rho(\mathbf{r})}\,. \tag{1.33}$$

To calculate the functional derivative of $F[\rho]$, one first needs to evaluate the differential $DF[\rho, h]$ using Eq. (1.31). In the second step, one has to cast the result in the form of Eq. (1.32).

Take the LDA for exchange energy as an example. The first differential of LDA is

$$\begin{aligned} DE_{\mathrm{x}}^{\mathrm{LDA}} &= -C_{\mathrm{x}} \left\{ \frac{d}{dt} \int \left[\rho(\mathbf{r}) + t h(\mathbf{r})\right]^{4/3} d\mathbf{r} \right\}_{t=0} && (1.34) \\ &= -\frac{4}{3} C_{\mathrm{x}} \int \rho^{1/3}(\mathbf{r}) h(\mathbf{r})\, d\mathbf{r}. && (1.35) \end{aligned}$$

By comparing this expression with Eq. (1.32), we find that the functional derivative of the LDA, called the LDA potential, is

$$v_{\mathrm{x}}^{\mathrm{LDA}} = -\frac{4}{3} C_{\mathrm{x}} \rho^{1/3}(\mathbf{r}). \tag{1.36}$$

The exchange-correlation potential for a density-dependent functional given by Eq. (1.22) can be obtained directly by functional differentiation. The first Gâteaux differential of such a functional is

$$\begin{aligned} DE_{\mathrm{xc}} &= \left\{ \frac{d}{dt} \int e_{\mathrm{xc}} \left(\rho + th, \nabla\rho + t\nabla h, \nabla^2\rho + t\nabla^2 h\right) d\mathbf{r} \right\}_{t=0} && (1.37) \\ &= \int \left(\frac{\partial e_{\mathrm{xc}}}{\partial \rho} h + \frac{\partial e_{\mathrm{xc}}}{\partial \nabla\rho} \nabla h + \frac{\partial e_{\mathrm{xc}}}{\partial \nabla^2\rho} \nabla^2 h \right) d\mathbf{r}. && (1.38) \end{aligned}$$

Applying integration by parts to the second and third terms of the above equation and using the fact that e_{xc} and its derivatives vanish at infinity, we obtain

$$DE_{\mathrm{xc}} = \int \left[\frac{\partial e_{\mathrm{xc}}}{\partial \rho} h - \nabla \cdot \left(\frac{\partial e_{\mathrm{xc}}}{\partial \nabla \rho} \right) h - \nabla \left(\frac{\partial e_{\mathrm{xc}}}{\partial \nabla^2 \rho} \right) \cdot \nabla h \right] d\mathbf{r}. \tag{1.39}$$

Applying integration by parts again to the third term of the above equation, we arrive at

$$DE_{\mathrm{xc}} = \int \left[\frac{\partial e_{\mathrm{xc}}}{\partial \rho} h - \nabla \cdot \left(\frac{\partial e_{\mathrm{xc}}}{\partial \nabla \rho} \right) h + \nabla^2 \left(\frac{\partial e_{\mathrm{xc}}}{\partial \nabla^2 \rho} \right) h \right] d\mathbf{r} \tag{1.40}$$

$$= \int \left(\frac{\partial e_{\mathrm{xc}}}{\partial \rho} - \nabla \cdot \frac{\partial e_{\mathrm{xc}}}{\partial \nabla \rho} + \nabla^2 \frac{\partial e_{\mathrm{xc}}}{\partial \nabla^2 \rho} \right) h(\mathbf{r})\, d\mathbf{r}. \tag{1.41}$$

Comparing Eq. (1.41) with Eq. (1.32), we find that functional derivative or potential of an explicit functional is

$$v_{\mathrm{xc}}([\rho]; \mathbf{r}) = \frac{\partial e_{\mathrm{xc}}}{\partial \rho} - \nabla \cdot \left(\frac{\partial e_{\mathrm{xc}}}{\partial \nabla \rho} \right) + \nabla^2 \left(\frac{\partial e_{\mathrm{xc}}}{\partial \nabla^2 \rho} \right). \tag{1.42}$$

Unfortunately, the exchange-correlation potential for a given orbital-dependent functional given by Eq. (1.23) cannot be obtained directly by functional differentiation. If we apply the chain rule for functional derivatives to E_{xc}, we obtain

$$v_{\mathrm{xc}} = \frac{\delta E_{\mathrm{xc}}}{\delta \rho(\mathbf{r})} \tag{1.43}$$

$$= \sum_{i=1}^{N} \int \frac{\delta E_{\mathrm{xc}}}{\delta \phi(\mathbf{r}')} \frac{\delta \phi(\mathbf{r}')}{\delta \rho(\mathbf{r})} d\mathbf{r}' + \text{c.c.}, \tag{1.44}$$

where c.c. stands for the complex conjugate of the preceding term. The second factor under the integral $\delta\phi(\mathbf{r}')/\delta\rho(\mathbf{r})$ cannot be evaluated directly. The functional derivative in Eq. (1.44) can be obtained numerically by the optimized effective potential (OEP) method [8, 26, 27]. Therefore, for a density functional, there is always a way to find its corresponding functional derivative, at least in principle.

A functional derivative has the properties similar to the properties of ordinary derivate

$$\frac{\delta}{\delta f(\mathbf{r})}(C_1F_1 + C_2F_2) = C_1\frac{\delta F_1}{\delta f(\mathbf{r})} + C_2\frac{\delta F_2}{\delta f(\mathbf{r})} \tag{1.45}$$

and

$$\frac{\delta}{\delta f(\mathbf{r})}(F_1F_2) = \frac{\delta F_1}{\delta f(\mathbf{r})}F_2 + F_1\frac{\delta F_2}{\delta f(\mathbf{r})}. \tag{1.46}$$

The chain rule for functional derivatives is

$$\frac{\delta F}{\delta g(\mathbf{r}')} = \int \frac{\delta F}{\delta f(\mathbf{r})}\frac{\delta f(\mathbf{r})}{\delta g(\mathbf{r}')}\,d\mathbf{r}. \tag{1.47}$$

We will employ the above properties in the following sections.

1.5 Model potentials

In DFT, one can approximate the exchange-correlation energy functional E_{xc}, then obtain the correspond potential v_{xc} by functional differentiation. An alternative approach is to model the exchange-correlation potential v_{xc} directly and then obtain the corresponding energy functional by functional integration. Let us review some of the directly approximated (so-called "model") potentials arising in the latter approach.

1.5.1 The potential of van Leeuwen and Baerends

Most existing exchange-correlation energy functionals, even at the meta-GGA level, have wrong asymptotic decay in their potential. In 1994, van Leeuwen and Baerends proposed a model potential (LB94) [28], aiming to correct this wrong behavior. The LB94 potential is given by

$$v_{\mathrm{x}\sigma}^{\mathrm{LB94}} = v_{\mathrm{x}\sigma}^{\mathrm{LDA}} - \rho_\sigma^{1/3}\frac{\beta x_\sigma^2}{1 + 3\beta x_\sigma \sinh^{-1} x_\sigma}, \tag{1.48}$$

where $\beta = 0.05$ is an empirical parameter and σ is the spin index. The quantity x_σ in the above equation, defined as

$$x_\sigma = \frac{|\nabla\rho|}{\rho^{4/3}}, \tag{1.49}$$

is a dimensionless reduced-density gradient.

1.5.2 Slater potential

The exact exchange energy functional of Eq. (1.17) is implicit, so its functional derivate or potential $v_{\mathrm{x}}^{\mathrm{exact}}$ cannot be obtained analytically by functional differentiation. It can only be evaluated numerically by the OEP method, which is inconvenient. Thus, a variety of approximations have been made to model $v_{\mathrm{x}}^{\mathrm{exact}}$ directly.

Usually, $v_{\mathrm{x}}^{\mathrm{exact}}$ is treated as a sum of the so-called Slater potential [4] and a response correction

$$v_{\mathrm{x}}^{\mathrm{exact}} = v_{\mathrm{x}}^{\mathrm{S}} + v_{\mathrm{x}}^{\mathrm{resp}}. \tag{1.50}$$

The decomposition of $v_{\mathrm{x}}^{\mathrm{exact}}$ is a useful strategy for modeling potentials, and the Slater potential is a starting point for many approximations.

The Slater potential is defined by

$$v_{\mathrm{x}\sigma}^{\mathrm{S}}(\mathbf{r}) = -\frac{1}{\rho_\sigma(\mathbf{r})} \int \frac{|\rho_\sigma(\mathbf{r}, \mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}', \tag{1.51}$$

where $\rho_\sigma(\mathbf{r}, \mathbf{r}') = \sum_{i=1}^{N_\sigma} \phi_{i\sigma}(\mathbf{r})\phi_{i\sigma}^*(\mathbf{r}')$ is the one-particle Kohn–Sham σ-spin density matrix The Slater potential has the correct $-1/r$ asymptotic decay, but it is deeper than the exact-exchange potential by a factor of $3/2$ for a uniform electron gas.

1.5.3 Becke–Johnson potential (BJ)

Becke and Johnson analyzed the difference between the exact exchange OEP and the Slater potential [29],

$$\Delta v_{\mathrm{x}\sigma} = v_{\mathrm{x}\sigma}^{\mathrm{OEP}} - v_{\mathrm{x}\sigma}^{\mathrm{S}}, \tag{1.52}$$

and proposed an approximation to $\Delta v_{\mathrm{x}\sigma}$ given by

$$\Delta v_{\mathrm{x}\sigma} = \frac{k_\sigma^{\mathrm{BJ}}}{2\pi}, \tag{1.53}$$

where $k_\sigma^{\mathrm{BJ}} = \sqrt{\frac{10}{3}\frac{\tau_\sigma}{\rho_\sigma}}$.

The Becke–Johnson potential is written as

$$v_{\mathrm{x}\sigma}^{\mathrm{BJ}} = v_{\mathrm{x}\sigma}^{\mathrm{S}} + \frac{k_\sigma^{\mathrm{BJ}}}{2\pi}. \tag{1.54}$$

The term $k_\sigma^{\mathrm{BJ}}/2\pi$ becomes a constant as $r \to \infty$. As a result, the Becke–Johnson potential behaves asymptotically as $-1/r + C$, where C is a system-dependent constant.

1.5.4 Räsänen–Pittalis–Proetto potential (RPP)

The Becke–Johnson potential was improved by Räsänen, Pittalis and Proetto [30]. They replaced the k_σ^{BJ} by

$$k_\sigma^{\mathrm{RPP}} = \sqrt{\frac{10}{3}\frac{(\tau_\sigma - \tau_\sigma^{\mathrm{W}})}{\rho_\sigma}}, \tag{1.55}$$

where $\tau_\sigma^{\mathrm{W}} = |\nabla\rho_\sigma|^2/8\rho_\sigma$ is the von Weizsäcker kinetic energy density.

The RPP potential is defined as

$$v_{x\sigma}^{\mathrm{RPP}} = v_{\mathrm{x}\sigma}^{\mathrm{S}} + \frac{k_\sigma^{\mathrm{RPP}}}{2\pi}. \tag{1.56}$$

The advantages of RPP potential are (i) it is exact for one- or two-electron systems. (ii) it has a correct $-1/r$ asymptotic decay since the term $k_\sigma^{\mathrm{RPP}}/2\pi$ becomes zero as $r \to \infty$.

1.5.5 Integration of model potentials

There are two questions associated with any model potential: (i) how to assign an energy expression to the potential; (ii) how to tell whether the potential is a functional derivative.

