

COMPUTING KINETIC ENERGY FROM ELECTRON DISTRIBUTION FUNCTIONS

Computing the Kinetic Energy from Electron Distribution Functions

By

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ABSTRACT

Approximating the kinetic energy as a functional of the electron density is a daunting, but important, task. For molecules in equilibrium geometries, the kinetic energy is equal in magnitude to the total electronic energy, so achieving the exquisite accuracy in the total energy that is needed for chemical applications requires similar accuracy for the kinetic energy functional. For this reason, most density functional theory (DFT) calculations use the Kohn-Sham method, which provides a good estimate for the kinetic energy. But the computational cost of Kohn-Sham DFT calculations has a direct dependence on the total number of electrons because the Kohn-Sham method is based on the orbital picture, with one orbital per electron. Explicit density functionals, where the kinetic energy is written explicitly in terms of the density, and not in terms of orbitals, are much faster to compute. Unfortunately, the explicit density functionals in the literature had disappointing accuracy. This dissertation introduces several new approaches for orbital-free density functional methods.

One can try to include information about the Pauli principle using the exchange hole. In the weighted density approximation (WDA), a model for the exchange hole is used to approximate the one-electron density matrix, which is then used to compute the kinetic energy. This thesis introduces a symmetric, normalized, weighted density approximation using the exchange hole of the uniform electron gas. Though the key results on kinetic energy are not accurate enough, an efficient algorithm is introduced which, with a more sophisticated hole model, might give better results.

The effects of electron correlation on the kinetic energy can be modeled by

moving beyond the one-electron distribution function (the electron density) to higher-order electron distributions (k-electron DFT). For example, one can model electron correlation directly using the pair electron density. In this thesis, we investigated two different functionals of the pair density, the Weizsäcker functional and the March-Santamaria functional. The Weizsäcker functional badly fails to describe the accurate kinetic energy due to the N -representability problem. The March-Santamaria functional is exact for a single Slater determinant, but fails to adequately model the effects of electron correlation on the kinetic energy.

Finally, we established a relation between Fisher information and Weizsäcker kinetic energy functional. This allowed us to propose generalisations of the Weizsäcker kinetic energy density functional. It is hoped that the link between information theory and kinetic energy might provide a new approach to deriving improved kinetic energy functionals.

Keywords: *Kinetic energy functional, Density functional theory (DFT), von-Weizsäcker functional, March-Santamaria functional, Thomas-Fermi model, density matrix, Two-point normalization, Pair-density functional theory (PDFT).*

To my parents, Dulal Chakrabarti and Mira Chakraborty
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PREFACE

This thesis investigates the kinetic energy functional in one- and many-electron density functional theory. It consists of an introduction, one book chapter, three journal articles (two published and one submitted), and concluding remarks. The introduction will be published as book chapter in 2012. In this section my contribution to each chapter is discussed.

Chapter I provides background on *ab initio* approaches to electronic structure theory and on density functional theory (DFT). It also introduces the basic mathematical ideas behind kinetic energy functionals and their numerical evaluation. It also provides a brief overview on the formal mathematical properties of kinetic energy functional. I composed Chapter I, which was then edited by my advisor (Paul Ayers).

Chapter II is a reprint of a book chapter, “Derivation of Generalized von-Weizsäcker Kinetic Energies from Quasiprobability Distribution Functions”, published as Chapter 2 in the book Statistical Complexity, edited by K.D. Sen. This chapter emerged from my quest to establish a relation between the Fisher information and the von Weizsäcker functional based on quasi-probability distributions. Prof. Ayers wrote a first draft of the chapter based on my typed research notes; I then edited and finalized the chapter.

Chapter III, is a reprint of a journal article, “Failure of the Weizsäcker Kinetic Energy Functional for One-, Two-, and Three-Electron Distribution Functions”, published in the *Journal Of Mathematical Chemistry*. While the many-electron Weizsäcker functional has often been mentioned in the literature, it had never before been

systematically tested. Our tests reveal that the Weizsäcker functional gives very poor results, which we attribute to the N -representability error of the Weizsäcker functional. I performed all of the research in this chapter; the manuscript was then prepared jointly with Prof. Ayers.

Chapter IV is a reprint of a journal article, “Failure of the March-Santamaria Kinetic Energy Functional for Two-Electron Distribution Functions”, published in *Journal Of Mathematical Chemistry*. This article addresses the other explicit pair density functional that is commonly discussed in the literature. While the March-Santamaria functional is exact for independent electrons, it deteriorates as the extent of electron correlation increases. We discuss why this occurs. I performed all the calculations and analysis in this chapter, and then Prof. Ayers and I prepared the manuscript together.

Chapter V is a preprint of a journal article on the evaluating the kinetic energy using a model exchange hole based on UEG model. It shows the success and failures of the proposed model, which is a type of generalized weighted density approximation. I have written the whole chapter, which was then edited by Prof. Ayers. This chapter also predicts some improved model, which have not yet been implemented.

Chapter VI summarizes the research in this thesis and discusses future prospects and proposals.

In all of the chapters, most of the scientific research—including writing the computer programs, selecting appropriate computational tests, generating numerical data, and analyzing the data—was performed by the author. Especially chapters I, II, V, and VI are based on the author’s independent research.

Chapter I

Introduction

I. A Quantum Mechanics in Chemistry

1. The Importance of Quantum Mechanics in Chemistry

Chemistry is the study of molecules and materials, with emphasis on how the atoms in existing molecules and materials can be rearranged and recombined to form new substances with useful properties. Chemical substances are composed of electrons and atomic nuclei; for the purposes of chemistry, electrons and nuclei are immutable pointlike particles with specified masses and charges. The behavior of chemical substances is governed by the electromagnetic force, especially the Coulombic attractions between negatively charged electrons and positively charged nuclei and the Coulombic repulsions between pairs of electrons and pairs of nuclei. (Other forces—gravitation, the forces that govern nuclear rearrangements—are either negligible or outside the scope of chemistry.) Atomic nuclei and electrons have very little mass, so their motion is therefore governed by the laws of quantum mechanics. Therefore, building predictive models for chemical phenomenon demands a quantum mechanical treatment.¹⁻³

The governing law of nonrelativistic molecular quantum mechanics is the time-dependent Schrödinger equation,

$$\hat{H}\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N; \mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_P; t) = i\hbar \frac{\partial \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N; \mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_P; t)}{\partial t} \quad (1)$$

where t is the time, $\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N$ are the positions of the electrons, $\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_P$ are the positions of the atomic nuclei, and $\hbar = h/2\pi$ is Planck's constant divided by 2π . The wave-function, Ψ , encapsulates all the observable information about any quantum-mechanical system. The Hamiltonian operator,

$$\hat{H}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N; \mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_P) = \hat{T}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N; \mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_P) + V(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N; \mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_P) \quad (2)$$

is the energy operator for the system. It is the sum of the kinetic energy operator,

$$\hat{T}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N; \mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_P) = \sum_{i=1}^N \frac{\hat{\mathbf{p}}_i \cdot \hat{\mathbf{p}}_i}{2m_e} + \sum_{\alpha=1}^P \frac{\hat{\mathbf{P}}_{\alpha} \cdot \hat{\mathbf{P}}_{\alpha}}{2M_{\alpha}} \quad (3)$$

and the potential energy function. The momentum operator in quantum mechanics is defined as

$$\hat{\mathbf{p}} = i\hbar \nabla. \quad (4)$$

In the absence of any external electromagnetic fields, the potential energy function is

$$V(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N; \mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_P) = \underbrace{-\sum_{i=1}^N \sum_{\alpha=1}^P \frac{Z_{\alpha} e^2}{4\pi\epsilon_0 |\mathbf{r}_i - \mathbf{R}_{\alpha}|}}_{\text{electron-nuclear attraction}} + \underbrace{\sum_{i=1}^{N-1} \sum_{j=i+1}^N \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_i - \mathbf{r}_j|}}_{\text{electron-electron repulsion}} + \underbrace{\sum_{\alpha=1}^{P-1} \sum_{\beta=\alpha+1}^P \frac{Z_{\alpha} Z_{\beta} e^2}{4\pi\epsilon_0 |\mathbf{R}_{\alpha} - \mathbf{R}_{\beta}|}}_{\text{nuclear-nuclear repulsion}} \quad (5)$$

In these equations, e denotes the charge on the electron, m_e denotes the mass of the electron, $Z_\alpha e$ is the charge on the α^{th} atomic nucleus, and M_α is the mass of the α^{th} atomic nucleus.

Substituting the form of the momentum operator into Eq. (3) allows us to rewrite the molecular Hamiltonian as

$$\begin{aligned} \hat{H}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N; \mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_P) = & \sum_{i=1}^N -\frac{\hbar^2}{2m_e} \nabla_i^2 + \sum_{\alpha=1}^P -\frac{\hbar^2}{2M_\alpha} \nabla_\alpha^2 - \sum_{i=1}^N \sum_{\alpha=1}^P \frac{Z_\alpha e^2}{4\pi\epsilon_0 |\mathbf{r}_i - \mathbf{R}_\alpha|} \\ & + \sum_{i=1}^{N-1} \sum_{j=i+1}^N \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_i - \mathbf{r}_j|} + \sum_{\alpha=1}^{P-1} \sum_{\beta=\alpha+1}^P \frac{Z_\alpha Z_\beta e^2}{4\pi\epsilon_0 |\mathbf{R}_\alpha - \mathbf{R}_\beta|} \end{aligned} \quad (6)$$

All chemical phenomena can be modeled by solving the time-dependent Schrödinger equation with an appropriate Hamiltonian, but this is only practical for very small systems because the computational cost of numerical techniques for solving the time-dependent Schrödinger equation grows exponentially with the number of particles.

In the absence of time-dependent external fields, the molecular Hamiltonian is time-independent. This allows us to remove the time-dependence from the Schrödinger equation, obtaining the time-independent Schrödinger equation,

$$\hat{H}\Psi_k = E_k \Psi_k \quad (7)$$

This is an eigenvalue equation. Furthermore, it is usually permissible to treat the atomic nuclei as classical particles. This assumption permeates chemistry; it is implicit in the concept of molecular structure, wherein the nuclei occupy fixed positions, surrounded by a swarm of electrons. Assuming that nuclei can be considered classically, the electrons only need to be treated quantum mechanically. This gives rise to the electronic Hamiltonian,

$$\hat{H}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \sum_{i=1}^N -\frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_{i=1}^N \sum_{\alpha=1}^P \frac{Z_{\alpha} e^2}{4\pi\epsilon_0 |\mathbf{r}_i - \mathbf{R}_{\alpha}|} + \sum_{i=1}^{N-1} \sum_{j=i+1}^N \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_i - \mathbf{r}_j|} \quad (8)$$

and the associated time-independent electronic Schrödinger equation,

$$\left[\sum_{i=1}^N -\frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_{i=1}^N \sum_{\alpha=1}^P \frac{Z_{\alpha} e^2}{4\pi\epsilon_0 |\mathbf{r}_i - \mathbf{R}_{\alpha}|} + \sum_{i=1}^{N-1} \sum_{j=i+1}^N \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_i - \mathbf{r}_j|} \right] \Psi_k(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = E_k \Psi_k(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \quad (9)$$

In quantum chemistry we typically use atomic units, where $\hbar = m_e = e^2/4\pi\epsilon_0 = 1$.

Henceforth we will use atomic units to simplify the notation.

When one or more of the atomic nuclei in a molecule has a large positive charge, the speed of an electron can be an appreciable fraction of the speed of light. In such cases, the electronic Schrödinger equation is inappropriate and one

should instead solve its relativistic generalization, which is called the Dirac-Coulomb equation. In practice, by making suitable approximations, almost all chemical phenomena can be described using the electronic Schrödinger equation or a small modification thereto.⁴ For this reason, we will only consider the electronic Schrödinger equation in the following discussion.

2. Spin and the Pauli Exclusion Principle

Because electrons are fermions, not every solution to the time-independent N -electron Schrödinger equation is a physically acceptable. Fermions are governed by the Pauli exclusion principle, so it is impossible for two electrons to exist in the same quantum state. The quantum state of an electron is specified by its position and its spin. While an electron can be located at any position in space, an electron can only have two types of spin, which are usually called $+1/2$ and $-1/2$, or up and down, or α and β . (However, when non-collinear magnetic fields are present or when relativistic effects are important, the Hamiltonian operator depends on spin and this simple picture breaks down.) The requirement that no two electrons with the same spin can be located at the same position in space arises from the anti-symmetry of the wave-function,

$$\Psi(\mathbf{r}_1, \sigma_1; \dots; \mathbf{r}_i, \sigma_i; \dots; \mathbf{r}_j, \sigma_j; \dots; \mathbf{r}_N, \sigma_N) = -\Psi(\mathbf{r}_1, \sigma_1; \dots; \mathbf{r}_j, \sigma_j; \dots; \mathbf{r}_i, \sigma_i; \dots; \mathbf{r}_N, \sigma_N). \quad (10)$$

That is, if one interchanges the spatial and spin coordinates of two electrons, the wave-function changes sign. Only the anti-symmetric solutions of the electronic Schrödinger equation represent electronic systems.