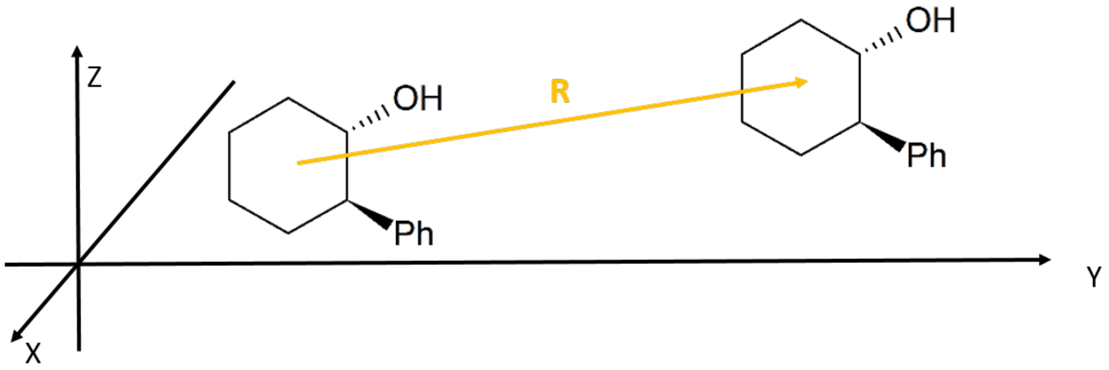
The first problem was studied by van Leeuwen and Baerends [31], followed by Gaiduk and Staroverov [32]. A potential that depends on the electron density explicitly can be turned into an energy functional by integrating v_{xc} along some path of electron densities

$$E_{\text{xc}}[\rho] = \int d\mathbf{r} \int_0^1 v_{\text{xc}}([\rho_\lambda]; \mathbf{r}) \frac{\partial \rho_\lambda(\mathbf{r})}{\partial \lambda} d\lambda, \tag{1.57}$$

where ρ_λ is a scaled electron density. This method generally requires knowing the potential as an explicit functional of the density

Functional derivatives should satisfy certain conditions. For example, their net forces on density must be zero; their parent functionals must be translationally invariant. By using these conditions, we may determine whether a given potential is a functional derivative.

1.6 Translational invariance and the zero-force theorem



In this section, we give a brief introduction about translational invariance and the net force on density. In the above figure, we displaced the molecule by a vector $\mathbf{R}$. The exchange energy of the displaced density, $E[\rho']$, and the original $E[\rho]$ are related by

$$E[\rho'] = E[\rho] + \mathbf{R} \cdot \int \nabla v_{\mathrm{x}}([\rho];\mathbf{r})\rho(\mathbf{r})d\mathbf{r}, \tag{1.58}$$

with

$$\rho'(\mathbf{r}) = \rho(\mathbf{r}+\mathbf{R}), \tag{1.59}$$

where $\mathbf{R}$ is an arbitrary vector. Any reasonable physical functional should not depend on position or coordinate. This property, known as translational invariance, requires that the second term on the right-hand side of the Eq. (1.58) be zero, so that the energy at different positions is the same. The integral in that term may be defined as the net force on the electron density

$$\mathbf{F} = -\int \nabla v_{\mathrm{x}}([\rho];\mathbf{r})\rho(\mathbf{r})d\mathbf{r}. \tag{1.60}$$

For a potential that is a functional derivative, its net force is always zero [33, 34], and its parent functional should be translationally invariant. Therefore, this property may be used to test whether a given potential is a functional derivative or not (more details will be discussed in Chapter 3).

1.7 Objectives of my study

The objective of my research is twofold: to develop a systematic method to convert a given orbital-dependent potential into an energy functional; to investigate the zero-force conditions for functional derivatives.

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Chapter 2

Construction of energy functionals from orbital-dependent potentials by integration along orbital-scaling paths

Unacceptably large errors of approximate DFT in calculations of band gaps of semiconductors, excitation energies, polarizabilities and other properties arise from the wrong asymptotic behavior and the lack of derivative discontinuity in the exchange-correlation potential $v_{\mathrm{xc}}([\rho];\mathbf{r})$. It is possible to reduce these errors by directly modeling the potential $v_{\mathrm{xc}}([\rho];\mathbf{r})$ as a function of Kohn–Sham orbitals. Several model potentials were proposed in the last two decades. For example, the potential of van Leeuwen and Baerends [1] corrected the wrong asymptotic behavior of the LDA potential. The Becke–Johnson and related potentials [2, 3] exhibited derivative discontinuities. Those model potentials give accurate predictions of band gaps in semiconductors, polarizabilities of molecular chains, and other molecular response properties [4–8]. Another advantage of directly approximating $v_{\mathrm{xc}}([\rho];\mathbf{r})$ is that the potential is a unique and simple function of $\mathbf{r}$, so it is more amenable to study and modeling.

Despite the appeal of model potentials, the methodology of calculating energy from these potentials or turning these potentials into energy functional is not yet fully developed. Gaiduk and Staroverov used the line integral method to convert model potentials into energy functionals [9]. They also successfully constructed a new functional from the non-integrable potential of van Leeuwen and Baerends (LB94) [10]. However, their method was restricted to explicitly density-dependent potentials and could not be applied to the more important class of orbital-dependent potentials, such as the Slater, BJ, and RPP potentials.

2.1 Motivation

The purpose of our reasearch in this chapter is to develop a systematic method for turning orbital-dependent potentials into energy functionals.

2.2 Methodology

2.2.1 Line integrals of Kohn–Sham potentials

Let us first recall how one can derive energy functionals from density-dependent potentials by line integrals. Given an integrable potential $v_{\text{xc}}(\mathbf{r})$, one can reconstruct its corresponding energy functional by integrating $v_{\text{xc}}(\mathbf{r})$ along a continuous line (path) of parametrized densities as

$$E_{\text{xc}}[\rho] = \int d\mathbf{r} \int_0^1 v_{\text{xc}}([\rho_\lambda];\mathbf{r}) \frac{\partial \rho_\lambda(\mathbf{r})}{\partial \lambda} d\lambda, \tag{2.1}$$

provided that the path $\rho_\lambda(\mathbf{r})$ is such that $E_{\text{xc}}[\rho_0] = 0$. This method first studied by Leeuwen and Baerends [11, 12] and by Gaiduk and Staroverov [9].

Let us focus on the van Leeuwen–Baerends formula. Suppose we are given an exchange-correlation functional $E_{\text{xc}}[\rho]$. First, we introduce a parametrized density ρ_λ, where λ is a parameter varying in the range $A \leq \lambda \leq B$. If $E_{\text{xc}}[\rho_\lambda]$ is piecewise differentiable function of λ in this interval, then we can write

$$E_{\text{xc}}[\rho_B] - E_{\text{xc}}[\rho_A] = \int_A^B \frac{dE_{\text{xc}}[\rho_\lambda]}{d\lambda} d\lambda. \tag{2.2}$$

The derivative of the function may be rewritten using the chain rule,

$$\frac{dE_{\text{xc}}[\rho_t]}{d\lambda} = \int \frac{\delta E[\rho_\lambda]}{\delta \rho_\lambda(\mathbf{r})} \frac{\partial \rho_\lambda(\mathbf{r})}{\partial \lambda} d\mathbf{r} = \int v([\rho_\lambda];\mathbf{r}) \frac{\partial \rho_\lambda(\mathbf{r})}{\partial \lambda} d\mathbf{r}. \tag{2.3}$$

Interchanging the order of integrals, we obtain

$$E_{\mathrm{xc}}[\rho_B] - E_{\mathrm{xc}}[\rho_A] = \int d\mathbf{r} \int_A^B v([\rho_\lambda]; \mathbf{r}) \frac{\partial \rho_\lambda(\mathbf{r})}{\partial \lambda} d\lambda. \tag{2.4}$$

If we choose $A = 0, B = 1$ and $E[\rho_0] = 0, \rho_1 = \rho$, then Eq. (2.4) reduces to Eq. (2.1). But, if this technique is applied to a potential that is not a functional derivative, the resulting energy functional will depend on how the path is chosen, meaning that the energy functional is not unique, and will not be suitable for computing electronic energies. However, in such cases integration of $v_{\mathrm{xc}}(\mathbf{r})$ can nevertheless be used to produce new energy functionals.

2.2.2 Density- and coordinate-scaling paths

The simplest path [11] for Eq. (2.1) is produced by scaling the density

$$\rho_q(\mathbf{r}) = q\rho(\mathbf{r}), \tag{2.5}$$

which we call here direct scaling. A line of scaled densities from $q = 0$ to $q = 1$ is called a Q path.

Another possibility is the number-conserving coordinate scaling [11]

$$\rho_\lambda(\mathbf{r}) = \lambda^3 \rho(\lambda \mathbf{r}). \tag{2.6}$$

A line of λ-scaled densities from $\lambda = 0$ to $\lambda = 1$ is called a Λ path.

2.2.3 Levy–Perdew virial relation

The Levy–Perdew virial relation is a special case of the line integral taken along the Λ path, applied to exchange functionals. Under uniform coordinate scaling, all valid exchange functionals satisfy the following equation [13, 14]

$$v_{\mathrm{x}}([\rho_\lambda];\mathbf{r}) = \lambda v_{\mathrm{x}}([\rho];\lambda\mathbf{r}). \tag{2.7}$$

Using Eq. (2.1) and (2.7), we find

$$E_{\mathrm{x}}[\rho] = \int_0^1 d\lambda \int \lambda v_{\mathrm{x}}([\rho];\mathbf{r})\lambda^2[3\rho(\lambda\mathbf{r}) + (\lambda\mathbf{r})\nabla_{\lambda\mathbf{r}}\rho(\lambda\mathbf{r})]d\mathbf{r}. \tag{2.8}$$

If we substitute $\lambda\mathbf{r} = \mathbf{r}'$, we obtain

$$E_{\mathrm{x}}[\rho] = \int_0^1 d\lambda \int v_{\mathrm{x}}([\rho];\mathbf{r}')[3\rho(\mathbf{r}') + \mathbf{r}'\cdot\nabla_{\mathbf{r}'}\rho(\mathbf{r}')]d\mathbf{r}'. \tag{2.9}$$

Noting that the integral over λ is simply 1, and switching back from $\mathbf{r}'$ to $\mathbf{r}$, we obtain the Levy–Perdew virial relation in the form

$$E_{\mathrm{x}}[\rho] = \int v_{\mathrm{x}}([\rho];\mathbf{r})[3\rho(\mathbf{r}) + \mathbf{r}\cdot\nabla\rho(\mathbf{r})]d\mathbf{r}. \tag{2.10}$$

2.2.4 Line integration along direct orbital-scaling (DOS) paths

Using the traditional line integral method it is not difficult to convert explicit potentials into energy functionals. However, application of this method to implicit (orbital-dependent) potentials is limited. One can integrate an orbital-dependent potential only through two particular paths: (i) the path of uniformly scaled densities, and (ii) the Aufbau path, which is based on the Janak theorem [15]. The drawback of approach (i) is that the functional $E_{\mathrm{x}}[\rho]$ constructed from $v_{\mathrm{x}}([\rho];\mathbf{r})$ may not be translationally invariant [10, 16] when the potential is not a functional derivative. Approach (ii) requires performing many self-consistent field (SCF) calculations to obtain a single energy value, which is impractical. All these problems can be resolved if we assume that the orbital-dependent potential $v_{\mathrm{xc}}([\phi_k];\mathbf{r})$ and the unknown parent functional $E_{\mathrm{xc}}[\phi_k]$ are related through the equation [17, 18]

$$\frac{\delta E_{\mathrm{xc}}}{\delta \phi_i^*} = v_{\mathrm{xc}} \phi_i. \tag{2.11}$$