When an electronic system is characterized by a specific anti-symmetric wave-function, the system is said to be in a pure state. Sometimes the system, however, is in a statistical mixture of several such states. Mixed states are described by the N -electron density matrices,

$$\Gamma_N(\mathbf{r}_1, \sigma_1; \dots; \mathbf{r}_N, \sigma_N; \mathbf{r}'_1, \sigma'_1; \dots; \mathbf{r}'_N, \sigma'_N) = \sum_{k=1}^{\text{\# of states}} p_k \Psi_k(\mathbf{r}_1, \sigma_1; \dots; \mathbf{r}_N, \sigma_N) \Psi_k^*(\mathbf{r}'_1, \sigma'_1; \dots; \mathbf{r}'_N, \sigma'_N) \quad (11)$$

where

$$1 = \sum_{k=1}^{\text{\# of states}} p_k \quad (12)$$

and

$$0 \leq p_k \leq 1 \quad (13)$$

The number p_k represents the probability of observing the system in the pure state described by the N -electron wave-function Ψ_k .

Equating the primed and unprimed coordinates in the N -electron density matrix gives the N -electron distribution function,

$$\begin{aligned}\rho_N(\mathbf{r}_1, \sigma_1; \dots; \mathbf{r}_N, \sigma_N) &= \Gamma_N(\mathbf{r}_1, \sigma_1; \dots; \mathbf{r}_N, \sigma_N; \mathbf{r}_1, \sigma_1; \dots; \mathbf{r}_N, \sigma_N) \\ &= \sum_{k=1}^{\text{\#of states}} p_k |\Psi_k(\mathbf{r}_1, \sigma_1; \dots; \mathbf{r}_N, \sigma_N)|^2\end{aligned}\quad (14)$$

The N -electron distribution function measures the probability of observing electrons with spins $\sigma_1, \sigma_2, \dots, \sigma_N$ at positions $\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N$.

The N -electron wave-function, the N -electron density matrix, and the N -electron density all completely determine the state of an electronic system. Only the N -electron distribution function, however, has a direct physical interpretation.

3. Variational Approaches to the Electronic Structure of Molecules

The N -electron Schrödinger equation is a $3N$ -dimensional partial differential equation. Numerical methods for solving this type of equation typically have computational costs that grow exponentially with the number of dimensions. For this reason, direct approaches for solving the electronic Schrödinger equation have only been applied to systems with ten or fewer electrons. To describe chemistry with quantum mechanics, approximations are required.

Conventional quantum chemistry uses two approaches to approximate the solutions of the electronic Schrödinger equation.¹⁻³ Wave-function-based approaches use a simplified form for the wave-function. Density-based approaches replace the wave-function with a simpler quantity that still contains all of the information needed to describe the properties of chemical substances. Both approaches rely on variational principles.

It seems that every physical law is subsumed by a deeper, more fundamental, variational principle.^{5,6} For example, the time-dependent Schrödinger equation is a particular manifestation of the quantum principle of stationary action. Similarly, the time-independent Schrödinger equation can be derived from the more fundamental stationary principle for the energy,

$$E_k = \underbrace{\text{stat}}_{\substack{\left| \Psi \right| = \sum_{\sigma_1=\alpha,\beta} \cdots \sum_{\sigma_N=\alpha,\beta} \int \cdots \int \Psi^*(\mathbf{r}_1, \sigma_1; \dots; \mathbf{r}_N, \sigma_N) \hat{H} \Psi(\mathbf{r}_1, \sigma_1; \dots; \mathbf{r}_N, \sigma_N) d\mathbf{r}_1 \dots d\mathbf{r}_N \\ \Psi(\mathbf{r}_1, \sigma_1; \dots; \mathbf{r}_N, \sigma_N) \text{ is antisymmetric}}} \left[\sum_{\sigma_1=\alpha,\beta} \cdots \sum_{\sigma_N=\alpha,\beta} \int \cdots \int \Psi^*(\mathbf{r}_1, \sigma_1; \dots; \mathbf{r}_N, \sigma_N) \hat{H} \Psi(\mathbf{r}_1, \sigma_1; \dots; \mathbf{r}_N, \sigma_N) d\mathbf{r}_1 \dots d\mathbf{r}_N \right] \quad (15)$$

The argument in this equation is the quantum mechanical expectation value for the energy of a quantum state described by the wave-function Ψ . (Quantum

mechanical expectation values like this can be written compactly using Dirac notation. For example,

$$\begin{aligned}\langle E \rangle &= \langle \Psi | \hat{H} | \Psi \rangle \\ &= \sum_{\sigma_1=\alpha,\beta} \sum_{\sigma_2=\alpha,\beta} \cdots \sum_{\sigma_N=\alpha,\beta} \iint \cdots \int \left[\Psi^*(\mathbf{r}_1, \sigma_1; \mathbf{r}_2, \sigma_2; \dots; \mathbf{r}_N, \sigma_N) \right. \\ &\quad \left. \times \hat{H} \Psi(\mathbf{r}_1, \sigma_1; \mathbf{r}_2, \sigma_2; \dots; \mathbf{r}_N, \sigma_N) \right] d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_N.\end{aligned}\tag{16}$$

Expression (15) indicates that one should search over all anti-symmetric N -electron wave-functions that are normalized to one,

$$1 = \langle \Psi | \Psi \rangle = \sum_{\sigma_1=\alpha,\beta} \sum_{\sigma_2=\alpha,\beta} \cdots \sum_{\sigma_N=\alpha,\beta} \iint \cdots \int |\Psi(\mathbf{r}_1, \sigma_1; \mathbf{r}_2, \sigma_2; \dots; \mathbf{r}_N, \sigma_N)|^2 d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_N,\tag{17}$$

and locate those wave-functions for which the expectation value of the energy is stationary, i.e., one should locate wave-functions for which a small, first-order, anti-symmetric, and normalization-preserving change in the wave-function produces only an (even smaller) second-order change in the energy. The stationary energy values so located are the eigenvalues of the time-independent electronic Schrödinger equation and the associated wave-functions,

$$\Psi_k = \arg \min_{\left\{ \Psi \mid \begin{array}{l} \langle \Psi | \Psi \rangle = 1 \\ \Psi \text{ is antisymmetric} \end{array} \right\}} \langle \Psi | \hat{H} | \Psi \rangle\tag{18}$$

are its eigenvectors.

If one uses a Lagrange multiplier called E to impose the normalization constraint, the variational principle can be rewritten as the functional differential equation,

$$0 = \frac{\delta}{\delta\Psi} \left(\langle \Psi | \hat{H} | \Psi \rangle - E \langle \Psi | \Psi \rangle \right). \quad (19)$$

By evaluating the functional derivatives, one discovers that the time-independent Schrödinger equation, Eq.(7), is the Euler-Lagrange equation for the stationary energy principle.

Functional derivatives appear throughout the following analysis. The derivative of a functional indicates how its value changes when the value of its argument changes,

$$dE = \int \frac{\delta E}{\delta\Psi(\tau)} \delta\Psi(\tau) d\tau \quad (20)$$

or, more explicitly,

$$E[\Psi + \Delta\Psi] - E[\Psi] = \int \frac{\delta E}{\delta\Psi(\tau)} \Delta\Psi(\tau) d\tau + \left(\begin{array}{l} \text{terms depending on second} \\ \text{and higher powers of } \Delta\Psi \end{array} \right). \quad (21)$$

Functional derivatives can be evaluated directly from the definition using Eq. (21)

.

4. Wave-function-Based Approaches

In wave-function-based approaches,¹⁻³ approximate solutions to the electronic Schrödinger equations are found by assuming that the wave-function has a simple, computationally tractable form. The parameters in the wave-function model are then determined using either the Schrödinger equation itself or, more commonly, the variational principle.

The simplest form of electronic wave-function that is normalized and anti-symmetric is a Slater determinant of one-electron wave-functions,

$$\Phi(\mathbf{r}_1, \sigma_1; \mathbf{r}_2, \sigma_2; \dots; \mathbf{r}_N, \sigma_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(\mathbf{r}_1)\sigma_1(1) & \phi_2(\mathbf{r}_1)\sigma_2(1) & \cdots & \phi_N(\mathbf{r}_1)\sigma_N(1) \\ \phi_1(\mathbf{r}_2)\sigma_1(2) & \phi_2(\mathbf{r}_2)\sigma_2(2) & \cdots & \phi_N(\mathbf{r}_2)\sigma_N(2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(\mathbf{r}_N)\sigma_1(N) & \phi_2(\mathbf{r}_N)\sigma_2(N) & \cdots & \phi_N(\mathbf{r}_N)\sigma_N(N) \end{vmatrix} \quad (22)$$

The one-electron wave-function are called orbitals; they are chosen to be orthogonal and normalized,

$$\delta_{ij} = \int \phi_i^*(\mathbf{r}) \phi_j(\mathbf{r}) d\mathbf{r} . \quad (23)$$

The Hartree-Fock method is derived by assuming that the wave-function is a Slater determinant, invoking the variational principle, and finding the stationary values of the energy. Evaluating the functional derivative in Eq. (19) reveals that

the Hartree-Fock orbitals can be determined by solving a system of one-electron Schrödinger equations,

$$\left\{ \left(-\frac{1}{2} \nabla^2 + \sum_{\alpha=1}^P \frac{-Z_{\alpha}}{|\mathbf{r} - \mathbf{R}_{\alpha}|} + \hat{w}[\phi_1, \dots, \phi_N; \mathbf{r}] \right) \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r}) \right\}_{i=1}^N \quad (24)$$

The operator $\hat{w}(\mathbf{r})$ represents the average potential energy that an electron in the spin-orbital ϕ_i feels due to the other electrons in the system. Because the electrons in Hartree-Fock theory feel only the average effects of the other electrons, the Hartree-Fock method is said to neglect electron correlation. The difference between the Hartree-Fock energy and the true energy is called the correlation energy,

$$E_c = E_{\text{HF}} - E_{\text{exact}} \quad (25)$$

For the ground state, the correlation energy is always positive: the Hartree-Fock energy is always too high. This is easily derived from the variational principle. The ground electronic state is the state with lowest energy, so in the ground state the stationary principle becomes a minimization,

$$E_0 = E_{\text{g.s.}} = \min_{\left\{ \begin{array}{l} \langle \Psi | \Psi \rangle = 1 \\ \Psi \text{ is antisymmetric} \end{array} \right\}} \langle \Psi | \hat{H} | \Psi \rangle \quad (26)$$

The ground-state energy in Hartree-Fock theory is obtained when the domain of the minimization is restricted to Slater determinants, which is a tiny subset of the set of all possible N -electron wave-functions. Therefore,

$$E_0 = \min_{\left\{ \Psi \mid \begin{array}{l} \langle \Psi | \Psi \rangle = 1 \\ \Psi \text{ is antisymmetric} \end{array} \right\}} \langle \Psi | \hat{H} | \Psi \rangle < \min_{\left\{ \Psi \mid \begin{array}{l} \langle \Psi | \Psi \rangle = 1 \\ \Psi \text{ is antisymmetric} \\ \Psi \text{ is a Slater determinant} \end{array} \right\}} \langle \Psi | \hat{H} | \Psi \rangle = E_{\text{HF}}.$$

(27)

The correlation energy is chemically important, so Hartree-Fock theory is unsuitable for modeling many chemical processes. Although Hartree-Fock theory often fails to give accurate predictions for chemical observables, the picture of electrons occupying one-electron orbitals that underlies the Hartree-Fock approximation is ubiquitous in chemistry.

The wave-function-based methods that are commonly used in computational chemistry either correct the Hartree-Fock method for the effects of electron correlation (using, e.g., many-body perturbation theory) or extend the Hartree-Fock method by using a more complicated form for the wave-function (e.g., the configuration interaction and coupled-cluster methods). The drawback of these methods is their high computational cost. One advantage of approaches based on optimizing the parameters in a model wave-function is that the energy obtained is a rigorous upper bound to the true energy. Therefore, when comparing

variational wave-function-based methods, the most accurate method is the one with the lowest energy. When comparing non-variational approaches, it is often impossible to decide which method is most accurate.

5. Density-Based Approaches

Wave-function-based approaches to the electronic Schrödinger equation are computationally daunting because the dimensionality of the wave-function grows as the number of electrons increases. Therefore, one confronts either exponentially increasing computational costs (if one chooses to explicitly account for the increasing dimensionality) or steadily decreasing computational accuracy (if one chooses a simple, computationally tractable, model wave-function with a lower effective dimension). Density-based approaches are based on the idea that there are alternative descriptors for electronic systems that are much simpler than the wave-function. The most popular such descriptor is the electron density.^{1,7-9}

The electron density is the probability of observing an electron at a specified point in space,

$$\begin{aligned}\rho(\mathbf{r}) &= \left\langle \Psi \left| \sum_{i=1}^N \delta(\mathbf{r}_i - \mathbf{r}) \right| \Psi \right\rangle \\ &= N \sum_{\sigma_1=\alpha,\beta} \sum_{\sigma_2=\alpha,\beta} \sum_{\sigma_3=\alpha,\beta} \cdots \sum_{\sigma_N=\alpha,\beta} \iint \cdots \int |\Psi(\mathbf{r}, \sigma_1; \mathbf{r}_2, \sigma_2; \mathbf{r}_3, \sigma_3; \dots; \mathbf{r}_N, \sigma_N)|^2 d\mathbf{r}_2 d\mathbf{r}_3 \dots d\mathbf{r}_N\end{aligned}\quad (28)$$

The electron density is defined so that it is normalized to the number of electrons,

$$N = \int \rho(\mathbf{r}) d\mathbf{r} \quad . \quad (29)$$

The probability of observing an electron at a point in space is always greater than or equal to zero, so the electron density is nonnegative,

$$0 \leq \rho(\mathbf{r}). \quad (30)$$

Somewhat surprisingly, every property of an electronic system can be determined from its electron density.¹⁰ In particular, the ground state energy can be determined from the variational principle for the electron density,

$$E_0 = \min_{\left\{ \rho \left| \begin{array}{l} 0 \leq \rho(\mathbf{r}) \\ N = \int \rho(\mathbf{r}) d\mathbf{r} \end{array} \right. \right\}} E_v[\rho] \quad (31)$$

The notation indicates that one should search over all nonnegative N -electron densities and find the one with lowest energy. That energy is the ground-state electronic energy, and its associated density is the ground state electron density. Unlike wave-function-based methods, where the energy functional,

$$E[\Psi] = \langle \Psi | \hat{H} | \Psi \rangle \quad (32)$$

is known exactly, in density-based methods the energy functional, $E_v[\rho]$, must be approximated. In density functional theory (DFT), one uses the electron density as the fundamental descriptor of an electronic system.

Developing improved approximations to the energy density functional, $E_v[\rho]$, is very difficult and, more than 80 years after the first approximations were proposed, approximating the energy functional is still a very active area of research.¹¹⁻¹⁴ This frustratingly slow progress has motivated researchers to consider alternative descriptors which contain more information than the electron density, but less information than the electronic wave-function.¹⁵ For example, the electron pair density, or two-electron distribution function, can also be used as the fundamental descriptor of an electronic system.^{16,17} More generally, the k -density, or k -electron distribution function,

$$\rho_k(\mathbf{q}_1, \mathbf{q}_2, \dots, \mathbf{q}_k) = \left\langle \Psi \left| \sum_{\substack{i_1=1 \\ i_2 \neq i_1}}^N \sum_{\substack{i_2=1 \\ i_3 \neq i_1}}^N \cdots \sum_{\substack{i_k=1 \\ i_k \neq i_1 \\ i_k \neq i_2 \\ \vdots \\ i_k \neq i_{k-1}}}^N \delta(\mathbf{r}_{i_1} - \mathbf{q}_1) \delta(\mathbf{r}_{i_2} - \mathbf{q}_2) \cdots \delta(\mathbf{r}_{i_k} - \mathbf{q}_k) \right| \Psi \right\rangle \quad (33)$$

can be used as the fundamental descriptor of chemical substances.^{18,19} The advantage of approaches based on the k -density, with $k \geq 2$, is that the potential energy can be evaluated exactly, so only the kinetic energy portion of $E_v[\rho_k]$ needs to be approximated. However, there has been very little work on designing kinetic energy functionals for higher-order electron distribution functions, and there has been even less testing of such functionals. This thesis attempts to explore new functionals (chapter 2) and test previously proposed functionals (chapters 3 and 4).

Most of the research on higher-order electron distribution functions has focused on the pair density.^{16,17,20} The pair density represents the probability of simultaneously observing one electron at \mathbf{r}_1 and another electron at \mathbf{r}_2 . It is normalized to the number of electron pairs,

$$N(N-1) = \iint \rho_2(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2. \quad (34)$$

As before, the ground state energy and pair density can be determined using a variational principle,

$$E_0 = \min_{\left\{ \begin{array}{l} 0 \leq \rho_2(\mathbf{r}_1, \mathbf{r}_2) \\ \rho_2(N(N-1)) = \iint \rho_2(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \\ \rho_2(\mathbf{r}_1, \mathbf{r}_2) \text{ is } N\text{-representable} \end{array} \right\}} E_v[\rho_2] \quad (35)$$

Using the pair density, instead of the electron density, as the fundamental descriptor of the system has two disadvantages. The first disadvantage is that the pair density is a six-dimensional function, so it is a more complicated mathematical object than the three-dimensional electron density function. The more severe disadvantage is that the minimization in Eq. (35) has a very difficult constraint, namely, the pair density must correspond to some N -electron system.¹⁹⁻²³ That is, there must exist some mixture of N -electron wave-functions for which

$$\rho_2(\mathbf{q}_1, \mathbf{q}_2) = \sum_{k=1}^{\text{\# of states}} p_k \left\langle \Psi_k \left| \sum_{i_1=1}^N \sum_{\substack{i_2=1 \\ i_2 \neq i_1}}^N \delta(\mathbf{r}_1 - \mathbf{q}_1) \delta(\mathbf{r}_2 - \mathbf{q}_2) \right| \Psi_k \right\rangle. \quad (36)$$

Such pair densities are said to be N -representable. Pair densities that are not N -representable do not describe N -electron systems. That is, the requirement that the variational principle for the pair density consider only N -representable functions is analogous to the requirement that the variational principle for the wave-function consider only normalized, anti-symmetric wave-functions.

Determining whether a given 6-dimensional function corresponds to an N -electron system is extraordinarily difficult, so in practice both the energy functional and the constraints on the minimization must be approximated in pair-density functional theory (2-DFT). These problems are exacerbated in methods based on even higher-order electron distribution functions because the

computational difficulty of working with the k -density and the difficulty of determining whether a given k -density is N -representable grow rapidly with k .

The difficulty of approximating the kinetic energy functional is removed if one considers, instead of the k -density, the k -electron reduced density matrices,²⁴⁻

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$$\Gamma_k(\mathbf{q}_1, \dots, \mathbf{q}_k; \mathbf{q}'_1, \dots, \mathbf{q}'_k) = \binom{N}{k} \int \dots \int \Gamma_N(\mathbf{q}_1, \dots, \mathbf{q}_k, \mathbf{r}_{k+1}, \dots, \mathbf{r}_N; \mathbf{q}'_1, \dots, \mathbf{q}'_k, \mathbf{r}_{k+1}, \dots, \mathbf{r}_N) d\mathbf{r}_{k+1} \dots d\mathbf{r}_N \quad (37)$$

Alternatively,

$$\Gamma_k(\mathbf{q}_1, \dots, \mathbf{q}_k; \mathbf{q}'_1, \dots, \mathbf{q}'_k) = \sum_{k=1}^{\# \text{ of states}} p_k \langle \Psi_k | \hat{\psi}^+(\mathbf{q}'_1) \hat{\psi}^+(\mathbf{q}'_2) \dots \hat{\psi}^+(\mathbf{q}'_k) \hat{\psi}(\mathbf{q}_k) \dots \hat{\psi}(\mathbf{q}_2) \hat{\psi}(\mathbf{q}_1) | \Psi_k \rangle \quad (38)$$

where $\hat{\psi}^+(\mathbf{q})$ ($\hat{\psi}(\mathbf{q})$) is the quantum mechanical field operator for creating (annihilating) an electron at the point \mathbf{q} . The k -electron distribution function (k -density) is obtained by setting the primed and unprimed variables equal in the k -electron density matrix (k -matrix),

$$\rho_k(\mathbf{q}_1, \dots, \mathbf{q}_k) = \Gamma_k(\mathbf{q}_1, \dots, \mathbf{q}_k; \mathbf{q}_1, \dots, \mathbf{q}_k) \quad (39)$$

In density matrix functional theory, the k -matrix is used as the fundamental descriptor of an electronic system. For $k \geq 2$, the exact energy

functional of the k -matrix is known explicitly, but the N -representability problem is still daunting.²¹ For $k = 1$, the exact energy functional is not known, but the exact kinetic energy functional is known and the N -representability problem is unproblematic.²⁸

By regarding the k -matrix as an integral kernel, one can define its eigenvectors and eigenvalues,

$$\iint \cdots \int \Gamma_k(\mathbf{q}_1, \dots, \mathbf{q}_k; \mathbf{q}'_1, \dots, \mathbf{q}'_k) \phi_i(\mathbf{q}'_1, \mathbf{q}'_2, \dots, \mathbf{q}'_k) d\mathbf{q}'_1 d\mathbf{q}'_2 \dots d\mathbf{q}'_k = n_i \phi_i(\mathbf{q}_1, \mathbf{q}_2, \dots, \mathbf{q}_k). \quad (40)$$

The eigenvectors of the k -matrix represent the natural k -electron states of the system, or k -bitals. The associated eigenvalues are the occupation numbers of these states, so that

$$\Gamma_k(\mathbf{q}_1, \dots, \mathbf{q}_k; \mathbf{q}'_1, \dots, \mathbf{q}'_k) = \sum_i n_i \phi_i(\mathbf{q}_1, \mathbf{q}_2, \dots, \mathbf{q}_k) \phi_i^*(\mathbf{q}'_1, \mathbf{q}'_2, \dots, \mathbf{q}'_k) \quad (41)$$

Most chemical applications using k -matrices are for $k = 1$ and/or $k = 2$.

The natural states of the 2-matrix,

$$\iint \Gamma_2(\mathbf{q}_1, \mathbf{q}_2; \mathbf{q}'_1, \mathbf{q}'_2) \phi_i(\mathbf{q}'_1, \mathbf{q}'_2) d\mathbf{r}'_1 d\mathbf{r}'_2 = n_i \phi_i(\mathbf{q}_1, \mathbf{q}_2) \quad (42)$$

are called the natural geminals. In order to obey the Pauli exclusion principle, no geminal can be occupied by more than $N - 1$ electrons. However, imposing

constraints on the geminal occupation numbers is not enough to ensure that the 2-matrix is N -representable.²⁹⁻³³

The 1-matrix is so important that it is given a special notation,

$$\gamma(\mathbf{q}, \mathbf{q}') = \Gamma_1(\mathbf{q}, \mathbf{q}') = \sum_i n_i \phi_i(\mathbf{q}) \phi_i^*(\mathbf{q}'). \quad (43)$$

If the coordinate \mathbf{q} is considered to include spin, then the Pauli principle indicates that the natural orbital occupation numbers are between zero and one, inclusive,

$$0 \leq n_i \leq 1. \quad (44)$$

(If spin is not included, then one can put up to two electrons in a single spatial orbital, so $0 \leq n_i \leq 2$.) An N -electron Slater determinant corresponds to a 1-matrix with N unit occupation numbers (corresponding to the spin-orbitals that appear in the Slater determinant); all the other natural orbital occupation numbers are zero. Because all the eigenvalues of a Slater determinantal 1-matrix are zero or one, the resulting 1-matrix is idempotent,

$$\int \gamma(\mathbf{q}, \mathbf{q}') \gamma(\mathbf{q}', \mathbf{q}'') d\mathbf{q}' = \gamma(\mathbf{q}, \mathbf{q}''). \quad (45)$$

More generally, it follows from Eq. (44) that the matrix $\gamma - \gamma^2$ is positive semidefinite,

$$0 \leq \gamma(\mathbf{q}, \mathbf{q}'') - \int \gamma(\mathbf{q}, \mathbf{q}') \gamma(\mathbf{q}', \mathbf{q}'') d\mathbf{q}'. \quad (46)$$

A matrix is positive semi-definite if and only if all its eigenvalues are nonnegative. Expression (46) (or the corresponding bounds on the natural orbital occupation numbers, (44)) is the N -representability constraint for the 1-matrix.²⁸ That is, every 1-matrix that satisfies (46) can be derived from an average of N -electron states, as in Eq. (38).

I. B Density Functional Theory (DFT)

1. Overview

In density-functional theory (DFT), the ground-state electron density replaces the wave-functionals the fundamental descriptor of an electronic system. This replacement is justified by the first Hohenberg-Kohn theorem, which indicates that the ground-state electron density determines all measurable properties of an electronic system, including the ground-state energy.¹⁰ The second Hohenberg-Kohn theorem indicates that the ground-state energy and ground-state density can be determined through the variational principle,³⁴

$$E_{g.s.} = \min_{\left\{ \begin{array}{l} 0 \leq \rho(\mathbf{r}) \\ N = \int \rho(\mathbf{r}) d\mathbf{r} \end{array} \right\}} E_v[\rho] \quad (47)$$

$$\rho_{g.s.}(\mathbf{r}) = \arg \min_{\left\{ \rho \left| \begin{array}{l} 0 \leq \rho(\mathbf{r}) \\ N = \int \rho(\mathbf{r}) d\mathbf{r} \end{array} \right. \right\}} E_v[\rho] \quad (48)$$

The constraints on the domain of electron densities included in the variational search ensure that the electron density is N -representable.^{35,36}

The primary difficulty in DFT is that the energy functional is unknown. This can be contrasted with the situation in wave-function theory, where the formula for evaluating the energy is explicit and computationally feasible, but the form of the exact wave-function is unknown and, because it is very complicated, probably unknowable. In DFT, the formerly intractable wave-function is replaced by the mathematically simple electron density, but the energy functional is unknown and, because it is very complicated, probably unknowable.