The same equation holds for explicit density functionals. Using this assumption and treating E_{xc} as a functional of orbitals, we may write Eq. (2.3) as

$$\frac{dE_{\mathrm{xc}}([\{\phi_{k\lambda}\}];\mathbf{r})}{d\lambda} = \sum_{i=1}^{N} \int \frac{\delta E_{\mathrm{xc}}([\{\phi_{k\lambda}\}];\mathbf{r})}{\delta \phi_{i\lambda}^*} \frac{\partial \phi_{i\lambda}^*}{\partial \lambda} d\mathbf{r} + \text{c.c.} = \sum_{i=1}^{N} \int v_{\mathrm{xc}}([\{\phi_{k\lambda}\}];\mathbf{r}) \phi_{i\lambda} \frac{\partial \phi_{i\lambda}^*}{\partial \lambda} d\mathbf{r} + \text{c.c.}, \tag{2.12}$$

where c.c. stands for the complex conjugate term. Then, we integrate this over some path of scaled orbitals, we obtain

$$E_{\mathrm{xc}}([\{\phi_{k\lambda}\}];\mathbf{r}) = \sum_{i=1}^{N} \int d\mathbf{r} \int_0^1 v_{\mathrm{xc}}([\{\phi_{k\lambda}\}];\mathbf{r}) \phi_{i\lambda}(\mathbf{r}) \frac{\partial \phi_{i\lambda}^*(\mathbf{r})}{\partial \lambda} d\lambda + \text{c.c.}. \tag{2.13}$$

For potentials that are explicit functionals of $\rho(\mathbf{r})$,

$$\frac{\partial \rho_\lambda(\mathbf{r})}{\partial \lambda} = \sum_{i=1}^{N} \left[\phi_{i\lambda}(\mathbf{r}) \frac{\partial \phi_{i\lambda}^*(\mathbf{r})}{\partial \lambda} \right] + \sum_{i=1}^{N} \left[\phi_{i\lambda}^*(\mathbf{r}) \frac{\partial \phi_{i\lambda}(\mathbf{r})}{\partial \lambda} \right], \tag{2.14}$$

so Eq. (2.13) correctly reduces to Eq. (2.1). Now, we can reconstruct energy functional not only from potentials that dependent on $\rho(\mathbf{r})$ explicitly, but also from orbital-dependent model potentials. Another advantage is that we are now free to use any density- or coordinate-scaling transformation of the orbital.

To test Eq. (2.13), we applied it to explicitly density-dependent potentials and to several orbital-dependent potentials. In all cases, we used direct orbital scaling (DOS)

$$\phi_{i\lambda} = \lambda \phi_i(\mathbf{r}),$$

where λ is real.

For future reference, we write out the following equations

$$\phi_{i\lambda} = \lambda\phi_i(\mathbf{r}) \ ; \quad \phi^*_{i\lambda} = \lambda\phi^*_i(\mathbf{r}) \tag{2.15}$$

$$\rho_\lambda(\mathbf{r}) = \lambda^2\rho(\mathbf{r}) \tag{2.16}$$

Let us now consider several examples.

2.3 Integration of potentials that are functional derivatives

2.3.1 Local-density approximation

The LDA exchange functional is

$$E_{\mathrm{x}}^{\mathrm{LDA}}[\rho] = -C_{\mathrm{x}}\int \rho^{4/3}d\mathbf{r}, \tag{2.17}$$

where $C_{\mathrm{x}} = (3/4)(3/\pi)^{1/3}$. The exchange potential is given by

$$v_{\mathrm{x}}^{\mathrm{LDA}} = -\frac{4}{3}C_{\mathrm{x}}\rho^{1/3}(\mathbf{r}). \tag{2.18}$$

Suppose we did not know what functional generated this potential. Let us apply our method to reconstruct its “unknown” functional.

We have

$$v_{\mathrm{x}}^{\mathrm{LDA}}([\{\phi_{k\lambda}\}];\mathbf{r}) = -\frac{4}{3}C_{\mathrm{x}}\rho_\lambda^{1/3}(\mathbf{r}) = \lambda^{2/3}v_{\mathrm{x}}^{\mathrm{LDA}}([\{\phi_k\}];\mathbf{r}). \tag{2.19}$$

Using Eq. (2.13)

$$\begin{aligned} E_{\mathrm{x}}^{\mathrm{LDA}}([\{\phi_k\}];\mathbf{r}) &= \sum_{i=1}^{N}\int d\mathbf{r}\int_0^1 \lambda^{5/3}v_{\mathrm{x}}([\{\phi_k\}];\mathbf{r})\phi^*_i(\mathbf{r})\phi_i(\mathbf{r})d\lambda + c.c \\ &= \frac{3}{4}\int \ v_{\mathrm{x}}^{\mathrm{LDA}}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} \\ &= -C_{\mathrm{x}}\int \rho^{4/3}d\mathbf{r}, \end{aligned} \tag{2.20}$$

which is the original LDA exchange energy functional.

2.3.2 Fermi–Amaldi potential (FA)

The Fermi–Amaldi exchange energy functional is defined as [19, 20]

$$E_{\mathrm{x}}^{\mathrm{FA}}[\rho] = -\frac{1}{2N}\int \frac{\rho(\mathbf{r}')\rho(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'d\mathbf{r}, \tag{2.21}$$

where N is the number of electrons. Here, we treat N as a constant.

The FA exchange potential is given by

$$v_{\mathrm{x}}^{\mathrm{FA}} = -\frac{1}{N}\int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'. \tag{2.22}$$

We have

$$\begin{aligned} v_{\mathrm{x}}^{\mathrm{FA}}([\{\phi_{k\lambda}\}];\mathbf{r}) &= -\frac{1}{N}\int \frac{\rho_\lambda(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' \\ &= -\frac{1}{N}\int \frac{\lambda^2\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'. \end{aligned} \tag{2.23}$$

Using Eq. (2.13), we obtain

$$\begin{aligned} E_{\mathrm{x}}^{\mathrm{FA}}([\{\phi_k\}];\mathbf{r}) &= \int \frac{2}{2+2}v_{\mathrm{x}}^{\mathrm{FA}}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} \\ &= -\frac{1}{2N}\int \frac{\rho(\mathbf{r}')\rho(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'d\mathbf{r}. \end{aligned} \tag{2.24}$$

The expression we obtained from Eq. (2.24) is the same as Fermi–Amaldi energy functional. For LDA and FA potential, which are both functional derivatives, the line integrals are path-independent.

2.4 Integration of potentials that are not functional derivatives

2.4.1 Van Leeuwen–Baerends potential

Now let us turn our attention to some model exchange potentials that are not functional derivatives. The van Leeuwen–Baerends potential is given by [1]

$$v_{\mathrm{x}\sigma}^{\mathrm{LB94}} = v_{\mathrm{x}\sigma}^{\mathrm{LDA}} - \rho_\sigma^{1/3} \frac{\beta x_\sigma^2}{1 + 3\beta x_\sigma \sinh^{-1} x_\sigma}, \tag{2.25}$$

where $\beta = 0.05$ and $x_\sigma = |\nabla \rho_\sigma| / \rho_\sigma^{4/3}$. The line integral of the LB94 potential under direct orbital-scaling path involves integration over the parameter λ, which cannot be done analytically. However, the necessary numerical integrals will be discussed in Section 2.5.

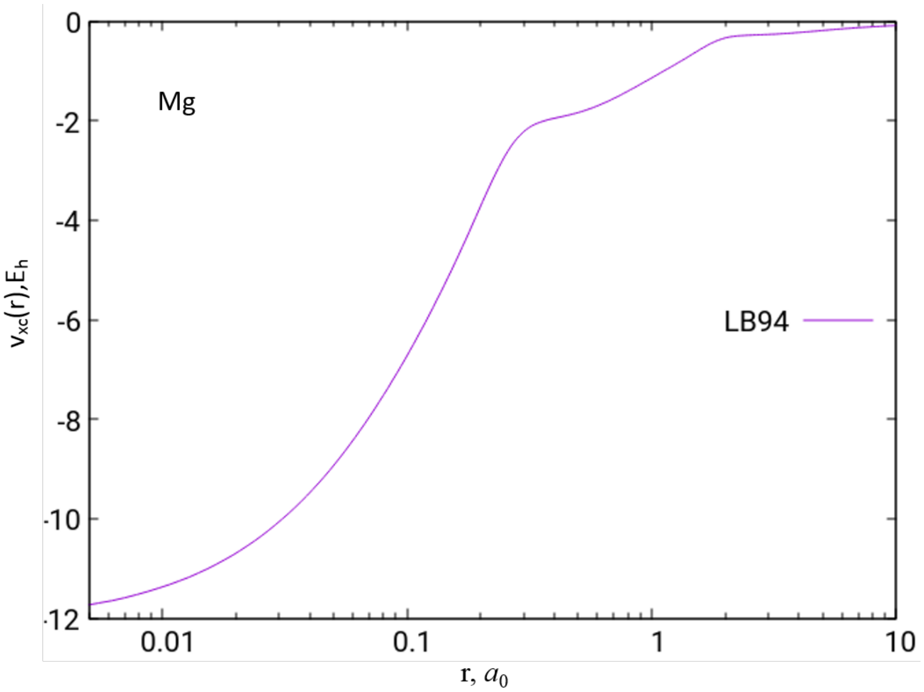


Figure 2.1: The LB94 exchange potential of the Mg atom based on HF/UGBS density

2.4.2 Slater potential

We will now apply our method to orbital-dependent potentials such as the Slater potential and related approximations. The Slater potential is defined by [21]

$$v_{\mathrm{x}\sigma}^{\mathrm{S}}(\mathbf{r}) = -\frac{1}{\rho_\sigma(\mathbf{r})} \int \frac{|\rho_\sigma(\mathbf{r}, \mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}', \tag{2.26}$$

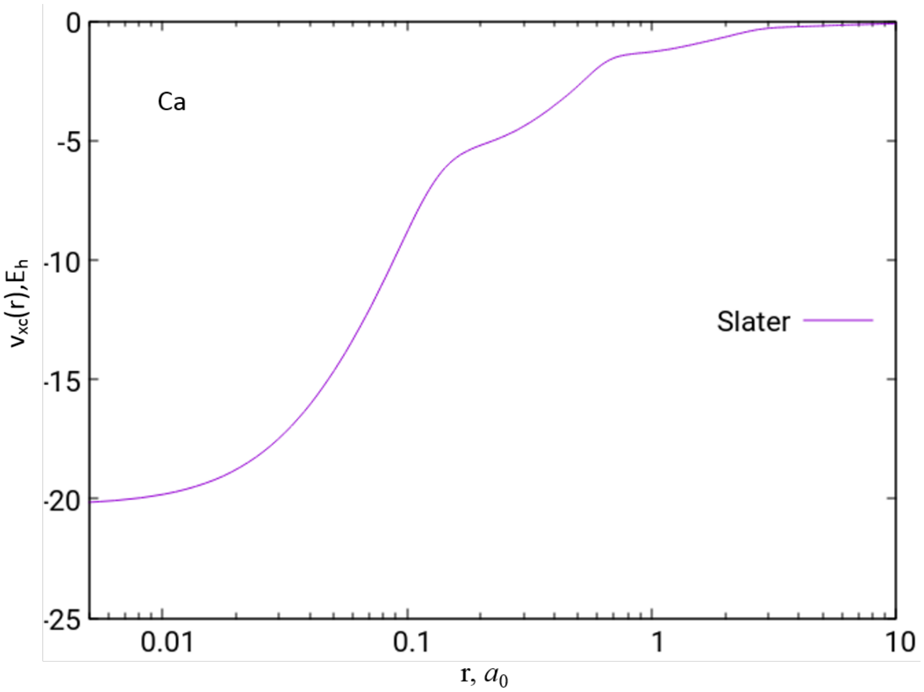


Figure 2.2: The Slater exchange potential of the Ca atom based on HF/UGBS density

where $\rho_\sigma(\mathbf{r}, \mathbf{r}') = \sum_{i=1}^{N_\sigma} \phi_{i\sigma}(\mathbf{r})\phi^*_{i\sigma}(\mathbf{r}')$ is the one-particle Kohn–Sham σ-spin density matrix.

In terms of scaled orbitals,

$$\begin{aligned} v^{\mathrm{S}}_{\mathrm{x}\sigma}([\{\phi_{k\lambda}\}]; \mathbf{r}) &= -\frac{1}{\lambda^2 \rho_\sigma(\mathbf{r})} \int \frac{|\sum_{j=1}^{N} \lambda^2 \phi_{i\sigma}(\mathbf{r})\phi^*_{i\sigma}(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \\ &= \lambda^2 v^{\mathrm{S}}_{\mathrm{x}\sigma}([\{\phi_k\}]; \mathbf{r}). \end{aligned} \tag{2.27}$$

Using Eq. (2.13), we obtain

$$\begin{aligned} E^{\mathrm{S}}_{\mathrm{x}\sigma}([\{\phi_k\}]; \mathbf{r}) &= \sum_{i=1}^{N} \int d\mathbf{r} \int_0^1 \lambda^3 v^{\mathrm{S}}_{\mathrm{x}\sigma}([\{\phi_k\}]; \mathbf{r})\phi^*_{i\sigma}(\mathbf{r})\phi_{i\sigma}(\mathbf{r}) d\lambda + \text{c.c.} \\ &= \frac{1}{2} \int v^{\mathrm{S}}_{\mathrm{x}\sigma}([\{\phi_k\}]; \mathbf{r})\rho_\sigma(\mathbf{r}) d\mathbf{r} \\ &= -\frac{1}{2} \int \int \frac{|\rho_\sigma(\mathbf{r}, \mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' d\mathbf{r}. \end{aligned} \tag{2.28}$$

Comparing Eq. (2.28) and Eq. (1.17), we find that the energy functional obtained from the Slater potential along the DOS path is identical to $E^{\mathrm{exact}}_{\mathrm{x}}$ of Eq. (1.17).

2.4.3 Becke–Johnson potential

The Becke–Johnson potential is given by [2]

$$v_{x\sigma}^{\mathrm{BJ}} = v_{x\sigma}^{\mathrm{S}} + \frac{k_{\sigma}^{\mathrm{BJ}}}{2\pi}, \tag{2.29}$$

where $k_{\sigma}^{\mathrm{BJ}} = \sqrt{\frac{10}{3}\frac{\tau_\sigma}{\rho_\sigma}}$.

We have

$$\nabla\phi_{i\lambda}(\mathbf{r}) = \frac{\partial\lambda\phi_i(\mathbf{r})}{\partial x} + \frac{\partial\lambda\phi_i(\mathbf{r})}{\partial y} + \frac{\partial\lambda\phi_i(\mathbf{r})}{\partial z} = \lambda\nabla\phi_i(\mathbf{r}). \tag{2.30}$$

So,

$$\tau_{\sigma\lambda}(\mathbf{r}) = \sum_{i=1}^{N}\frac{1}{2}|\lambda\nabla\phi_{i\sigma}(\mathbf{r})|^2 = \lambda^2\tau_\sigma(\mathbf{r}). \tag{2.31}$$

Then, we obtain

$$k_{\sigma\lambda}^{\mathrm{BJ}}(\mathbf{r}) = \sqrt{\frac{10}{3}\frac{\lambda^2\tau_\sigma(\mathbf{r})}{\lambda^2\rho_\sigma(\mathbf{r})}} = k_{\sigma}^{\mathrm{BJ}}(\mathbf{r}). \tag{2.32}$$

Using Eq. (2.13) and Eq. (2.32), we obtain the second part of the Becke–Johnson functional $E_{x\sigma}^{\mathrm{BJ-2}}$,

$$\begin{aligned} E_{x\sigma}^{\mathrm{BJ-2}}([\{\phi_{k\lambda}\}];\mathbf{r}) &= \int \frac{1}{2\pi}\sqrt{\frac{10}{3}\tau_\sigma(\mathbf{r})\rho_\sigma(\mathbf{r})}\ d\mathbf{r} \\ &= \int \frac{k_{\sigma}^{\mathrm{BJ}}(\mathbf{r})}{2\pi}\rho_\sigma(\mathbf{r})d\mathbf{r}. \end{aligned} \tag{2.33}$$

So,

$$\begin{aligned} E_{x\sigma}^{\mathrm{BJ}}([\{\phi_k\}];\mathbf{r}) &= -\frac{1}{2}\int\int \frac{|\rho_\sigma(\mathbf{r},\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'d\mathbf{r} + \int \frac{1}{2\pi}\sqrt{\frac{10}{3}\tau(\mathbf{r})\rho(\mathbf{r})}\ d\mathbf{r} \\ &= E_{x\sigma}^{\mathrm{exact}}[\rho] + \int \frac{k_{\sigma}^{\mathrm{BJ}}(\mathbf{r})}{2\pi}\rho_\sigma(\mathbf{r})d\mathbf{r}. \end{aligned} \tag{2.34}$$

The energy functional obtained from the BJ potential along DOS path is a sum of $E_{\mathrm{x}}^{\mathrm{exact}}$ and an additional integral of $k_{\sigma}^{\mathrm{BJ}}/2\pi$ times density. This additional integral is not zero for N-electron systems. As a result, the BJ–DOS functional deviates from $E_{\mathrm{x}}^{\mathrm{exact}}$.

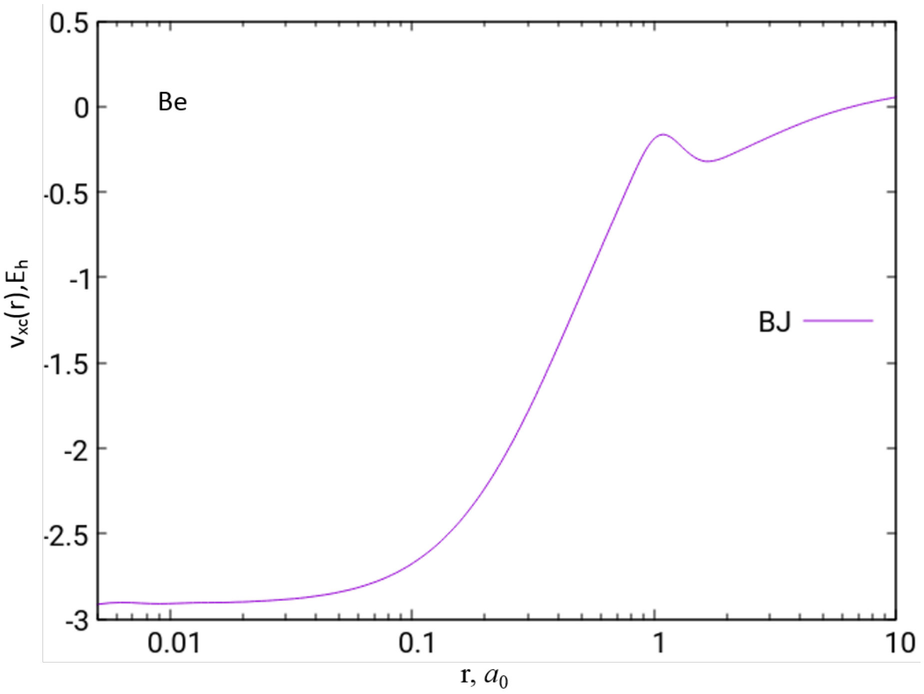


Figure 2.3: The BJ exchange potential of the Be atom based on HF/UGBS density

2.4.4 Räsänen–Pittalis–Proetto potential

The Räsänen–Pittalis–Proetto potential is given by [3]

$$v_{\mathrm{x}\sigma}^{\mathrm{RPP}} = v_{\mathrm{x}\sigma}^{\mathrm{S}} + \frac{k_{\sigma}^{\mathrm{RPP}}}{2\pi}, \tag{2.35}$$

where $k_{\sigma}^{\mathrm{RPP}} = \sqrt{\frac{10}{3}\frac{(\tau_{\sigma}-\tau_{\sigma}^{\mathrm{W}})}{\rho_{\sigma}}}$ and $\tau_{\sigma}^{\mathrm{W}} = |\nabla\rho_{\sigma}|^2/8\rho_{\sigma}$.

Similarly, we have

$$\tau_{\sigma\lambda}^{\mathrm{W}} = \frac{|\nabla\rho_{\sigma}|^2}{8\rho_{\sigma}} = \lambda^2\tau_{\sigma}^{\mathrm{W}}. \tag{2.36}$$

Using Eq. (2.13), we obtain

$$E_{\mathrm{x}}^{\mathrm{RPP}}([\{\phi_k\}];\mathbf{r}) = E_{\mathrm{x}}^{\mathrm{exact}}[\rho] + \frac{1}{2\pi}\int\sqrt{\frac{10}{3}\frac{(\tau_\sigma - \tau_\sigma^{\mathrm{W}})}{\rho_\sigma}}\rho(\mathbf{r})\,d\mathbf{r} \tag{2.37}$$

$$= E_{\mathrm{x}\sigma}^{\mathrm{exact}}[\rho] + \int\frac{k_\sigma^{\mathrm{RPP}}(\mathbf{r})}{2\pi}\rho_\sigma(\mathbf{r})d\mathbf{r}. \tag{2.38}$$

The energy functional obtained from the RPP potential along DOS path has a similar formula to the BJ–DOS functional, but the k_σ^{BJ} under the integral is replaced by k_σ^{RPP}. For one- or two-electron systems, as discussed in Chapter 1, k_σ^{RPP} becomes zero, and thus, the RPP–DOS functional becomes exact.

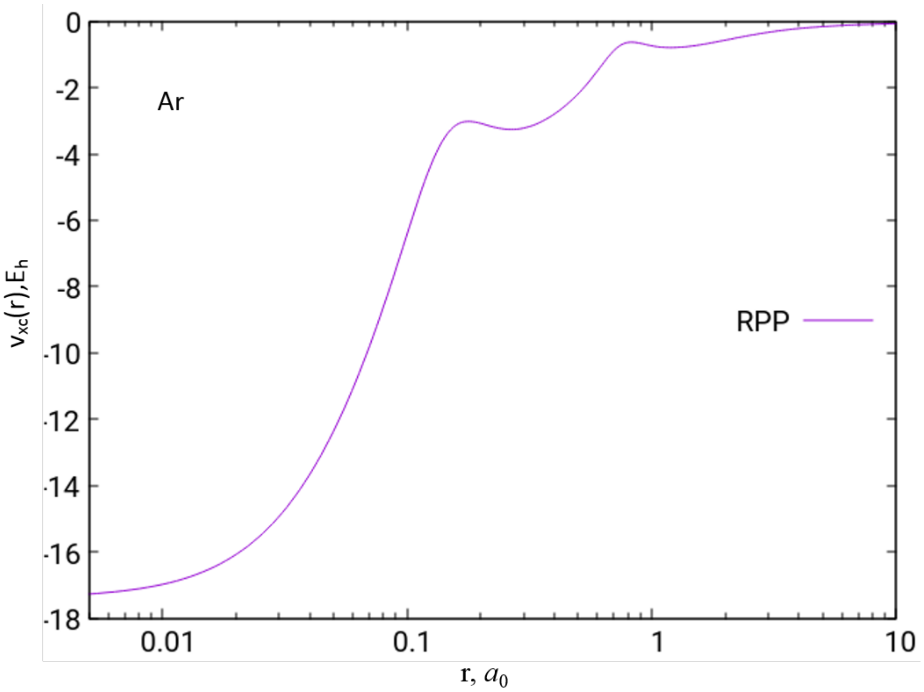


Figure 2.4: The RPP exchange potential of the Ar atom based on HF/UGBS density

2.4.5 Uniform coordinate scaling

Under uniform coordinate scaling, all exchange potentials satisfy Eq. (2.7). Using the following equation,

$$\begin{aligned} \frac{\partial \phi_{i\lambda}(\mathbf{r})}{\partial \lambda} &= \frac{\partial \lambda^{3/2} \phi_i(\lambda \mathbf{r})}{\partial \lambda} \\ &= \frac{3}{2} \lambda^{1/2} \phi_i(\lambda \mathbf{r}) + \lambda^{3/2} \nabla_{\lambda \mathbf{r}} \phi_i(\lambda \mathbf{r}) \cdot \mathbf{r}, \end{aligned} \tag{2.39}$$

our line integral method of Eq. (2.13) also reduces to the Levy–Perdew virial relation, Eq. (2.10).