Some progress can be made by decomposing the energy into contributions from the kinetic energy, electron-nuclear attraction potential energy, and the electron-electron repulsion potential energy:

$$E_v[\rho] = T[\rho] + V_{ne}[\rho; v] + V_{ee}[\rho]. \quad (49)$$

The electron-nuclear attraction energy has a simple explicit form,

$$V_{ne}[\rho; v] = \int \rho(\mathbf{r}) v(\mathbf{r}) d\mathbf{r} \quad (50)$$

where $v(\mathbf{r})$ is the external potential that binds the electrons. For a molecular system, the external potential is simply

$$v(\mathbf{r}) = -\sum_{\alpha=1}^P \frac{Z_{\alpha}}{|\mathbf{r} - \mathbf{R}_{\alpha}|}. \quad (51)$$

The electron-electron repulsion contribution is often decomposed into classical electrostatic repulsion energy, plus corrections for the Pauli principle (exchange) and electron correlation,

$$V_{ee}[\rho] = J[\rho] + V_x[\rho] + V_c[\rho] = J[\rho] + V_{xc}[\rho] \quad (52)$$

The classical Coulomb repulsion energy is by far the largest contribution to the electron-electron repulsion; it is also known in an explicit form,

$$J[\rho] = \frac{1}{2} \iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'. \quad (53)$$

The exchange and correlation contributions must be approximated, but acceptably accurate models were available even in the 1930's (e.g., the Fermi-Amaldi model and the Dirac model for exchange;^{37,38} the Wigner model for correlation³⁹).

The kinetic energy functional is more problematic. There is no classical kinetic energy expression, analogous to Eq. (50) and Eq.(53), which can be used as a building block. A semiclassical expression in powers of Planck's constant^{40,41} gives, at leading order, the approximate functional of Thomas and Fermi.^{42,43} This approximation is much less accurate than analogous expressions, Eqs. (50) and Eq. (53), for the potential energy contributions to the energy. This is partly

because for a stable geometric arrangement of the atomic nuclei, the virial theorem indicates that the kinetic energy of a molecule has the same magnitude as the electronic energy, $T[\rho_{g.s.}] = -E_{g.s.}$. Merely determining the order of magnitude of chemical equilibrium constants and reaction rates requires errors of less than .001 atomic units (1 milliHartree) in energy; for a moderately large molecule this means part-per-million accuracy in the energy is required. Kinetic energy functionals must also be accurate to within a few parts-per-million. This exquisite accuracy is unattainable with Thomas-Fermi theory, where the errors in the kinetic energy are about 10%.

2. Kohn-Sham Density-Functional Theory (KS-DFT)

The difficulty of developing good kinetic energy functionals motivated Kohn and Sham to design a model system whose kinetic energy closely resembles that of the target electronic system.⁴⁴ As a model system, they chose a system of non-interacting fermions with the same density as the target electronic system. The exact ground-state wave-function for a system of non-interacting fermions is a Slater determinant, so the 1-matrix of the model system is idempotent. The kinetic energy of the non-interacting system can then be computed from the Slater determinant,

$$T_s[\rho] = \left\langle \Phi_s \left| \sum_{i=1}^N -\frac{1}{2} \nabla_i^2 \right| \Phi_s \right\rangle, \quad (54)$$

from the 1-matrix,

$$T_s[\rho] = \sum_{\sigma=\alpha,\beta} \iint \delta(\mathbf{r}-\mathbf{r}') \left(-\frac{1}{2} \nabla_{\mathbf{r}}^2 \gamma^{\sigma\sigma}(\mathbf{r},\mathbf{r}') \right) d\mathbf{r} d\mathbf{r}' \quad (55)$$

or from the occupied Kohn-Sham orbitals,

$$T_s[\rho] = \sum_{\sigma=\alpha,\beta} \sum_{\{i \in \text{occupied orbitals}\}} \left\langle \phi_i^\sigma \left| -\frac{1}{2} \nabla^2 \right| \phi_i^\sigma \right\rangle. \quad (56)$$

The remaining contribution to the kinetic energy is due to electron correlation,

$$T_c[\rho] = T[\rho] - T_s[\rho] \geq 0. \quad (57)$$

The Kohn-Sham approximation to the kinetic energy, $T_s[\rho]$ is extremely accurate. The correlation-kinetic energy, $T_c[\rho]$, is usually smaller than the magnitude of the correlation energy.

The unknown portions of the energy functional - the correlation-kinetic energy, the exchange potential energy, and the correlation potential energy - are added together to define the exchange-correlation energy,

$$E_{xc}[\rho] = T_c[\rho] + V_{xc}[\rho]. \quad (58)$$

In Kohn-Sham DFT, the only portion of the total energy,

$$E_v[\rho] = T_s[\rho] + \int \rho(\mathbf{r}) v(\mathbf{r}) d\mathbf{r} + J[\rho] + E_{xc}[\rho] \quad (59)$$

that needs to be approximated is the exchange-correlation energy functional. This is why the pursuit for better exchange-correlation functionals is the dominant research topic in DFT^{11-14,45}. Good approximations to the exchange-correlation functional exist, and it is increasingly difficult to design new exchange-correlation functionals that are significantly better than existing functionals like,⁴⁶ for example, the ubiquitous B3LYP functional.⁴⁷⁻⁵¹

Kohn-Sham DFT is effective because the exchange-correlation energy is a relatively small number. For this reason, a relatively inaccurate functional for the exchange-correlation energy (with, for example, about a 1% error) can give results that are accurate enough to be useful for computational chemistry. By contrast, a kinetic energy functional with a 1% error is worthless for quantitative chemical modeling.

Substituting Eq. (54) into Eq. (59) and invoking the variational principle gives rise to the Kohn-Sham equations,

$$\left(-\frac{1}{2}\nabla^2 + v_s^\sigma(\mathbf{r})\right)\phi_i^\sigma(\mathbf{r}) = \epsilon_i^\sigma \phi_i^\sigma(\mathbf{r}). \quad (60)$$

The potential that enters into this equation is called the Kohn-Sham potential,

$$v_s^\sigma(\mathbf{r}) = v(\mathbf{r}) + v_J[\rho^\sigma; \mathbf{r}] + v_{xc}[\rho^\sigma; \mathbf{r}] \quad (61)$$

The Coulomb potential,

$$v_J[\rho^\sigma; \mathbf{r}] = \int \frac{\rho^\alpha(\mathbf{r}') + \rho^\beta(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' = \frac{\delta J[\rho^\alpha, \rho^\beta]}{\delta \rho^\sigma(\mathbf{r})} \quad (62)$$

is the functional derivative of the classical Coulomb repulsion energy. The exchange-correlation potential is the functional derivative of the exchange correlation energy,

$$v_{xc}[\rho^\sigma; \mathbf{r}] = \frac{\delta E_{xc}[\rho^\alpha, \rho^\beta]}{\delta \rho^\sigma(\mathbf{r})}. \quad (63)$$

The energy of the non-interacting reference system is

$$\begin{aligned} E_s[v_s; N] &= \sum_{\sigma=\alpha, \beta} \sum_{\{i \in \text{occupied orbitals}\}} \mathcal{E}_i^\sigma = \sum_{\sigma=\alpha, \beta} \sum_{\{i \in \text{occupied orbitals}\}} \left\langle \phi_i^\sigma \left| -\frac{1}{2} \nabla^2 + v_s(\mathbf{r}) \right| \phi_i^\sigma \right\rangle \\ &= \sum_{\sigma=\alpha, \beta} T_s[\rho^\sigma] + \int \rho^\sigma(\mathbf{r}) v_s(\mathbf{r}) d\mathbf{r} \end{aligned} \quad (64)$$

The energy of the true system of interacting electrons is

$$E_{g.s.} = E_s[v_s^\sigma; N] + E_{xc}[\rho^\alpha, \rho^\beta] - J[\rho^\alpha, \rho^\beta] - \sum_{\sigma=\alpha, \beta} \int \rho^\sigma(\mathbf{r}) v_{xc}^\sigma(\mathbf{r}) d\mathbf{r}. \quad (65)$$

The value of other observable properties has a similar form. Because the electron density of the non-interacting system and the interacting system is the

same, the value of any property can be written as the sum of its value in the non-interacting system plus a correction that is a density functional,

$$\begin{aligned} Q[\rho^\alpha, \rho^\beta] &= Q_s[\rho^\alpha, \rho^\beta] + Q_{\text{correction}}[\rho^\alpha, \rho^\beta] \\ &= \langle \Phi_s | \hat{Q} | \Phi_s \rangle + Q_{\text{correction}}[\rho^\alpha, \rho^\beta]. \end{aligned} \quad (66)$$

The most important example in this chapter is the exact kinetic energy, which can be written as

$$T[\rho^\alpha, \rho^\beta] = T_s[\rho^\alpha, \rho^\beta] + T_c[\rho^\alpha, \rho^\beta] = \langle \Phi_s | \hat{T} | \Phi_s \rangle + T_c[\rho^\alpha, \rho^\beta]. \quad (67)$$

The utility of Kohn-Sham DFT arises because the properties of the non-interacting reference system often closely resemble properties of the target interacting-electron system.

3. Orbital-Free Density Functional Theory (OF-DFT)

Almost all DFT-based computations use the Kohn-Sham method. This approach, however, arguably violates the spirit of DFT. The simplicity and computational efficiency of DFT is compromised because instead of needing to determine just one 3-dimensional function (the electron density), in Kohn-Sham DFT one must determine N 3-dimensional functions (the Kohn-Sham spin-orbitals). The conceptual beauty of DFT is compromised because, unlike the

electron density, which is a physical observable with a simple interpretation, the Kohn-Sham orbitals are neither physically observable nor directly interpreted. For these reasons, there is still interest in orbital-free DFT (OF-DFT), wherein the kinetic energy is written as an explicit functional of the electron density. The dominant research topic in OF-DFT is the pursuit of better kinetic energy functionals.⁵²⁻⁶⁰

Because the accuracy and reliability of present-day kinetic-energy functionals is poor, OF-DFT is usually used either for the specific types of systems where existing functionals are reliable (simple metals and similar materials;^{61,62} warm dense matter⁶³) or applications where low-cost, low-accuracy models for the kinetic energy suffice. For example, OF-DFT is useful for massive molecular dynamics simulations of material fracture and deformation.^{64,65} It is also useful for embedding high-level calculations inside lower level calculations and for dividing systems into subsystems; in these cases the kinetic energy functional is used to model the “kinetic energy pressure” for the surroundings that keeps the electrons confined to a particular subsystem^{55,66-73}. Finally, sometimes OF-DFT is used to provide a qualitative description of a substance’s electronic structure. For example, even very approximate kinetic-energy functionals can be used to provide a picture of the electron pairing in molecules and materials.⁷⁴⁻⁷⁸

4. Properties of the Kinetic Energy Functional

The conventional approach to deriving new density functionals is to first make a list of properties of the exact functional; these properties then constrain the types of functionals that need to be considered.

Most researchers choose to model not the total kinetic energy, $T[\rho]$, but just the Kohn-Sham piece, $T_s[\rho]$. Partly this is because accurate approximations to the correlation-kinetic energy, $T_c[\rho]$, are already available from KS-DFT. In particular, most OF-DFT programs use the same energy expression that is used in Kohn-Sham,

$$E_v[\rho] = \tilde{T}_s[\rho] + J[\rho] + \tilde{E}_{xc}[\rho] + \int \rho(\mathbf{r})v(\mathbf{r})d\mathbf{r} \quad (68)$$

so that standard approximate exchange-correlation functionals from KS-DFT can be used. In Eq.(68), the functionals that must be approximated in practical calculations are decorated with a \sim . When Eq. (68) is used, the correlation-kinetic energy contribution is included in the exchange-correlation energy functional.

The other reason that researchers choose to approximate the Kohn-Sham kinetic energy is that this functional has simpler mathematical properties. For example, the Kohn-Sham kinetic energy is homogeneous of degree two with respect to coordinate scaling of the electron density,⁷⁹

$$T_s[\rho_\alpha] = \alpha^2 T_s[\rho_{\alpha=1}] \quad (69)$$

$$\rho_\alpha(x, y, z) = \alpha^3 \rho(\alpha x, \alpha y, \alpha z). \quad (70)$$

From this equation, one can derive the virial equation for the Kohn-Sham kinetic energy,⁷⁹⁻⁸¹

$$\begin{aligned} T_s[\rho] &= \frac{1}{2} \int \rho(\mathbf{r}) \mathbf{r} \cdot \nabla v_s(\mathbf{r}) d\mathbf{r} = \frac{-1}{2} \int \rho(\mathbf{r}) \mathbf{r} \cdot \nabla \frac{\delta T_s[\rho]}{\delta \rho(\mathbf{r})} d\mathbf{r} \\ &= -\frac{1}{2} \int v_s(\mathbf{r}) (3\rho(\mathbf{r}) - \mathbf{r} \cdot \nabla \rho(\mathbf{r})) d\mathbf{r} = \frac{1}{2} \int \frac{\delta T_s[\rho]}{\delta \rho(\mathbf{r})} (3\rho(\mathbf{r}) - \mathbf{r} \cdot \nabla \rho(\mathbf{r})) d\mathbf{r} \end{aligned} \quad (71)$$

This expression is much simpler than the corresponding expression for the total kinetic energy.⁸²⁻⁸⁴

Coordinate scaling requirements seem arbitrary, but because they are equivalent to the virial relationship, functionals that violate coordinate-scaling conditions often have poor variational properties.⁸⁵ Moreover, scaling the atomic charge in isoelectronic series of ions changes the density in a way that is qualitatively similar to coordinate scaling,⁸⁶ so failing to describe coordinate scaling correctly usually gives poor results for isoelectronic series.