2.5 Results and discussion

In Table 2.1, we listed total energies obtained from various orbital-dependent exchange-only model potentials for selected atoms and molecules along the DOS and Λ paths. For the Slater potential, the proposed DOS path gave better energies than all other paths relative to the reference exact (HF) values. For other potentials, the Λ-path energies were most reasonable.

The energies obtained from the BJ potential along DOS path were significantly higher than the exact values (see Table 2.1). One important reason for this is that the BJ potential is upshifted [2, 15] relative to the other potentials (see Figure 2.5). We shifted $v_{\mathrm{x}\sigma}^{\mathrm{BJ}}$, so that the highest occupied orbital energies were equal to their HF orbital energies. In Table 2.3, the results given by the shifted BJ potential were better than from the unshifted potential.

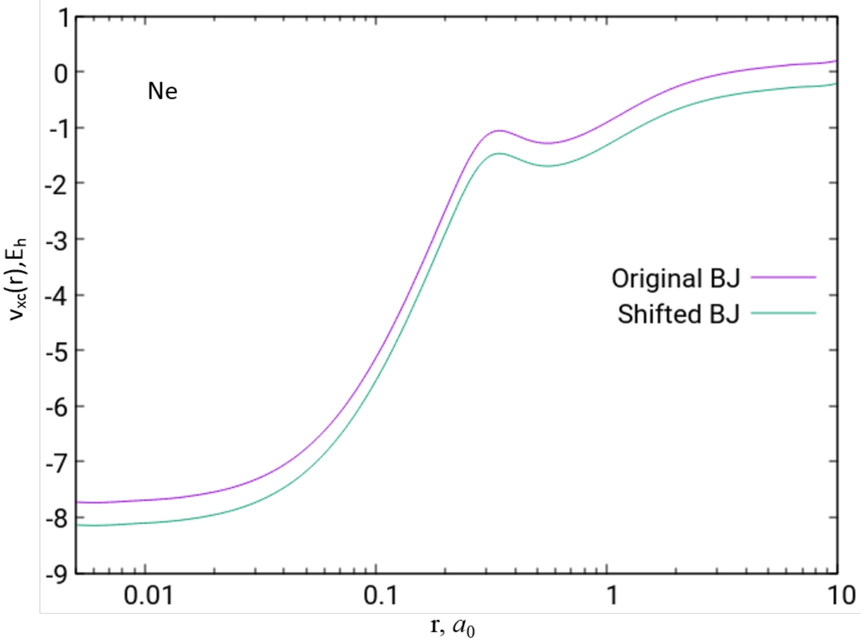


Figure 2.5: The original and shifted BJ exchange potentials of the Ne atom based on HF/UGBS density

The RPP–DOS functional produces better results than the BJ–DOS functional. The energies of H and He atoms obtained from RPP potentials along DOS path are the same as the exact values (see Table 2.1), which indicates the RPP–DOS functional is exact for one- or two-electron systems.

The energy expression of LB94 along DOS path involves integrals over the parameter λ, which cannot be evaluated analytically. Therefore, we wrote a subroutine performing the Gauss–Legendre quadrature with $256 \times N$ point grids [22, 23]. Our results were reported in Table 2.2. We also refined the DOS-LB94 functional by changing the value of β from 0.05 to 0.025 so that it satisfied the second-order gradient expansion of GGA. The refined LB94 functional along DOS path gave reasonable results, even better than whose from Λ path. We also found that the energies of selected atoms obtained from the LB94 and refined

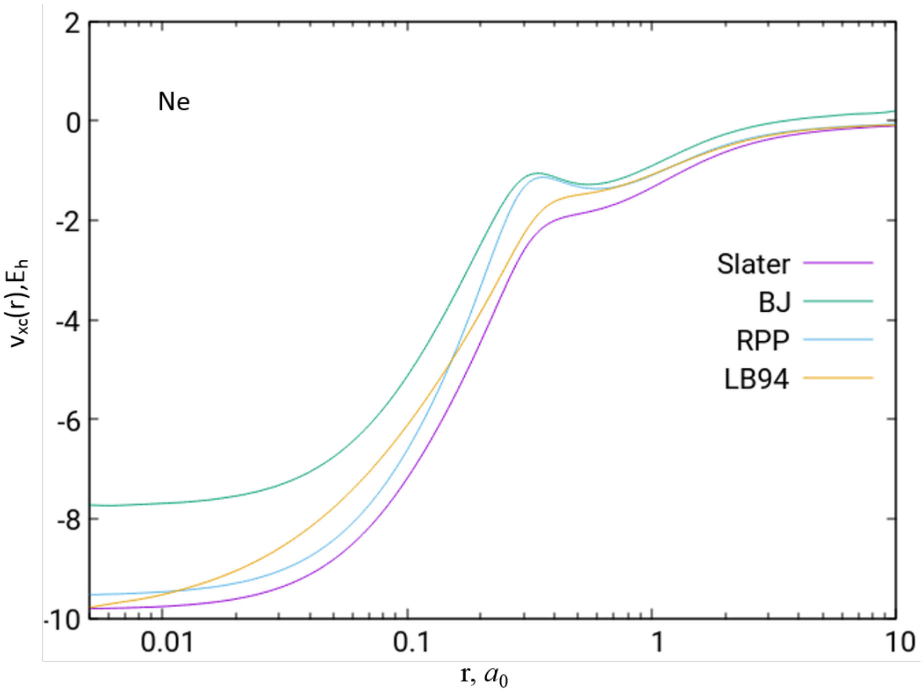
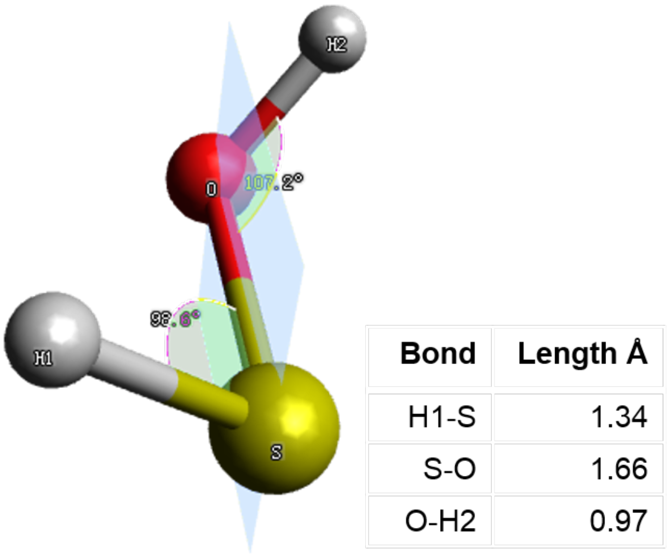


Figure 2.6: The Slater, BJ, RPP and LB94 exchange potentials of the Ne atom based on HF/UGBS density

LB94 potentials along the DOS paths were the same as the energies reported by Gaiduk and Staroverov along the Q path [10], which shows that for a density-dependent potential, our line integral expressed in Eq. (2.13) correctly reduces to Eq. (2.1).

We also tested the translational invariance of the energy expression arising by integration along the DOS path. As discussed in Section 1.6, the difference of the energies between the displaced and original molecule is proportional to the displacement vector $\mathbf{R}$. We displaced two test molecules (H_2O and HSOH) by $\mathbf{R} = (0, 0, 5)$Å, so that the energy differences can be easily observed. The results reported in Table 2.4 and 2.5 show that the energies obtained by integrating the Slater, Becke–Johnson, Räsänen–Pittalis–Proetto potentials along the DOS path at two different places are always the same, meaning that the corresponding energy



Bond	Length Å
H1-S	1.34
S-O	1.66
O-H2	0.97

Figure 2.7: Structure of HSOH molecule

expressions are translationally invariant. This is to be contrasted with the energy expressions obtained by integrating the same potentials along the Λ-paths, which are strongly position-dependent.

Table 2.1: Total ground-state energies (in hartrees) obtained from the Slater, Becke–Johnson, Räsänen–Pittalis–Proetto exchange-only potentials by integration along DOS and Λ paths. All values are for HF/cc-pVTZ densities (Grid=399590).

	Slater		Becke–Johnson		RPP		HF/cc-pVTZ
	DOS	Λ	DOS	Λ	DOS	Λ	
H	−0.4998	−0.4998	−0.2944	−0.5007	−0.4998	−0.4998	−0.4998
He	−2.8612	−2.8612	−2.1679	−2.7857	−2.8612	−2.8612	−2.8612
Li	−7.4327	−7.5389	−6.2274	−7.3771	−7.3320	−7.5522	−7.4327
Be	−14.5729	−14.9126	−12.7462	−14.5317	−14.2464	−14.9416	−14.5729
B	−24.5321	−25.1396	−21.9464	−24.4697	−23.8471	−25.0435	−24.5321
N	−54.4007	−55.7559	−49.8808	−54.1410	−52.5111	−54.9486	−54.4007
Na	−161.8580	−165.5980	−152.2437	−161.0215	−156.3319	−162.5022	−161.8580
MAE	0.0000	0.8784	2.9501	0.1903	1.2183	0.3131	
Molecules at the MP2/6-31G* geometries							
H_2O	−76.0561	−78.2515	−69.8975	−75.8002	72.8987	−76.7435	−76.0561
CH_4	−40.2133	−41.4833	−35.7680	−40.4514	−38.3002	−40.6189	−40.2133

MAE: Mean absolute error

Table 2.2: Total ground-state (in hartrees) energies obtained from the LB94 and refined LB94 exchange-only potentials by integration along DOS path and Λ paths. All values are for HF/cc-pVTZ densities (Grid=399590).

	LB94		revLB94	HF/cc-pVTZ
	DOS	Λ	DOS	
H	−0.6307	−0.4657	−0.5006	−0.4998
He	−3.3133	−2.8191	−2.8721	−2.8612
Li	−8.1969	−7.3555	−7.4439	−7.4327
Be	−15.7065	−14.5420	−14.5844	−14.5729
B	−26.1085	−24.5764	−24.5458	−24.5321
N	−56.9620	−54.5857	−54.4122	−54.4007
Ne	−133.0357	−129.3972	−128.5677	−128.5319
Na	−166.9842	−162.8578	−161.8765	−161.8580
P	−348.5923	−342.4021	−340.6820	−340.7163
Ar	−537.0174	−529.1603	−526.7488	−526.8131
kr	−2779.4403	−2761.9119	−2751.8550	−2752.0521
MAE	5.6106	1.4701	0.0372	

Table 2.3: Total ground-state energies (in hartrees) obtained from shifted BJ potential calculated for the HF/cc-pVTZ densities.

	Becke–Johnson Potential			HF/cc-pVTZ
	DOS	DOS shifted	Λ	
H	−0.2945	−0.5000	−0.5000	−0.5000
He	−2.1781	−2.8433	−2.7784	−2.8617
Li	−6.2255	−6.5079	−7.3809	−7.4328
Be	−12.7431	−13.2920	−14.5400	−14.5730
B	−21.9504	−22.7712	−24.4755	−24.5331

Table 2.4: Total ground-state (in hartrees) energies of H_2O at different positions obtained from different exchange-only potentials by integration along DOS and Λ paths.

Position	Total Energy						
	Slater		BJ		RPP		HF/cc–pVTZ
	DOS	Λ	DOS	Λ	DOS	Λ	
Initial[a]	−76.0561	−78.2547	−69.8976	−75.8040	−72.8987	−76.7377	−76.0561
Displaced[b]	−76.0561	−78.1176	−69.8976	−75.6467	−72.8987	−76.9825	−76.0561

Table 2.5: Total ground-state (in hartrees) energies of HSOH at different positions obtained from different exchange-only potentials by integration along DOS and Λ paths.

Position	Total Energy						
	Slater		BJ		RPP		HF/cc-pVTZ
	DOS	Λ	DOS	Λ	DOS	Λ	
Initial[c]	−473.5717	−483.7200	−450.2699	-472.3416	−459.3102	−475.5704	−473.5717
Displaced[d]	−473.5717	−483.8716	−450.2699	−472.5100	−459.3102	−475.4311	−473.5717

Displaced[c,d] position: Both H_2O and HSOH molecules are translated by $\mathbf{R}$, where $\mathbf{R}$=(0, 0, 5)

2.6 Analysis of integrating $v_{\mathbf{x}}^{\mathbf{Slater}} + v_{\mathbf{x}}^{\mathbf{resp}}$ along the DOS path

As discussed in Chapter 1, $v_{\mathrm{x}}^{\mathrm{exact}}$ is usually treated as a sum of the Slater potential and a response correction

$$v_{\mathrm{x}}^{\mathrm{exact}} = v_{\mathrm{x}}^{\mathrm{Slater}} + v_{\mathrm{x}}^{\mathrm{resp}}. \tag{2.40}$$

Since $v_{\mathrm{x}}^{\mathrm{exact}}$ is a functional derivative of $E_{\mathrm{x}}^{\mathrm{exact}}$, the line integral of $v_{\mathrm{x}}^{\mathrm{exact}}$ is path-independent. Integrating $v_{\mathrm{x}}^{\mathrm{exact}}$ along any path should always give $E_{\mathrm{x}}^{\mathrm{exact}}$.

Integrating each side of Eq. (2.40) along the DOS path, we have

$$E_{\mathrm{x}}^{\mathrm{exact}} = E_{\mathrm{x}}^{\mathrm{exact}} + \left(\sum_{i=1}^{N} \int d\mathbf{r} \int_0^1 v_{\mathrm{x}}^{\mathrm{resp}}([\{\phi_{k\lambda}\}];\mathbf{r}) \phi_{i\lambda}(\mathbf{r}) \frac{\partial \phi_{i\lambda}^*(\mathbf{r})}{\partial \lambda} d\lambda + \mathrm{c.c.} \right), \tag{2.41}$$

where $v_{\mathrm{x}}^{\mathrm{resp}}([\{\phi_{k\lambda}\}];\mathbf{r})$ in terms of scaled orbitals.

The terms in the brackets of the above equation should be zero

$$\sum_{i=1}^{N} \int d\mathbf{r} \int_0^1 v_{\mathrm{x}}^{\mathrm{resp},\lambda} \phi_{i\lambda}(\mathbf{r}) \frac{\partial \phi_{i\lambda}^*(\mathbf{r})}{\partial \lambda} d\lambda + \mathrm{c.c.} = 0, \tag{2.42}$$

which indicates that the line integral of $v_{\mathrm{x}}^{\mathrm{resp}}$ should vanish for any system.

2.7 Summary

We developed a systematic method for turning orbital-dependent model potentials into energy functionals. As stated in Section 2.2, when v_{xc} is not a functional derivative, the resulting energy functional will depend on the integration path chosen. Therefore, our proposed line integral expressed in Eq. (2.13) can be used as a method to define a new functional approximation. The line integral along the DOS path can be applied not only to density-dependent potentials, but also to orbital-dependent potentials. It is more general than the traditional line integral introduced by van Leeuwen and Baerends.

We also applied direct orbital scaling to several model exchange potentials, and the results were acceptable. The finding that the line integral of $v_{\mathrm{x}}^{\mathrm{resp}}$ should vanish may be used as a constraint in approximating $v_{\mathrm{x}}^{\mathrm{resp}}$.

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Chapter 3

Tests for the functional derivatives

In Chapter 2, we developed a systematic method for turning orbital-dependent model potentials into energy functionals. A model potential may not be a functional derivate. The zero-force theorem may be used to test whether a given potential is not a functional derivate. In this chapter, we focus on understanding and analyzing this theorem in application to various model potentials in calculations with finite basis sets.

3.1 The zero-force theorem

Any acceptable exchange functional should be invariant with respect to translation and rotation of the density, and it should satisfy the Levy–Perdew virial relation [1–3]:

$$E_{\mathrm{x}}[\rho] = -\int \rho(\mathbf{r})\mathbf{r} \cdot \nabla v_{\mathrm{x}}([\rho];\mathbf{r})d\mathbf{r}.$$

Translational and rotational invariance mean that the energy of a system should not depend on the system's position and orientation with respect to coordinate axes. For example, if we move a molecule from its original position by $\mathbf{R}$, the density $\rho(\mathbf{r})$ becomes $\rho(\mathbf{r}') = \rho(\mathbf{r}+\mathbf{R})$. The exchange energy functional of the displaced molecule is

$$E_{\mathrm{x}}[\rho'] = -\int \rho(\mathbf{r}+\mathbf{R})\mathbf{r} \cdot \nabla_{\mathbf{r}} v_{\mathrm{x}}([\rho];\mathbf{r}+\mathbf{R})d\mathbf{r}. \tag{3.1}$$

After substituting $\mathbf{r}' = \mathbf{r}+\mathbf{R}$ in Eq. (3.1) and replacing $\mathbf{r}'$ with $\mathbf{r}$ we have

$$E_{\mathrm{x}}[\rho'] = E_{\mathrm{x}}[\rho] + \mathbf{R} \cdot \int \rho(\mathbf{r})\nabla v_{\mathrm{x}}([\rho];\mathbf{r})d\mathbf{r}. \tag{3.2}$$

Since the displaced molecule should have the same energy as the undisplaced one, the second term on the right-hand side of Eq. (3.2) must vanish for an arbitrary $\mathbf{R}$, which requires

$$\int \rho(\mathbf{r})\nabla v_{\mathrm{x}}([\rho];\mathbf{r})d\mathbf{r} = 0 \tag{3.3}$$

or, after integration by parts,

$$\int v_{\mathrm{x}}([\rho];\mathbf{r})\nabla\rho(\mathbf{r})d\mathbf{r} = 0. \tag{3.4}$$

Similarly, rotational invariance requires

$$\int \rho(\mathbf{r})\mathbf{r} \times \nabla v_{\mathrm{x}}([\rho];\mathbf{r})d\mathbf{r} = 0 \tag{3.5}$$

or, after integration by parts,

$$\int v_{\mathrm{x}}([\rho];\mathbf{r})\mathbf{r} \times \nabla\rho(\mathbf{r})d\mathbf{r} = 0. \tag{3.6}$$

In electrostatics, a particle of charge q in an electric field $\mathbf{E}$ experiences the force

$$\mathbf{F} = q\mathbf{E}. \tag{3.7}$$

Now the electric field can be written as the gradient of a scalar potential v,

$$\mathbf{E} = -\nabla v. \tag{3.8}$$

Therefore, the quantity $-\rho(\mathbf{r})\nabla v_{\mathrm{x}}(\mathbf{r})d\mathbf{r}$ may be interpreted as the exchange force acting on the charge $\rho(\mathbf{r})d\mathbf{r}$. Since the electron density is the distribution of electrons for a given system, we may define the total net exchange force on the electron density

$$\mathbf{F} \equiv -\int \rho(\mathbf{r})\nabla v_{\mathrm{x}}([\rho];\mathbf{r})d\mathbf{r}. \tag{3.9}$$

Translational invariance requires this force to be zero. In addition, Levy and Perdew, van Leeuwen and Baerends independently showed that functional derivatives satisfy Eq. (3.3-3.6) [1,4]. Eq. (3.3) and (3.5) are known as the "zero-force" and "zero-torque" theorems [3,5]. Levy and Perdew derived these conditions by employing the Hellmann–Feynman theorem [1], whereas van Leeuwen and Baerends deduced them by using a line integral along the Λ path [4].

If the zero-force and zero-torque theorems do not hold for an approximate v_{x}, then the potential is not translationally and rotationally invariant, and it is not a functional derivative [4]. Evidence given by Gaiduk and Staroverov showed that all existing model potentials violate these conditions and therefore have no parent energy functionals [6]. Thus, the zero-force and zero-torque theorems can be used as tests for determining whether a given potential is not a functional derivative and for examining the properties of a potential.

3.2 Motivation

Although Levy and Perdew, van Leeuwen and Baerends showed that functional derivatives satisfy the zero-force test, they assumed a complete (infinite) basis set. However, in practice, researchers use finite basis sets in any computational calculations, and it is possible that functional derivative tests may produce different results when the calculations are done using a finite basis set. One of our goals in this chapter is to prove that potentials derived from explicit density functionals such as LDA and GGA satisfy the zero-force theorem in any finite basis set. Another goal is to apply these theorems to a new type of model potentials recently developed by Ryabinkin, Kohut and Staroverov (RKS).

3.3 Basis set and basis-set limit

Most *ab initio* and density-functional calculations are performed using a finite set of basis functions that is called a basis set. In DFT, specifically, a Kohn-Sham orbital ϕ_i^{KS} is expressed as a linear combination of basis functions χ_μ,

$$\phi_i^{\mathrm{KS}} = \sum_\mu C_{\mu i} \chi_\mu, \tag{3.10}$$

where $C_{\mu i}$ are the coefficients determined from by solving the Kohn-Sham equations. A Kohn-Sham orbital ϕ_i^{KS} can only be expanded exactly if a complete (infinite) set of basis functions χ_μ is used. However, in practice, one has to use a finite basis set. Therefore, it is important to choose a basis set so that ϕ_i^{KS} can be accurately represented. In this way, the electron density can be written in terms of basis functions,

$$\rho = \sum_\mu \sum_\nu P_{\mu\nu} \chi_\mu \chi_\nu \tag{3.11}$$

where P is the density matrix.

There are two types of basis functions: Slater-type orbitals (STO) and Gaussian-type orbitals (GTO). An STO can be written as

$$\phi^{\mathrm{STO}} = N x^a y^b z^c e^{-\zeta r^2}, \tag{3.12}$$

where N is a normalization constant, a, b, c are related to the angular momentum $L = a+b+c$, while ζ determines the spatial extent of the orbital. Similarly, a GTO can be expressed as

$$\phi^{\mathrm{GTO}} = N x^a y^b z^c e^{-\zeta r}, \tag{3.13}$$

In general, STOs give more accurate results, but they take longer to compute integrals. A combination of n GTOs to mimic an STO is called an STO-nG basis. For example, a basis using 3 GTOs to approximate an STO is called STO-3G.

3.3.1 Types of basis sets

The STO-3G basis set is known as a single-ζ basis set, or a minimal basis set, which indicates that only one basis function is used to define an atomic orbital (AO). For example, N atom has five STO-3G basis functions roughly corresponding to the AOs: $1s, 2s, 2p_x, 2p_y, 2p_z$.

One can increase the accuracy and flexibility of a basis set by using more than one function to define each AO. A double-ζ basis uses two functions for each AO. Similarly, a triple-ζ basis uses three functions. Examples of this type basis set are cc-pCVXZ, where X=D, T, Q, 5, 6,... (D=double, T=triples, Q=quadruple, etc.). The acronym stands for 'correlation-consistent polarized core and valence (double/triple/quadruple/etc.) zeta'.