Another important constraint related to the variational principle is the N -representability of the kinetic energy functional. The kinetic energy functional is N -

representable if and only, for every noninteracting system, the kinetic energy functional gives a higher energy than the kinetic energy portion of the energy. That is, if for all electron densities $\rho(\mathbf{r})$ and for all Kohn-Sham potentials $v_s(\mathbf{r})$,

$$\tilde{T}_s[\rho] \geq E_s[v_s; N] - \int \rho(\mathbf{r}) v_s(\mathbf{r}) d\mathbf{r}, \quad (72)$$

then the functional $\tilde{T}_s[\rho]$ is N -representable. This, ensures that the energy computed with an approximated kinetic-energy functional is always an upper bound to the KS-DFT energy. It also ensures that there exists an N -representable 1-matrix that has this electron density and this kinetic energy,

$$\begin{aligned} \rho(\mathbf{r}) &= \gamma(\mathbf{r}, \mathbf{r}) \\ \tilde{T}_s &= \iint \delta(\mathbf{r} - \mathbf{r}') \left(-\frac{1}{2} \nabla_{\mathbf{r}}^2 \gamma(\mathbf{r}, \mathbf{r}') \right) d\mathbf{r} d\mathbf{r}' \end{aligned} \quad (73)$$

5. Approaches to the Kinetic-Energy Functional

a) 1-electron density matrix models

In molecular quantum mechanics, the kinetic energy is usually computed from the 1-matrix,

$$T_s[\rho] = \iint \delta(\mathbf{r} - \mathbf{r}') \left(-\frac{1}{2} \nabla_{\mathbf{r}}^2 \gamma_s[\rho; \mathbf{r}, \mathbf{r}'] \right) d\mathbf{r} d\mathbf{r}'. \quad (74)$$

For finite systems, integration by parts lets one rewrite the kinetic energy in a form where its non-negativity is manifest,

$$T_s[\rho] = \iint \delta(\mathbf{r} - \mathbf{r}') \left(\frac{1}{2} \nabla \cdot \nabla' \gamma_s[\rho; \mathbf{r}, \mathbf{r}'] \right) d\mathbf{r} d\mathbf{r}'. \quad (75)$$

These two formulas give the same result for any well-behaved 1-matrix.

If one can model the non-interacting 1-matrix, $\gamma_s(\mathbf{r}, \mathbf{r}')$, as a functional of the electron density, then, using Eq. (74) or Eq. (75), then one can compute the kinetic energy. This is the most straightforward approach for deriving kinetic-energy functionals, and the Thomas-Fermi functional and the Weizsäcker functional can both be derived in this way. (Indeed, all of the most popular functionals can be derived in several different ways.) In chapter 5, we present a new approach, based on the weighted density approximation,⁸⁷ for modeling the 1-matrix and then we will derive the functional associated with that approach.

b) Exchange hole models

For an idempotent density matrix γ , Eq. (75) and

$$T_s[\rho] = \iint \frac{|\nabla(\gamma[\rho; \mathbf{r}, \mathbf{r}'])|^2}{8(\gamma[\rho; \mathbf{r}, \mathbf{r}'])^2} d\mathbf{r} d\mathbf{r}' \quad (76)$$

give identical results.⁸⁸ This expression can be rewritten in terms of the exchange hole,

$$h_x^{\sigma\sigma}(\mathbf{r}, \mathbf{r}') = -\frac{|\gamma^{\sigma\sigma}(\mathbf{r}, \mathbf{r}')|^2}{\rho^\sigma(\mathbf{r})\rho^\sigma(\mathbf{r}')} . \quad (77)$$

giving¹⁸

$$T_s[\rho^\alpha, \rho^\beta] = \sum_{\sigma=\alpha, \beta} \left[\int \frac{|\nabla \rho^\sigma(\mathbf{r})|^2}{8\rho^\sigma(\mathbf{r})} d\mathbf{r} - \iint \rho^\sigma(\mathbf{r})\rho^\sigma(\mathbf{r}') \frac{|\nabla h_x^{\sigma\sigma}[\rho^\sigma; \mathbf{r}, \mathbf{r}']|^2}{8h_x^{\sigma\sigma}[\rho^\sigma; \mathbf{r}, \mathbf{r}']} d\mathbf{r}d\mathbf{r}' \right] \quad (78)$$

Therefore, if one can model the exchange hole in terms of the electron density, one can build a density functional. This link between the exchange hole and the kinetic energy motivates the use of exchange-energy expressions to derive kinetic-energy functionals. When this is done, the kinetic-energy functionals are said to be conjoint.⁸⁹

c) Momentum density models

The kinetic energy is most easily computed in momentum space, where the classical expression,

$$T_s[\rho] = \int \frac{1}{2} p^2 \Pi_s[\rho; \mathbf{p}] d\mathbf{p} \quad (79)$$

is valid. Therefore, if one can model the momentum density, $\Pi_s(\mathbf{p})$, using the electron density, one has derived a kinetic energy functional. The Thomas-Fermi functional can be derived in this way. In chapter 2, we derive a generalization of the Weizsäcker functional using a model for the momentum density.

d) Quasi-probability distribution models

When approximating the potential-energy portions of the energy, it was very helpful to start with the result from classical electrostatics and then add a correction for quantum mechanics. A similar approach for the kinetic energy can be derived using the quasi-probability distribution function, $F(\mathbf{r}, \mathbf{p})$. In classical physics, the classical phase-space probability distribution function gives the probability of observing a particle at \mathbf{r} with momentum \mathbf{p} . The Heisenberg uncertainty principle indicates that the position and momentum cannot be observed simultaneously, so there is no unique analogue to the classical quantity. Instead, one has a quasi-probability distribution function,^{90,91}

$$F_s(\mathbf{r}, \mathbf{p}) = \left(\frac{1}{2\pi} \right)^6 \iiint e^{-i\tau \mathbf{p}} e^{-i\boldsymbol{\theta}(\mathbf{r}-\mathbf{u})} f(\boldsymbol{\theta}, \tau) \gamma_s(\mathbf{u} + \frac{1}{2}\tau, \mathbf{u} - \frac{1}{2}\tau) d\mathbf{u} d\boldsymbol{\theta} d\tau$$

(80)

where $f_1(\boldsymbol{\theta}, \boldsymbol{\tau})$ is any integrable function that satisfies the constraints

$$1 = f(\boldsymbol{\theta}, \boldsymbol{\tau}) = f(\boldsymbol{\theta}, \mathbf{0}). \quad (81)$$

$$(f(\boldsymbol{\theta}, \boldsymbol{\tau}))^* = f(-\boldsymbol{\theta}, -\boldsymbol{\tau}) \quad (82)$$

The Heisenberg uncertainty principle is captured by the fact there are many different choices for $f(\boldsymbol{\theta}, \boldsymbol{\tau})$. Equivalently, the quantum-classical correspondence is not unique; this is why, for example, there are two (and even more) equivalent forms for the kinetic energy, Eqs. (74) and (75). All $f(\boldsymbol{\theta}, \boldsymbol{\tau})$ that are consistent with Eq. (81) provide a suitable classical correspondence; the most popular choice, $f(\boldsymbol{\theta}, \boldsymbol{\tau}) = 1$, corresponds to the Wigner quasi-probability distribution function.^{92,93}

Given a quasi-probability distribution function, the electron density and momentum density are given by

$$\rho(\mathbf{r}) = \int F_s(\mathbf{r}, \mathbf{p}) d\mathbf{p} \quad (83)$$

and

$$\Pi_s(\mathbf{p}) = \int F_s(\mathbf{r}, \mathbf{p}) d\mathbf{r}. \quad (84)$$

If one can model the quasi-probability distribution function using the electron density, then the kinetic energy can be expressed using⁹⁴⁻⁹⁷

$$T_s[\rho] = \iint \frac{1}{2} p^2 F_s[\rho; \mathbf{r}, \mathbf{p}] d\mathbf{r} d\mathbf{p}. \quad (85)$$

This approach to deriving kinetic energy functionals was pioneered by Ghosh, Berkowitz, Lee, and Parr.⁹⁸⁻¹⁰⁰ The Thomas-Fermi model, and generalizations thereto, have been derived using this approach.⁹⁹

e) Local Kinetic Energy Models

Using the quasi-probability distribution function as an intermediary, the local kinetic energy can be defined as⁹⁴

$$t_s(\mathbf{r}) = \int \frac{1}{2} p^2 F_s[\rho; \mathbf{r}, \mathbf{p}] d\mathbf{p} \quad (86)$$

Because the quasi-probability distribution is not uniquely defined, neither is the local kinetic energy.⁹⁴⁻⁹⁷ If one can model the local kinetic energy using the electron density, then the kinetic energy functional can be written as,

$$T_s[\rho] = \int t_s[\rho; \mathbf{r}] d\mathbf{r} \quad (87)$$

Most kinetic energy functionals are expressions with the form of Eq. (87).

f) Local Temperature Models

By analogy to the classical expression for the kinetic energy of a monatomic ideal gas, $k.e. = \frac{3}{2}k_B\Theta\rho$, Ghosh et al. proposed writing the local kinetic energy as^{98,101}

$$t_s(\mathbf{r}) = \frac{3}{2}\Theta(\mathbf{r})\rho(\mathbf{r}) \quad (88)$$

where $\Theta(\mathbf{r})$ is the local temperature.¹⁰² Therefore, if one can build a model for the local temperature from the electron density; one can derive a kinetic energy functional,

$$T_s[\rho] = \int \frac{3}{2}\Theta[\rho;\mathbf{r}]\rho(\mathbf{r})d\mathbf{r}. \quad (89)$$

This approach can also be used to derive Thomas-Fermi-like functionals.⁹⁹

g) Other Approaches

There are other, even less conventional, approaches for deriving kinetic-energy functionals. There are recent approaches using hydrodynamic tensors,^{103,104} semiclassical expansions,¹⁰⁵⁻¹⁰⁷ information theory,¹⁰⁸⁻¹¹⁴ the theory of moments,^{86,115-118} analysis of quantum fluctuations,¹¹⁹⁻¹²¹ and higher-order electron distribution functions.^{18,109,121,122}

I. C One-Point Approximate Orbital-Free Kinetic Energy Functionals

1. Thomas-Fermi-based Functionals

In the following two sections we will briefly summarize the main families of kinetic energy functionals. Many functionals are necessarily omitted; the intention is to provide the flavor of mainstream approaches, rather than an encyclopedic list of functionals.

The first kinetic energy density functional was derived, independently, by Thomas and Fermi, in 1927 and 1928, respectively.^{42,43} The Thomas-Fermi functional is the simplest local density approximation.

In a uniform electron gas (UEG) of non-interacting fermions with density ρ , the local kinetic energy per fermion is a constant,

$$\tau(\rho) = \frac{(3\pi)^{2/3}}{10} \rho^{2/3}(\mathbf{r}) \quad (90)$$

The local kinetic energy per unit volume is then the probability of observing a fermion at the point \mathbf{r} times the local kinetic energy per fermion,

$$t[\rho] = \rho(\mathbf{r}) \tau(\rho) \quad (91)$$

Integrating over all volume gives the Thomas-Fermi functional,

$$T_s^{\text{TF}}[\rho] = C_F \int \rho^{5/3}(\mathbf{r}) d\mathbf{r} \quad (92)$$

with

$$C_F = \frac{(3\pi)^{2/3}}{10}. \quad (93)$$

If one chooses a model system other than the uniform electron gas, the value of the constant, C_F , changes.⁹⁹ However, the exponent, 5/3, is required by the coordinate scaling condition, Eq.(69), and should not be changed.

When the number of electrons per unit volume is very large, the number of occupied states becomes very large and most of the fermions are in states with very high quantum numbers. This is the classical limit. If one neglects relativistic effects, then the relative error in the Thomas-Fermi kinetic energy of neutral atoms goes to zero as the atomic number increases. However, the absolute error of the Thomas-Fermi kinetic energy is not small for any atom in the periodic table.¹²³⁻¹²⁵

The Thomas-Fermi model does not suffice for chemistry. In Thomas-Fermi theory, all atomic anions are predicted to be unstable. Also, the energy of a molecule is always greater than the energy of the isolated atoms, so Thomas-Fermi theory predicts that no molecule is stable. This result is called the Teller nonbinding theorem.¹²³⁻¹²⁶

For the electron density of closed-shell atoms, the Thomas-Fermi kinetic energy is in error by about 5%. Variational minimization of the density increases, this error to about 10% and leads to electron densities that diverge at the atomic nucleus.¹²⁷ Adding constraints to force the correct electron-nuclear cusp conditions on the electron density,¹²⁸ like other attempts to improve the simple Thomas-Fermi model, give disappointing results.

2. Gradient-Corrected Thomas-Fermi Functionals

a) Overview

Since the Thomas-Fermi functional is exact for the uniform electron gas, its failings must arise because the electron densities of chemical substances are far from uniform. This suggests that we construct the gradient expansion about the uniform electron gas limit; such functionals will be exact for nearly uniform electron gasses. An alternative perspective is to recall that Thomas-Fermi theory is exact in the classical, high-quantum number, limit. The gradient expansion can be derived as a Maclaurin series in powers of \hbar ; it adds additional quantum effects into the Thomas-Fermi model.

The second-order gradient expansion approximation is⁴⁰

$$\begin{aligned}
 T_s^{\text{GEA2}}[\rho] &= C_F \int \left[\rho^{5/3}(\mathbf{r}) + \frac{|\nabla \rho(\mathbf{r})|^2}{72\rho(\mathbf{r})} \right] d\mathbf{r} \\
 &= T_s^{\text{TF}}[\rho] + \frac{1}{9} T_w[\rho]
 \end{aligned}
 \tag{94}$$

Here,

$$T_w[\rho] = \int \frac{|\nabla \rho(\mathbf{r})|^2}{8\rho(\mathbf{r})} d\mathbf{r}
 \tag{95}$$

is the kinetic energy functional proposed by von Weizsäcker.¹²⁹ The error in $T^{\text{GEA2}}[\rho]$ is about 1% of the total energy; this error is still several thousand times larger than the minimum error acceptable for chemical applications.⁵⁶

The gradient expansion was extended to fourth order,¹³⁰

$$\begin{aligned}
 T^{\text{GEA4}}[\rho] &= T^{\text{GEA2}}[\rho] + \frac{1}{540(3\pi)^{2/3}} \int \rho^{5/3}(\mathbf{r}) \left[\left(\frac{\nabla^2 \rho(\mathbf{r})}{\rho^{5/3}(\mathbf{r})} \right)^2 + \frac{1}{3} \left(\frac{|\nabla \rho(\mathbf{r})|}{\rho^{4/3}(\mathbf{r})} \right)^4 \right. \\
 &\quad \left. - \frac{9}{8} \left(\frac{\nabla^2 \rho(\mathbf{r})}{\rho^{5/3}(\mathbf{r})} \right) \left(\frac{|\nabla \rho(\mathbf{r})|}{\rho^{4/3}(\mathbf{r})} \right)^2 \right] d\mathbf{r}
 \end{aligned}
 \tag{96}$$

and later to sixth order.¹³¹ The fourth-order results are generally an improvement upon the second-order results, but they are still woefully inadequate for modeling chemical reaction energies.^{132,133} The sixth-order functional diverges because of the cusp in the electron density at the location of atomic nuclei.¹³¹ Molecular

electron densities are too different from the uniform electron gas for the gradient expansion to converge.

The divergence of the gradient expansion motivated researchers to consider generalized gradient approximations for the kinetic energy. Examining the form of the convergent terms in the gradient expansion, it is observed that the kinetic energy starts with a Thomas-Fermi term, which is then embellished by a dimensionless enhancement factor. (See Eq. (96).) That is, it is reasonable to propose kinetic energy functionals of the form,

$$T_s^{\text{GGA}}[\rho] = C_F \int \rho^{5/3}(\mathbf{r}) F_{\text{enh}}[s(\rho), p(\rho)] d\mathbf{r} \quad (97)$$

where

$$s[\rho; \mathbf{r}] = \frac{1}{2(3\pi^2)^{1/3}} \frac{|\nabla \rho(\mathbf{r})|}{\rho^{4/3}(\mathbf{r})} \quad (98)$$

is the reduced gradient,

$$p[\rho; \mathbf{r}] = \frac{1}{4(3\pi^2)^{2/3}} \frac{\nabla^2 \rho(\mathbf{r})}{\rho^{5/3}(\mathbf{r})} \quad (99)$$

is the reduced Laplacian, and (ideally)

$$F_{\text{enh}}(0,0) = 1. \quad (100)$$

The functional in Eq. (97) is exact for the uniform electron gas if and only if Eq. (100) is satisfied. According to the conjointness hypothesis, it is reasonable to choose the same enhancement functional for kinetic energy functionals that one uses for exchange-energy functionals.⁸⁹

Many generalized gradient approximations for the kinetic energy have been proposed.^{59,60,134} A few of the more popular and innovative approximations are now presented.

b) Linear combinations of the Thomas-Fermi and von Weizsäcker functionals

The simplest approach to improving the gradient expansion is to reweight the Weizsäcker correction to the gradient expansion; such approximations are called TF+ λ vW approximations,

$$T_s^{\text{TF}+\lambda\text{vW}}[\rho] = T_s^{\text{TF}}[\rho] + \lambda T_w[\rho]. \quad (101)$$

Popular choices include the gradient expansion ($\lambda=1/9$),⁴⁰ $\lambda = 1/5$,¹³⁵ and $\lambda = 1$.^{87,136} Thakkar proposed choosing $\lambda = b/9$, where b is a system-dependent constant (analogous to the α parameter in $X\alpha$ theory).⁵⁸ Pearson and Gordon analyzed the gradient expansion as an asymptotic series and wrote λ as a functional of the reduced gradient, so that the gradient correction is only applied

in regions where the gradient is small enough for this correction to be reliable.¹³⁷

In chapter 5, we will provide a justification for the $\lambda=1$ functional.

c) ***N*-dependent functionals**

In this case, the enhancement factor is considered to be a simple function of the number of electrons, N .¹³⁸ The most common form for the enhancement factor, based on the asymptotic expansion of atomic kinetic energies,¹³⁹⁻¹⁴¹ is

$$F_{\text{enh}}^{\text{TF-}N}(N) = 1 + \frac{a}{N^{1/3}} + \frac{b}{N^{2/3}}. \quad (102)$$

where a and b are parameters to be fit.

Unfortunately N -dependent functionals are not size consistent. If one considers ten atoms very far from each other, the energy of the system should be the sum of the isolated atomic energies. This is not true for N -dependent functionals because one uses a different functional for the isolated atoms and the super-system (because they have different numbers of electrons).

d) **Rational Function Approximation**

Often the enhancement factor is written as a rational function; this is motivated by the observation that the gradient expansion diverges and the

knowledge that Pade approximants are often very effective approaches for the re-summation of divergent series. A representative functional of this form is the DePristo-Kress functional,¹⁴²

$$F_{\text{enh}}^{\text{DK}}(x) = \frac{1 + 0.95x(\mathbf{r}) + 14.28111x^2(\mathbf{r}) - 19.57962x^3(\mathbf{r}) + 26.6477x^4(\mathbf{r})}{1 - 0.05x(\mathbf{r}) + 9.99802x^2(\mathbf{r}) + 2.96085x^3(\mathbf{r})} \quad (103)$$

where

$$x(\mathbf{r}) = \frac{\frac{1}{9}t_w[\rho; \mathbf{r}]}{t_s^{\text{TF}}[\rho; \mathbf{r}]} \quad (104)$$

and $t_w[\rho; \mathbf{r}]$ and $t_s^{\text{TF}}[\rho; \mathbf{r}]$ are the local kinetic energies in the Weizsäcker (Eq. (95)) and Thomas-Fermi (Eq. (92)) functionals, respectively.

e) Conjoint Gradient Corrected Functionals

The conjointness hypothesis is based on the similarity between kinetic-energy and exchange-energy functionals.⁸⁹ This can be motivated, for example, by the form for the kinetic energy in terms of the exchange hole, Eq. (78). A kinetic-energy functional is conjoint to an exchange-energy functional if it uses the same enhancement factor as the exchange functional. (Sometimes the parameters in the enhancement factor are adjusted, often they are not.) Many popular generalized

gradient approximations for the kinetic energy are built using the conjointness hypothesis.^{89,143-148} The PW91 functional has a typical form,

$$F_{\text{enh}}^{\text{PW91}}(s) = \frac{1 + 0.19645s \cdot \text{arcsinh}(7.7956s) + s^2(0.2743 - 0.1508e^{-100s^2})}{1 + 0.19645s \cdot \text{arcsinh}(7.7956s) + 0.004s^4} \quad (105)$$

where s is the reduced gradient; cf. Eq. (98).

The most successful GGA forms based on conjointness are the PBE-motivated forms,

$$F_{\text{enh}}^{\text{PBE}}(s) = 1 + \sum_{k=1}^{n-1} C_k \left[\frac{s^2}{1 + a_k s^2} \right]^k \quad (106)$$

with $n = 2$ and $n = 4$. The popular PBE-TW functional is an $n = 2$ functional.

f) Functionals consistent with non-uniform coordinate scaling.

The uniform density scaling condition in Eq. (69) was generalized to nonuniform density scaling,

$$\rho_{\alpha,\beta,\gamma}(x, y, z) = \alpha \cdot \beta \cdot \gamma \cdot \rho(\alpha x, \beta y, \gamma z) \quad (107)$$

by Ou-Yang and Levy.¹⁴⁹ Based on these conditions, Ou-Yang and Levy proposed two new kinetic energy functionals (OL1 and OL2). The Thakkar

functional, which was fit to the kinetic energies of 77 molecules, satisfies the non-uniform scaling constraints and is reported to be one of the most accurate GGA functionals,⁵⁸

$$F_{\text{enh}}^{T92}(s) = 1 + \frac{0.0055(2(6\pi^2)^{1/3}s)^2}{1 + 0.0253(2(6\pi^2)^{1/3}s)\text{arcsinh}(2(6\pi^2)^{1/3}s)} - \frac{0.072(2(6\pi^2)^{1/3}s)}{1 + 2^{5/3}(2(6\pi^2)^{1/3}s)} \quad (108)$$

3. Weizsäcker-based Functionals

The Thomas-Fermi kinetic energy is accurate when the electron density is almost constant and when the number of electrons per unit volume is very large (because one is approaching the classical limit). The Weizsäcker functional is accurate in complementary situations: the Weizsäcker functional is exact for one-electron systems and two-electron systems with a non-degenerate ground state; it is also accurate in regions where the electron density is changing very rapidly (e.g., near the atomic nuclei) and in all regions of a system where the dominant contribution to the electron density comes from a single Kohn-Sham orbital (e.g., the asymptotic regions far from the atomic nuclei). Moreover, unlike the Thomas-Fermi functional, the Weizsäcker functional is consistent with chemical binding. This suggests that the Weizsäcker functional, instead of the Thomas-Fermi

functional, might be a better starting point for chemical applications of OF-DFT.¹⁵⁰

The Weizsäcker functional is a lower bound to the true kinetic energy, but it is a very weak lower bound.^{18,109,151-154} It is even less accurate than the Thomas-Fermi functional.

4. Corrected Weizsäcker-based Functionals

a) Weizsäcker Plus Thomas-Fermi Functionals

The simplest approach to correcting the Weizsäcker functional is to add a fraction of Thomas-Fermi functional, forming a $vW+\lambda TF$ functional,

$$T_s^{vW+\lambda TF}[\rho] = T_w[\rho] + \lambda T_s^{TF}[\rho]. \quad (109)$$

The only choice for λ that is consistent with the uniform electron gas limit is $\lambda=1$; unfortunately that functional gives answers far above the true kinetic energy.^{87,136,155}

This model can be improved by making the mixing factor, λ , system dependent. Several authors considered making λ depend on N .^{108,156} These functionals give reasonable results for atomic kinetic energies but, unfortunately, they are not size consistent. Moreover, when they are used in a variational optimization, atomic densities have no shell structure.¹⁵⁷

$$\lambda(N) = \left(1 - \frac{2}{N}\right) \left(1 - \frac{A_1}{N^{1/3}} + \frac{A_2}{N^{2/3}}\right) \quad (110)$$

Shell structure is retained if one chooses λ so that it varies at different points in space,¹⁵⁸

$$T_s^{\text{DG}}[\rho] = T_w[\rho] + C_F \int \lambda(\mathbf{r}) \rho^{5/3}(\mathbf{r}) d\mathbf{r}. \quad (111)$$

b) Enhancement Factors from the Pauli Potential

The Weizsäcker functional is exact for non-interacting bosons. The correction to the Weizsäcker functional, then, is solely due to the Pauli principle. The Pauli kinetic energy can then be defined as,

$$T_\theta[\rho] = T_s[\rho] - T_w[\rho] \geq 0. \quad (112)$$

Because the Weizsäcker kinetic energy functional is a lower bound, the Pauli kinetic energy is always positive.^{18,109,151-154} If one differentiates the resulting energy function, one obtains a differential equation for the square root of the electron density,^{153,159,160}

$$\left(\frac{-1}{2}\nabla^2 + v_s(\mathbf{r}) + v_\theta(\mathbf{r})\right)\sqrt{\rho(\mathbf{r})} = \varepsilon\sqrt{\rho(\mathbf{r})} \quad (113)$$

where the Pauli potential is¹⁵³

$$v_\theta(\mathbf{r}) = \frac{\delta T_\theta[\rho]}{\delta \rho(\mathbf{r})} = \frac{1}{\rho(\mathbf{r})} \left(t_\theta(\mathbf{r}) + \sum_{\{\epsilon \in \text{occupied orbitals}\}} (\varepsilon_{\text{HOMO}} - \varepsilon_i) |\phi_i(\mathbf{r})|^2 \right) \geq 0$$

(114)

Here $t_\theta(\mathbf{r})$ is the local Pauli kinetic energy, which is defined as

$$t_\theta(\mathbf{r}) = \frac{1}{2} \left[\nabla \cdot \nabla' \gamma_s(\mathbf{r}, \mathbf{r}') \right]_{\mathbf{r}=\mathbf{r}'} - \frac{1}{2} \left| \nabla \sqrt{\rho(\mathbf{r})} \right|^2 \quad (115)$$

where $\gamma_s(\mathbf{r}, \mathbf{r}')$ is the Kohn-Sham 1-matrix. Beyond its conceptual utility,¹⁶¹ the approach based on the Pauli potential is useful for its computational ease: solving Eq. (113) is equivalent in difficulty to solving the Kohn-Sham equations for a 1-electron system.