Another type of basis sets is called a split-valence basis, which uses only one basis function for each core AO, but two or more functions for each valence AO. The reason for this is that core orbitals are weakly affected by their surroundings; valence orbitals, on the other hand, must adapt to chemical bonding. Some of the commonly used split-valence basis sets developed by Pople and co-workers are known by such names as 3-21G, 4-31G and 6-31G. In this case, the first number represents the number of primitive Gaussians functions used for each core AO, and the numbers after the hyphen represent the numbers of primitive functions used for the valence functions. A universal Gaussian basis set (UGBS) is a large basis set that uses the same set of exponents for all primitive GTOs, and only the range of these exponents varies from one element to another.

3.3.2 Basis-set limit

Generally, the more basis functions are used, the more accurate results are obtained. In DFT calculations, a larger basis set is needed to approach the basis set limit. The basis set limit can be extrapolated from several calculations using two or more basis sets.

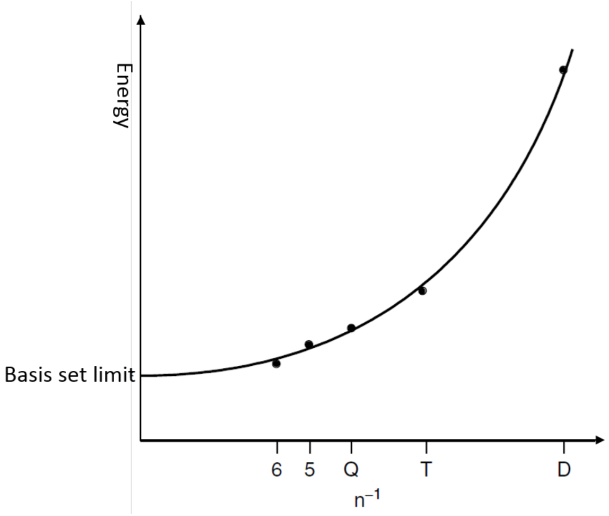

Figure 3.1: Extrapolation to the basis-set limit.

Fig 3.1 is an example of an extrapolation method to estimate the energy of a given system at the basis-set limit using the cc-pVXZ basis sets, where X=D, T, Q, 5, 6.

3.4 Zero-force condition for LDA and GGA exchange functionals

Let us focus on the zero-force condition for LDA and GGA exchange potentials. The LDA exchange potential is written as $v_{\mathrm{x}}^{\mathrm{LDA}} = -C'_{\mathrm{x}}\rho^{1/3}(\mathbf{r})$, where $C'_{\mathrm{x}} = (3/\pi)^{1/3}$. Ignoring the constant C'_{x}, the zero-force theorem for the LDA potential requires that

$$\int \rho^{1/3}(\mathbf{r})\nabla\rho(\mathbf{r})d\mathbf{r} = 0. \tag{3.14}$$

Applying integration by parts to the left-hand side of the above equation, we obtain

$$\int \rho^{1/3}(\mathbf{r})\nabla\rho(\mathbf{r})d\mathbf{r} = \rho^{4/3}(\mathbf{r})|_{-\infty}^{+\infty} - \int \rho(\mathbf{r})\nabla\rho^{1/3}(\mathbf{r})d\mathbf{r}. \tag{3.15}$$

Since the electron density of any finite system vanishes at infinity, the first term at the right-hand side of the above equation is zero. Using this fact and rearranging Eq. (3.15), we obtain

$$\int \left[\rho^{1/3}(\mathbf{r})\nabla\rho(\mathbf{r}) + \rho(\mathbf{r})\nabla\rho^{1/3}(\mathbf{r})\right] d\mathbf{r} = 0. \tag{3.16}$$

Because

$$\nabla\rho(\mathbf{r}) = \nabla[\rho^{1/3}(\mathbf{r})\rho^{1/3}(\mathbf{r})\rho^{1/3}(\mathbf{r})] = 3[\rho^{2/3}(\mathbf{r})\nabla\rho^{1/3}(\mathbf{r})], \tag{3.17}$$

combining (3.17) to Eq (3.16), we obtain

$$4\int \rho(\mathbf{r})\nabla\rho^{1/3}(\mathbf{r})d\mathbf{r} = 0. \tag{3.18}$$

The critical step of our proof is Eq. (3.15). Eq. (3.15) holds as long as the density vanishes at infinity. As shown in Eq. (3.13), every basis function has an exponential decay. Thus, any electron density expressed in a GTO- or STO-type basis set (written as a combination of basis functions) vanishes at infinity. Therefore, we proved that the LDA exchange potential satisfies the zero-force theorem in any basis set as long as the density is integrable, that is, tends to zero at infinity. All densities of finite systems are integrable.

The above analysis is also applicable to any local potential of the form

$$v = C\rho^n(\mathbf{r}), \tag{3.19}$$

where C and n are constants.

Let us now consider a functional of the form

$$F[\rho] = \int f(\mathbf{r}, \rho, \nabla\rho, \nabla^2\rho) d\mathbf{r}, \tag{3.20}$$

where the function f is integrable that is, vanishes sufficiently fast at infinity. For convenience, let us first analyze its gradient

$$\nabla f(\mathbf{r}, \rho, \nabla\rho, \nabla^2\rho) = \frac{\partial f}{\partial x}\mathbf{i} + \frac{\partial f}{\partial y}\mathbf{j} + \frac{\partial f}{\partial z}\mathbf{k}, \tag{3.21}$$

where $\mathbf{i}$, $\mathbf{j}$, $\mathbf{k}$ are unit vectors. Applying the chain rule to the right-hand side of the above equation, we obtain

$$\frac{\partial f}{\partial x} = \frac{\partial f}{\partial \rho}\frac{\partial \rho}{\partial x} + \frac{\partial f}{\partial \nabla\rho} \cdot \frac{\partial \nabla\rho}{\partial x} + \frac{\partial f}{\partial \nabla^2\rho}\frac{\partial \nabla^2\rho}{\partial x}. \tag{3.22}$$

$\frac{\partial f}{\partial y}$ and $\frac{\partial f}{\partial z}$ have the similar formula with respect to y and z. Therefore, we may write ∇f as

$$\nabla f = \frac{\partial f}{\partial \rho}\nabla\rho + \left(\frac{\partial f}{\partial \nabla\rho} \cdot \nabla\right)\nabla\rho + \frac{\partial f}{\partial \nabla^2\rho}\nabla\left(\nabla^2\rho\right), \tag{3.23}$$

where $\nabla\left(\nabla^2\rho\right)$ is a vector whose components are $\frac{\partial^2\nabla\rho}{\partial x}, \frac{\partial^2\nabla\rho}{\partial y}, \frac{\partial^2\nabla\rho}{\partial z}$.

According to the gradient theorem, the fact that $f(\mathbf{r}, \rho, \nabla\rho, \nabla^2\rho)$ vanishes at infinity implies that

$$\int \nabla f(\mathbf{r}, \rho, \nabla\rho, \nabla^2\rho) d\mathbf{r} = 0. \tag{3.24}$$

Substitution of Eq. (3.23) into Eq. (3.24) gives

$$\int \left[\frac{\partial f}{\partial \rho}\nabla\rho + \left(\frac{\partial f}{\partial \nabla\rho} \cdot \nabla\right)\nabla\rho + \frac{\partial f}{\partial \nabla^2\rho}\nabla\left(\nabla^2\rho\right)\right] d\mathbf{r} = 0. \tag{3.25}$$

Integrating by parts the second and third terms under the above integral and assuming that the products of the gradients of f and $\rho(\mathbf{r})$ vanish at infinity we obtain

$$\int \left[\frac{\partial f}{\partial \rho}\nabla\rho - \nabla \cdot \left(\frac{\partial f}{\partial \nabla\rho}\right)\nabla\rho - \nabla\left(\frac{\partial f}{\partial \nabla^2\rho}\right)\nabla^2\rho\right] d\mathbf{r} = 0. \tag{3.26}$$

Integrating by parts the third term under the above integral again we have

$$\begin{gathered}\int\left[\frac{\partial f}{\partial\rho}\nabla\rho-\nabla\cdot\left(\frac{\partial f}{\partial\nabla\rho}\right)\nabla\rho+\nabla^2\left(\frac{\partial f}{\partial\nabla^2\rho}\right)\nabla\rho\right]d\mathbf{r}= \\ \int\nabla\rho\left[\frac{\partial f}{\partial\rho}-\nabla\cdot\left(\frac{\partial f}{\partial\nabla\rho}\right)+\nabla^2\left(\frac{\partial f}{\partial\nabla^2\rho}\right)\right]d\mathbf{r}=0.\end{gathered} \tag{3.27}$$

In Section 1.4, we showed that the functional derivative of a given explicit functional is

$$\frac{\delta F}{\delta\rho}=\frac{\partial f}{\partial\rho}-\nabla\cdot\left(\frac{\partial f}{\partial\nabla\rho}\right)+\nabla^2\left(\frac{\partial f}{\partial\nabla^2\rho}\right), \tag{3.28}$$

so Eq. (3.27) in fact says

$$\int\left(\frac{\delta F}{\delta\rho}\right)\nabla\rho\,d\mathbf{r}=0. \tag{3.29}$$

The above proof holds if the products of derivatives of f and $\rho(\mathbf{r})$ vanish at infinity. In that case, the functional derivative of any generalized gradient approximation satisfes the zero-force theorem for any basis set.

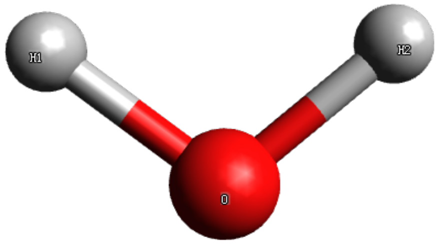

Figure 3.2: Structure of H_2O molecule.

Unfortunately, the zero-force test may give a false positive, meaning that for a molecule with at least one symmetry element the net force from a potential that is not a functional derivative may vanish by symmetry. For example, the total net forces of H_2O molecule from

Table 3.1: Cartesian components and total magnitudes of net forces (in hartrees/bohr) for the H_2O molecule calculated from LB94 potentials using different basis sets and Grid=Ultrafine.

	F_x	F_y	F_z	$\mid \mathbf{F} \mid$
6-31G*	0.000000	0.000000	0.000000	0.000000
cc-pVQZ	0.000000	0.000000	0.000000	0.000000

the LB94 exchange potential (not a functional derivative) are zero (see Table 3.1). This is because the force on the left H atom of H_2O is canceled by the force on the right H atom, so that the total forces vanish. In order to avoid false positives, we use an artificial asymmetric cluster of 4 H atoms (H_4) throughout this chapter (Fig 3.3)

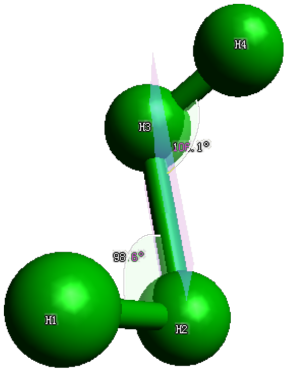

Figure 3.3: Structure of H_4 molecule.

To illustrate our findings for H_4, we applied the zero-force tests to LDA exchange potential using different basis sets, compared with the LB94 exchange potential which is not a functional derivative. The results are listed in Table 3.2.

Table 3.2: Cartesian components and total magnitudes of net forces (in hartrees/bohr) for the H_4 molecule calculated from the LDA and LB94 potentials using different basis sets and Grid=Ultrafine.