The non-negativity constraints on the Pauli correction and its potential give stringent constraints on the types of functionals that can be considered. The most popular form for the kinetic energy has attempted to modify the enhancement factors from Thomas-Fermi-based kinetic energy functionals, defining,¹⁶²

$$T_\theta[\rho] = \int C_F \rho^{5/3}(\mathbf{r}) F_\theta(s(\mathbf{r})) d\mathbf{r} \quad (116)$$

with the modified enhancement factors

$$F_\theta(s) = F_{\text{enh}}(s) - \frac{5}{3} s^2. \quad (117)$$

The resulting functionals, however, become negative (and even diverge) near the atomic nuclei.¹⁶³ This problem is avoided by using so-called reduced gradient approximations, where the Pauli kinetic energy has the form⁶⁰

$$T_{\theta}[\rho] = \int C_F \rho^{5/3}(\mathbf{r}) F_{\theta}(\kappa_2, \kappa_4) d\mathbf{r} \quad (118)$$

where

$$\kappa_2 = s + b \cdot p \quad (119)$$

and

$$\kappa_4 = s^4 + \frac{18}{13} p^2 - \frac{30}{13} s^2 p \quad (120)$$

are specific linear combinations of the reduced gradient, s , and the reduced Laplacian, p . (Cf. Eqs. (98) and (99)).

I. D Two-Point Approximate Orbital-Free Kinetic Energy Functionals

1. Functionals Based on the Non-interacting Response Kernel

The functionals considered in the previous section are all semi-local: the local kinetic energy at the point \mathbf{r} depends only on the electron density and its derivatives at the point \mathbf{r} . Improved models for the kinetic energy require considering how the electron density at other points, \mathbf{r}' , affect the local kinetic energy at the point \mathbf{r} . Without including these effects, the oscillations in electron

density that are essential for differentiating between core and valence electrons in atoms and molecules cannot be recovered.

Most nonlocal functionals aim to reproduce the Kohn-Sham linear response function,

$$\chi_s(\mathbf{r}, \mathbf{r}') = \left(\frac{\delta \rho(\mathbf{r})}{\delta v_s(\mathbf{r}')}\right)_\mu. \quad (121)$$

The Kohn-Sham linear response predicts long- and short-range density oscillations in the nearly uniform electron gas; in particular, it captures how the electron density becomes non-uniform when the Kohn-Sham potential is changed by an external perturbation,

$$d\rho(\mathbf{r}) = \int \chi_s(\mathbf{r}, \mathbf{r}') \delta v_s(\mathbf{r}') d\mathbf{r}'. \quad (122)$$

For the uniform electron gas, the response function depends only on the distance between the perturbation and the point, at which the density-change is measured,

$$d\rho(\mathbf{r}) = \int \chi_s(|\mathbf{r} - \mathbf{r}'|) \delta v_s(\mathbf{r}') d\mathbf{r}' \quad (123)$$

and the Fourier transform of the response function; known as Lindhard function;¹⁶⁴ can be determined analytically¹⁶⁵

$$\chi_{\text{Lind}}(\eta) = -\frac{k_F}{\pi^2} \left(\frac{1}{2} + \frac{1-\eta^2}{4\eta} \ln \left| \frac{1+\eta}{1-\eta} \right| \right). \quad (124)$$

Here

$$k_F = (3\pi^2 \rho)^{1/3} \quad (125)$$

is the Fermi wave-vector and

$$\eta = \frac{q}{2k_F} \quad (126)$$

is the scaled Fermi momentum.

The response kernel, provides a useful constraint on kinetic energy functionals because the second derivative of the non-interacting kinetic energy is related to the inverse of the linear response function,

$$\frac{\delta^2 T_s[\rho]}{\delta \rho(\mathbf{r}) \delta \rho(\mathbf{r}')} = -\chi_s^{-1}(\mathbf{r}, \mathbf{r}'). \quad (127)$$

Taking the Fourier transform of both sides, one may require that, in the uniform electron gas limit,

$$\hat{F} \left[\frac{\delta^2 T_s[\rho]}{\delta \rho(\mathbf{r}) \delta \rho(\mathbf{r})} \right] = \frac{-1}{\chi_{\text{Lind}}(\eta)}. \quad (128)$$

This constraint cannot be satisfied by any semi-local functional. That is, as semi-local functional is incapable of describing how the kinetic energy of the uniform electron gas changes when it is simultaneously perturbed away from uniformity at two different points. The idea that imposing the correct linear response would improve the description of non-uniform electron densities emerged from the work

of Chacon, Alvarellos, and Tarazona¹⁶⁶ and from the work of Herring.¹⁵⁵ Many functionals that reproduce the Lindhard response have been proposed in the intervening years.^{59,65,134,167-175} These functionals are among the most accurate functionals available, but they are difficult to formulate in real space and they are still inadequate when one is far from the uniform electron gas limit. For this reason, these functionals are much more useful for solid-state physics than they are for molecular chemistry.

While there are many ways to design functionals that are consistent with the Lindhard response, most functionals are based on one of two approaches. The first approach was pioneered by Chacon, Alvarellows, and Tarazona. The CAT functionals have the form,¹⁶⁶

$$T_s^{\text{CAT}}[\rho] = T_w[\rho] - \alpha T_s^{\text{TF}}[\rho] + (1 + \alpha) \int C_F \rho(\mathbf{r}) (\tilde{\rho}_\beta(\mathbf{r}))^{2/3\beta} d\mathbf{r} \quad (129)$$

where $\tilde{\rho}_\beta(\mathbf{r})$ is an effective electron density, averaged over a nonlocal integral kernel,

$$\tilde{\rho}_\beta(\mathbf{r}) = \int \rho^\beta(\mathbf{r}') \Omega(k_F(\mathbf{r})|\mathbf{r} - \mathbf{r}'|) d\mathbf{r}'. \quad (130)$$

The function $\Omega(k_F(\mathbf{r})|\mathbf{r} - \mathbf{r}'|)$ is chosen so that the Lindhard response is recovered in the uniform electron gas limit. The parameters α and β can be used to satisfy constraints and fit reference data.

There are several generalizations of this functional form; most differ in whether the Fermi wave-vector in Eq. (130) is considered to be constant,^{65,167,169,174} vary with \mathbf{r} (as shown in Eq. (130)), or replaced by a symmetrized form based on the generalized p -mean,¹⁷¹

$$k_F(\mathbf{r}, \mathbf{r}') = \left(\frac{k_F^p(\mathbf{r}) + k_F^p(\mathbf{r}')}{2} \right)^{1/p}. \quad (131)$$

The symmetrized form seems to be the best for recovering shell structure in the electron density.¹⁷¹ Taking the Fermi momentum to be constant has computational advantages because the kinetic energy functional can be evaluated very quickly as a double-convolution of densities with the weighting function. In this case, the form of the functional also simplifies, becoming,

$$T_s^{\text{SND A}}[\rho] = T_w[\rho] - \alpha T_s^{\text{TF}}[\rho] + (1 + \alpha) (2k_F^3) \int C_F \rho^{5/3+\beta}(\mathbf{r}) \omega(2k_F |\mathbf{r} - \mathbf{r}'|) \rho^\beta(\mathbf{r}') d\mathbf{r} \quad (132)$$

The weighting factor in the function is again chosen to ensure that the Lindhard response is recovered. Functionals like Eq. (132) are called simplified nonlocal density approximations.^{65,167,169,174}

2. The Weighted Density Approximation (WDA)

a) Overview

The idea behind the CAT functional and its generalizations is that if the linear response function of the uniform electron gas is correct, then at least some of the shell structure in the uniform electron gas will also be reproduced. The shell structure, however, is directly implied by the exchange hole (cf. Eq.(77)) and therefore also by the 1-matrix. The conventional weighted density approximation is based on the desire to recover the 1-matrix of the uniform electron gas perfectly.^{87,176,177} The main difference between the various types of WDA-functionals and the various types of CAT-functionals, then, is that the nonlocal function that is being reproduced is the 1-matrix for WDAs, but the response kernel for CATs.

WDAs are especially convenient for molecular systems because it is impossible to write the Lindhard response function explicitly in real space. However, the 1-matrix of the uniform electron gas has the simple real-space form,

$$\gamma_{\text{UEG}}^{\sigma\sigma}[\rho^\sigma; \mathbf{r}, \mathbf{r}'] = \sqrt{\rho^\sigma(\mathbf{r})\rho^\sigma(\mathbf{r}')} g_{\text{UEG}}^{\sigma\sigma}[\rho^\sigma; \mathbf{r}, \mathbf{r}'], \quad (133)$$

where

$$g_{\text{UEG}}^{\sigma\sigma}(k_F^\sigma|\mathbf{r}-\mathbf{r}'|) = 3 \left(\frac{\sin(k_F^\sigma|\mathbf{r}-\mathbf{r}'|) - (k_F^\sigma|\mathbf{r}-\mathbf{r}'|)\cos(k_F^\sigma|\mathbf{r}-\mathbf{r}'|)}{(k_F^\sigma|\mathbf{r}-\mathbf{r}'|)^3} \right). \quad (134)$$

Another nice feature of WDAs is that after one has determined the density matrix, one automatically obtains not only an approximation to the kinetic energy,

$$T_s^{\text{WDA-UEG}}[\rho^\alpha, \rho^\beta] = \sum_{\sigma=\alpha,\beta} \delta(\mathbf{r}-\mathbf{r}') \left(\frac{1}{2} \nabla \cdot \nabla' \gamma_{\text{UEG}}^{\sigma\sigma}[\rho^\sigma; \mathbf{r}, \mathbf{r}'] \right) d\mathbf{r} d\mathbf{r}' \quad (135)$$

but also an approximation to the exchange energy,

$$E_x^{\text{WDA-UEG}}[\rho^\alpha, \rho^\beta] = \sum_{\sigma=\alpha,\beta} \left(\frac{-1}{2} \right) \iint \frac{\left(\gamma_{\text{UEG}}^{\sigma\sigma}[\rho^\sigma; \mathbf{r}, \mathbf{r}'] \right)^2}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}'. \quad (136)$$

b) Types of Weighted Density Approximations

When one makes a weighted density approximation, one must make three choices. First one must choose the form of the model 1-matrix. The 1-matrix of the uniform electron gas is one choice, but certainly it is not the only choice. (For example, a Gaussian model for the density matrix is prevalent in the literature.^{99,178,179})

Second, one must choose how the Fermi momentum enters into the formula. It is possible to choose k_F^σ to be a constant, equal to the average value of the Fermi wave-vector. This will not be accurate for atoms and molecules, though, where the electron density varies over many orders of magnitude. Second, one can choose the Fermi wave vector to be dependent on one of the points, $k_F^\sigma(\mathbf{r})$. The resulting 1-matrix,

$$\gamma_{\text{UEG}}^{\sigma\sigma}[\rho^\sigma; \mathbf{r}, \mathbf{r}'] = \sqrt{\rho^\sigma(\mathbf{r})\rho^\sigma(\mathbf{r}')} g_{\text{UEG}}^{\sigma\sigma}(k_F^\sigma(\mathbf{r})|\mathbf{r}-\mathbf{r}'|), \quad (137)$$

however, is not symmetric. Finally, one can force the 1-matrix to be symmetric. One way to do this is to add the 1-matrix to its transpose,

$$\gamma_{\text{UEG}}^{\sigma\sigma}[\rho^\sigma; \mathbf{r}, \mathbf{r}'] = \sqrt{\rho^\sigma(\mathbf{r})\rho^\sigma(\mathbf{r}')} \left(g_{\text{UEG}}^{\sigma\sigma}(k_F^\sigma(\mathbf{r})|\mathbf{r}-\mathbf{r}'|) + g_{\text{UEG}}^{\sigma\sigma}(k_F^\sigma(\mathbf{r}')|\mathbf{r}-\mathbf{r}'|) \right) \quad (138)$$

This choice has been proposed in the literature,^{180,181} but seemingly never tested. Instead, one might use the generalized p -mean from Eq. (131),

$$\gamma_{\text{UEG}}^{\sigma\sigma}[\rho^\sigma; \mathbf{r}, \mathbf{r}'] = \sqrt{\rho^\sigma(\mathbf{r})\rho^\sigma(\mathbf{r}')} g_{\text{UEG}}^{\sigma\sigma}(k_F^\sigma(\mathbf{r}, \mathbf{r}')|\mathbf{r}-\mathbf{r}'|). \quad (139)$$

This form is symmetric. Note that the three different choices here correspond exactly to the three different choices that can be made when the Lindhard response function is used to define a nonlocal weighting function.

Finally, the one must choose how the Fermi wave-vector is to be determined. It is easiest to use the classical local-density approximation,

$$k_{F,\text{LDA}}^\sigma(\mathbf{r}) = \left(6\pi^2 \rho^\sigma(\mathbf{r})\right)^{1/3}. \quad (140)$$

Alternatively, one can determine the “effective value” of the Fermi wave-vector by imposing a constraint. We want the 1-matrix to be idempotent, so we would like to satisfy the equations,

$$\left\{ \int \gamma^{\sigma\sigma} \left[k_F^\sigma(\mathbf{r}); \mathbf{r}, \mathbf{r}' \right] \gamma^{\sigma\sigma} \left[k_F^\sigma(\mathbf{r}''); \mathbf{r}', \mathbf{r}'' \right] d\mathbf{r}' = \gamma^{\sigma\sigma} \left[k_F^\sigma(\mathbf{r}); \mathbf{r}, \mathbf{r}'' \right] \right\}_{\sigma=\alpha,\beta} \quad (141)$$

This system of nonlinear equations is overdetermined because there is an equation for every pair of points, $(\mathbf{r}, \mathbf{r}'')$, but there is only one unknown at each point, $k_F(\mathbf{r})$. We could try to make a more sophisticated model for the density matrix, but if we force idempotency exactly, then the method is equivalent to Kohn-Sham, and will have computational cost similar to Kohn-Sham.