	F_x	F_y	F_z	$\mid \mathbf{F} \mid$
LDA				
6-31G*	0.000000	0.000000	0.000000	0.000000
cc-pVQZ	0.000000	0.000000	0.000000	0.000000
UGBS1O	0.000000	0.000000	0.000000	0.000000
UGBS2O	0.000000	0.000000	0.000000	0.000000
LB94				
6-31G*	0.000002	−0.000060	−0.000047	0.000076
cc-pVQZ	0.000075	−0.000261	−0.000093	0.000287
UGBS1O	0.000015	−0.000397	−0.000167	0.000431

In Table 3.2, the magnitudes of net forces and their components were calculated from a potential that is a functional derivatives (LDA) and a potential that is not a functional derivative (LB94). As we can see, the forces obtained from a functional derivative are always zero for any basis set used. However, a potential that is not a functional derivative always violates the zero-force theorem for any basis set.

3.5 Zero-force test for the RKS potential

Orbital-dependent functionals directly constructed from Kohn–Sham orbitals provide better description of molecular properties than the LDA and GGA [7–10]. However, they pose distinctive challenges since they are implicit functionals of the density. In particular, their functional derivatives (Kohn–Sham potentials) cannot be obtained in closed form by explicit functional differentiation of E_{xc} with respect to the density, but may be computed numerically via the optimized effective potential (OEP) method [11–13]. The exchange-only OEP method minimizes the HF total energy expression within the Kohn–Sham scheme

$$v_{\mathrm{x}}^{\mathrm{OEP}}(\mathbf{r}) = \frac{\delta E_{\mathrm{x}}^{\mathrm{exact}}}{\delta \rho(\mathbf{r})}, \tag{3.30}$$

where $E_{\mathrm{x}}^{\mathrm{exact}}$ is the HF exchange energy expression written in terms of Kohn–Sham orbitals.

To obtain $v_{\mathrm{x}}^{\mathrm{OEP}}(\mathbf{r})$ in practice, one has to solve the OEP integral equation, which can be easily done only for systems with spherical symmetry [12]. For atomic and molecular systems, a linear combination of atomic orbitals procedure is required [14, 15], where the orbitals as well as the local potential are expanded in finite basis sets. Unfortunately, the auxiliary basis set turns the OEP method into an ill-posed problem, and the solution of an integral equation depends on what auxiliary basis is chosen.

Because of the high computational cost and the lack of effective OEP solvers, several approximations were developed, such as the Krieger–Li–Iafrate (KLI) [16], localized Hartree–Fock [17] and Becke–Johnson (BJ) approximations [18]. However, all these approximations are not functional derivatives, meaning that they violate the zero-force and zero-torque theorems.

Recently, Ryabinkin, Kohut and Staroverov developed a method to compute the Kohn–

Sham exchange-correlation potential corresponding to a HF electron density [19, 20]. This potential is almost indistinguishable from the exact-exchange OEP, and is dramatically better than all existing models, while having the same low computational cost as KLI and BJ potentials. The RKS potential for a Hartree-Fock wave function may be written as

$$v_{\mathrm{xc}}^{\mathrm{HF}} = v_{\mathrm{xc}}^{\mathrm{hole}} + \bar{\epsilon}^{\mathrm{KS}} - \bar{\epsilon}^{\mathrm{HF}}(\mathbf{r}) + \frac{\tau_{\mathrm{P}}^{\mathrm{HF}}(\mathbf{r})}{\rho^{\mathrm{HF}}(\mathbf{r})} - \frac{\tau_{\mathrm{P}}^{\mathrm{KS}}(\mathbf{r})}{\rho^{\mathrm{KS}}(\mathbf{r})}. \tag{3.31}$$

Here $v_{\mathrm{xc}}^{\mathrm{hole}}$ is the exchange-correlation hole potential of the interacting system built in terms of the HF orbitals

$$v_{\mathrm{xc}}^{\mathrm{hole}} = -\frac{1}{2\rho^{\mathrm{HF}}(\mathbf{r})} \int \frac{|\gamma^{\mathrm{HF}}(\mathbf{r}, \mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}', \tag{3.32}$$

where $\gamma^{\mathrm{HF}}(\mathbf{r}, \mathbf{r}') = \sum_{i=1}^{N} \phi_i^{\mathrm{HF}}(\mathbf{r}) \phi_i^{\mathrm{HF}*}(\mathbf{r}')$ is the spinless reduced density matrix, ϕ_i^{HF} is the spatial part of the ith HF spin orbital, $\bar{\epsilon}^{\mathrm{KS}}(\mathbf{r})$ and $\bar{\epsilon}^{\mathrm{HF}}(\mathbf{r})$ are Kohn–Sham and Hartree–Fock average local ionization energies, given by

$$\bar{\epsilon}^{\mathrm{KS}}(\mathbf{r}) = \frac{1}{\rho^{\mathrm{KS}}(\mathbf{r})} \sum_{i=1}^{N} \epsilon_i^{\mathrm{KS}} |\phi_i^{\mathrm{KS}}(\mathbf{r})|^2, \tag{3.33}$$

$$\bar{\epsilon}^{\mathrm{HF}}(\mathbf{r}) = \frac{1}{\rho^{\mathrm{HF}}(\mathbf{r})} \sum_{i=1}^{N} \epsilon_i^{\mathrm{HF}} |\phi_i^{\mathrm{HF}}(\mathbf{r})|^2, \tag{3.34}$$

where ϵ_i^{KS} and ϵ_i^{HF} are the eigenvalues of Kohn–Sham and Hartree–Fock equations, and $\tau_{\mathrm{P}}^{\mathrm{HF}}(\mathbf{r})$ and $\tau_{\mathrm{P}}^{\mathrm{KS}}(\mathbf{r})$ are Hartree–Fock and Kohn–Sham Pauli kinetic energy densities, defined by

$$\tau_{\mathrm{P}}^{\mathrm{HF}}(\mathbf{r}) = \frac{1}{2\rho^{\mathrm{HF}}} \sum_{i<j}^{N} |\phi_i^{\mathrm{HF}}(\mathbf{r}) \nabla \phi_j^{\mathrm{HF}}(\mathbf{r}) - \phi_j^{\mathrm{HF}}(\mathbf{r}) \nabla \phi_i^{\mathrm{HF}}(\mathbf{r})|^2, \tag{3.35}$$

$$\tau_{\mathrm{P}}^{\mathrm{KS}}(\mathbf{r}) = \frac{1}{2\rho^{\mathrm{KS}}} \sum_{i<j}^{N} |\phi_i^{\mathrm{KS}}(\mathbf{r}) \nabla \phi_j^{\mathrm{KS}}(\mathbf{r}) - \phi_j^{\mathrm{KS}}(\mathbf{r}) \nabla \phi_i^{\mathrm{KS}}(\mathbf{r})|^2, \tag{3.36}$$

In Equation (3.30), $\rho^{\mathrm{KS}} = \rho^{\mathrm{HF}}$, but $\tau_{\mathrm{P}}^{\mathrm{KS}} \neq \tau_{\mathrm{P}}^{\mathrm{HF}}$ and $\bar{\epsilon}^{\mathrm{KS}} \neq \bar{\epsilon}^{\mathrm{HF}}$.

3.5.1 Results and discussion

The RKS potential is almost indistinguishable from the exact OEP when large basis sets are employed [19, 20]. This indicates that the RKS potential is exact in the basis-set limit, and that it is a functional derivative. We wish to find out whether the RKS potential satisfies the zero-force theorem when different basis sets and grids are employed. Therefore, we applied systematic zero-force tests to RKS potentials. All calculations were performed using the modified Gaussian 09 program.

In Table 3.3, the magnitudes of net forces and their components were calculated from the RKS potential using different basis sets and integration grids. The integration grid needs to be specified (by using keyword Grid= *mmmnnn*) for numerical integrations in Gaussian 09 program, where *mmmnnn* is a positive integer, which requests a grid with *mmm* radial shells around each atom and *nnn* angular points in each shell. For example, Grid=399,590 means it has 399 radial shells and 590 angular points per shell. Generally, the more grids used, the more accurate results obtained. For H atom, keyword 'Ultrafine' requests a 99,590 grid. In our calculations, we used three different grids. The net forces and their components did not change as the grids changed, but the magnitude of the net forces decreases as the basis sets increases. The RKS potential passed the zero-force when a very large UGBS2O basis set was used.

As discussed in Section 3.4, a potential that is not a functional derivative always violates the zero-force theorem, while a potential that is a functional derivative satisfies the zero-force theorem for any basis set. The interesting finding is that the net force obtained from RKS potential decreases as the basis set increases. They passed the test when the large basis set

Table 3.3: Cartesian components and total magnitudes of net forces (in hartrees/bohr) for the H_4 molecule calculated from RKS potentials using different basis sets and grids.

	F_x	F_y	F_z	$\mid \mathbf{F} \mid$
Grid=UltraFine				
6-31G*	−0.000360	0.000164	−0.000089	0.000405
cc-pVQZ	−0.000053	0.000023	−0.000023	0.000062
UGBS1O	−0.000027	−0.000025	−0.000020	0.000042
UGBS2O	−0.000003	0.000003	0.000000	0.000004
Grid=399,590				
6-31G*	−0.000360	0.000164	−0.000089	0.000405
cc-pVQZ	−0.000053	0.000023	−0.000023	0.000062
UGBS1O	−0.000027	−0.000025	−0.000020	0.000042
UGBS2O	−0.000003	0.000003	0.000000	0.000004
Grid=999,974				
6-31G*	−0.000360	0.000164	−0.000089	0.000405
cc-pVQZ	−0.000053	0.000023	−0.000023	0.000062
UGBS1O	−0.000027	−0.000025	−0.000020	0.000042
UGBS2O	−0.000003	0.000003	0.000000	0.000004

UGBS2O was used, which indicates that the RKS potential is an almost exact functional derivate of $E_{\mathrm{x}}^{\mathrm{exact}}$. Our result confirm that the RKS potential is virtually indistinguishable from the exact OEP when the large universal Gaussian basis set is employed. RKS potentials are defined in such a way that $\rho^{\mathrm{KS}} = \rho^{\mathrm{HF}}$ only in the basis-set limit (infinite basis). When a small (finite) basis set is used, ρ^{KS} does not equal to ρ^{HF} exactly. In this case, the RKS potential is not a functional derivative and violates the zero-force theorem.

3.6 Summary

We proved analytically that any functional derivative of an explicit density functional satisfies the zero-force theorem. For RKS potentials generated using finite basis set, net exchange-correlation force decreases as the basis set increases. The RKS potential becomes indistinguishable from the exact OEP in the basis-set limit.

Violation of the zero-force theorem by a given v_{xc} indicates that (i) the potential is not translationally invariant, or (ii) it is not a functional derivative. However, passing the zero-force test is not sufficient to ensure that the trial potential is a functional derivative. In addition, even if a functional derivative satisfies the zero-force theorem, its parent functional may not be translationally invariant.

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Curriculum Vitae

Hanqing Zhao

EDUCATION

Master of Science in Chemistry, Polytechnic Institute of New York University, 2014

Bachelor of Science in Applied Chemistry, Wuhan University, 2007

Minor Degree: Biotechnology

WORK & INTERNSHIP EXPERIENCE

Research volunteer, Prof. Mark E. Tuckerman's Laboratory of NYU, 2013–2014

Research Assistant, Prof. Richard Gross's Laboratory of NYU–Poly, 2013

Assistant engineer, Zhongleng Asia Pacific (Tianjin) Energy Technology Co., Ltd., 2012

High School Chemistry Teacher, Jingxi Fuzhou Innovation School, 2008–2012

Chemical Technician, Tianjin Zhentao Plexiglass Product Factory, 2008

HONORS & AWARDS

Graduate Innovation Fellowship, NYU–Poly, 2012

Graduate Innovation Fellowship, NYU–Poly, 2013

GRADUATE COURSES TAKEN AT UWO

SCICOMP 9502A	Scientific Computing	84
CHEM 9444A	Computer Simulations in Chemistry	86