The simplest thing to do is to reduce the dimensionality of the system by setting $\mathbf{r} = \mathbf{r}''$ in the idempotency condition, Eq. (141). One then has a set of nonlinear equations, one for each grid point,

$$\left\{ \int \gamma^{\sigma\sigma} \left[k_F^\sigma(\mathbf{r}); \mathbf{r}, \mathbf{r}' \right] \gamma^{\sigma\sigma} \left[k_F^\sigma(\mathbf{r}); \mathbf{r}', \mathbf{r} \right] d\mathbf{r}' = \rho^\sigma(\mathbf{r}) \right\}_{\sigma=\alpha,\beta}. \quad (142)$$

This can be rewritten in terms of the exchange hole,

$$\left\{ \int \rho^\sigma(\mathbf{r}') h_x^{\sigma\sigma} \left[k_F^\sigma(\mathbf{r}); \mathbf{r}, \mathbf{r}' \right] d\mathbf{r}' = -1 \right\}_{\sigma=\alpha,\beta}. \quad (143)$$

This condition, then, ensures that the functionals are self-interaction free, and that each σ -spin electron excludes another σ -spin electron from its immediate vicinity. If the non-symmetric form of the 1-matrix is used, then the nonlinear equations (142) are decoupled; in this case the equations can be solved using Newton's method in one dimension. If the symmetric form of the 1-matrix (cf. Eq.(139)) is used, then the nonlinear equations in Eq. (142) are coupled. We solve these equations using a limited-memory bad-Broyden method to update an approximation to the inverse Jacobian, which we choose as the inverse of the diagonal of the Jacobian. This allows us to solve Eq. (142) in about ten iterations, so that the cost of the symmetrized WDA 1-matrix method is only one order of magnitude slower than the cost of the asymmetric WDA 1-matrix. Further details on this approach can be found in Chapter 5.

When one is considering the exchange energy, all these variants give different results: for example, if one solves for the effective Fermi vector in Eq. (142) using the asymmetric form of the 1-matrix (Eq. (137)), and then symmetrizes the 1-matrix using the p -mean, the exchange energy one computes is different from what one would have obtained without symmetrization. That is,

even if one uses the same values of $k_F(\mathbf{r})$, the following formulas give different results

$$\begin{aligned}
 & -\frac{1}{2} \iint \frac{\left(\sqrt{\rho(\mathbf{r})\rho(\mathbf{r}')} g(k_F(\mathbf{r})|\mathbf{r}-\mathbf{r}'|) \right)^2}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \\
 & \neq -\frac{1}{2} \iint \frac{\left(\sqrt{\rho(\mathbf{r})\rho(\mathbf{r}')} g\left(\left\{ \frac{k_F^p(\mathbf{r})+k_F^p(\mathbf{r}')}{2} \right\}^{1/p} |\mathbf{r}-\mathbf{r}'| \right) \right)^2}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}'
 \end{aligned} \tag{144}$$

That is, for the exchange energy, the results change if you symmetrize the 1-matrix after determining $k_F(\mathbf{r})$. However, the formulas for the kinetic energy are the same,

$$\begin{aligned}
 & \iint \delta(\mathbf{r}-\mathbf{r}') \left(\frac{-1}{2} \nabla_{\mathbf{r}}^2 \sqrt{\rho(\mathbf{r})\rho(\mathbf{r}')} g(k_F(\mathbf{r})|\mathbf{r}-\mathbf{r}'|) \right) d\mathbf{r} d\mathbf{r}' \\
 & = \iint \delta(\mathbf{r}-\mathbf{r}') \left(\frac{-1}{2} \nabla_{\mathbf{r}}^2 \sqrt{\rho(\mathbf{r})\rho(\mathbf{r}')} g\left(\left\{ \frac{k_F^p(\mathbf{r})+k_F^p(\mathbf{r}')}{2} \right\}^{1/p} |\mathbf{r}-\mathbf{r}'| \right) \right) d\mathbf{r} d\mathbf{r}'
 \end{aligned} \tag{145}$$

Moreover, Eq. (145) can be simplified to a simple three-dimensional integral,^{87,169}

$$T_s^{\text{WDA}}[\rho^\alpha, \rho^\beta] = \sum_{\sigma=\alpha, \beta} T_w[\rho^\sigma] - \frac{3}{2} g''(0) \int \rho^\sigma(\mathbf{r}) (k_F^\sigma(\mathbf{r}))^2 d\mathbf{r} \tag{146}$$

where $g''(0)$, the curvature of the 1-matrix model at the origin, equals $-1/5$ for the uniform electron gas models. Notice that, this formula does not depend on the value of p in Eq. (131).

c) Results

If one chooses the formula for the Fermi vector that is appropriate for the uniform electron gas, Eq. (140), one recovers the TF+vW ($\lambda=1$) functional. Although this functional is exact for the uniform electron gas, the kinetic energies it assigns to atoms and molecular systems are far too high.^{87,136}

The conventional weighted density approximation for the kinetic energy results when the effective Fermi vector is determined by substituting the asymmetric 1-matrix, Eq.(137), into the diagonal idempotency condition, Eq. (142). This functional is also exact for the uniform electron gas, but the kinetic energies of atoms and molecules are still predicted to be far too high.^{87,176,177} Indeed, this functional is only slightly more accurate than the Thomas-Fermi functional. This is surprising since the WDA and the TF functional were derived from the same formula for the 1-matrix, but the WDA adds an additional exact constraint.

When the effective Fermi vector is determined by substituting the symmetric 1-matrix, Eq. (139), into the diagonal idempotency condition, the results are much better. This functional is also exact for the uniform electron gas, but now the kinetic energies of atoms and molecules are only slightly too high. The performance of this symmetrized WDA is comparable to the second-order gradient expansion. This seems to be a general result: the accuracy of the symmetrized WDA for exchange is comparable to conventional second-order gradient-corrected density functionals.

d) Other Related Approaches

By using local scaling transformation of the electron density,¹⁸²⁻¹⁹⁰ one can rewrite any kinetic energy functional as a 1-point, non-symmetric, weighted density approximation.^{187,190} Specifically, one has

$$\rho^{\text{WDA}}(\mathbf{r}) = \left(\frac{\tilde{t}[\rho; \mathbf{r}] - t_w(\mathbf{r}) + \frac{1}{4} \nabla^2 \rho(\vec{r})}{c_F \rho(\mathbf{r})} \right)^{3/2} \quad (147)$$

where $\tilde{t}[\rho; \mathbf{r}]$ is the local kinetic energy of the approximate functional and $t_w(\mathbf{r})$ is the local Weizsäcker kinetic energy, $t_w(\mathbf{r}) = |\nabla \rho(\mathbf{r})| / 8 \rho(\mathbf{r})$. This indicates that every approximate kinetic energy functional can be reproduced by a suitable weighted density approximation or a suitable local scaling transformation. That is,

both the weighted density approximation and the local scaling transformation are completely general, and in principle exact, approaches for developing kinetic energy functionals.

There are many other approaches that relates to the weighted density approximation; most of these approaches are designed to be more computationally efficient than the conventional WDA.^{87,176,191} We briefly mention the average density approximation (ADA),¹⁹² the modified weighted density approximation (MWDA),¹⁹³ the semi-local average density approximation (SADA),^{173,194} the reduced weighted density approximation,¹⁸⁰ and the generalized weighted density approximation.^{180,181}

I. E Approximate Kinetic Energy Functionals in k -Density Functional Theory

It seems extremely difficult to approximate the kinetic energy as an explicit functional of the electron density. In wave-function-based methods, when a single-particle theory fails to give satisfactory results, one has recourse to a hierarchy of increasingly complicated approaches. In particular, one builds better and better models by considering first two-particle correlations, then three-particle correlations, etc. The CCSDTQ... and CISDTQ... hierarchies are of this form.

For most chemical systems, these hierarchies quickly converge to the exact answer.

There is a similar hierarchy in density-functional theory: instead of using the one-electron distribution function (the electron density), one can use the two-electron distribution function (the pair density),^{16,17,195} the three-electron distribution function, etc..^{18,19,122} Using higher-order electron distribution function as the fundamental descriptor for an electronic system should give increasingly accurate results for chemical properties, including the electronic kinetic energy.

Chemists and physicists have done a lot of theoretical work on the pair-density-based theory,^{15-20,22,23,122,195-225} but there are few systematic tests of the approximate kinetic energy functionals that have been proposed. Chapters 3 and 4 of the thesis test two of the simplest functionals.

The Weizsäcker functional can be generalized to higher-order electron distribution functions (see, for example, Chapter 2),^{18,129,198-200,205}

$$T_w[\rho_k] = \frac{(N-k)!}{2(N-1)!} \iint \cdots \int \left| \nabla_{\mathbf{r}_1} \sqrt{\rho_k(\mathbf{r}_1, \dots, \mathbf{r}_k)} \right|^2 d\mathbf{r}_1 \cdots d\mathbf{r}_k. \quad (148)$$

The resulting theory is discussed, and numerically assessed, in Chapter 3. This approach has many features in common with the Weizsäcker-based approaches discussed in section III.D. For example, the k -electron distribution function can be

determined by solving for the ground state of an effective k -electron Schrödinger equation,

$$\left(\sum_{i=1}^k \frac{-1}{2} \nabla_i^2 + v(\mathbf{r}_k) + \frac{(N-1)}{(k-1)} \sum_{j=1}^{i-1} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + v_\theta(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_k) \right) \sqrt{\rho_k(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_k)} = \mathcal{E} \sqrt{\rho_k(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_k)} \quad (149)$$

where $v_\theta(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_k)$ is a potential that accounts for the effects of the Pauli exclusion principle.^{199,200}

One might hope that, just as the wave-function-based hierarchy rapidly converges to the exact kinetic energy, the hierarchy based on electron distribution functions would also. This is not true of the Weizsäcker functional: only a very small portion of the error in the Weizsäcker kinetic energy functional is corrected when one considers the 2-electron distribution function. Similarly, results for the 3-electron distribution function are only slightly better than those for the 2-electron distribution function. The Weizsäcker kinetic energy functional does not appear to be a good starting point for methods based on the k -electron distribution function.

The March-Santamaria formula for the kinetic energy density functional, cf. Eq.(76), is actually a functional for the non-interacting 2-fermion distribution

function.^{18,88} Substituting the *interacting* distribution function into this expression gives,

$$T^{\text{MS}}[\rho_k] = \iint \frac{|\nabla_{\mathbf{r}}(\rho_2(\mathbf{r}, \mathbf{r}') - \rho(\mathbf{r})\rho(\mathbf{r}'))|^2}{8(\rho_2(\mathbf{r}, \mathbf{r}') - \rho(\mathbf{r})\rho(\mathbf{r}'))} d\mathbf{r}d\mathbf{r}' \quad (150)$$

Since this functional is exact in Hartree-Fock theory, one might expect that it would give even better results when correlated pair densities were used. As shown in chapter 4, this is not the case: the quality of Eq. (150) actually *deteriorates* as the amount of electron correlation increases.

The effectiveness of Kohn-Sham theory arises because it imposes the Pauli principle by computing the kinetic energy from an N -electron wave-function or, equivalently, an N -representable 1-matrix. The previous results suggest that something similar should be done in higher-order density functional theories. Some results of this sort already exist in the literature. Ayers and Levy have proposed using a Slater determinant to approximate the kinetic energy and then computing the correlation-kinetic energy by comparing the true pair density to the non-interacting model pair density.²⁰⁴ Higuchi and Higuchi have proposed to compute the kinetic energy directly, using either Slater determinants or correlated wave-functions.^{206-209,219,220,224,225} Gonis *et al.* have proposed computing the kinetic energy using a model 2-matrix (albeit one that is not necessarily N -

representable).^{196,197} Approaches like these are much more computationally demanding than wave-function-free approaches like the ones we tried, but they seem to be required.

I. F Summary

Thomas and Fermi derived the first approximate kinetic energy density functional in 1927 and 1928, respectively.^{42,43} For the next decade, researchers patiently pursued better kinetic energy density functionals, but there were no major improvements until 1965, when Kohn and Sham revolutionized the field by introducing orbitals to approximate the kinetic energy.⁴⁴ The Kohn-Sham orbital-based density-functional theory (DFT) has come to dominate applications in chemistry and physics.

However, there is still interest in old-fashioned, Thomas-Fermi-like, orbital-free density functional theory. Part of this interest is practical: in Kohn-Sham DFT, one must determine the form of N 3-dimensional functions (the occupied Kohn-Sham orbitals), but in orbital-free DFT, one need determine only one 3-dimensional function (the electron density) (Note that, the computational cost for OF-DFT is at the order of $\sim N$ compared to Kohn-Sham method, which is at the order of $\sim N^3$). The computational cost for the k -order density functionals

is at the order of $\sim N^k$). Therefore, orbital-free DFT methods are computationally easier than Kohn-Sham DFT. Some of the interest is certainly aesthetic: density-based methods are appealing precisely because they avoid the conceptual and computational complexity inherent in the wave-function. At a practical level, however, the Kohn-Sham approach is indistinguishable from wave-function-based “Hartree plus correction” and “Hartree-Fock plus correction” approaches. Finally, some of the interest is intellectual: the literature on kinetic energy density functionals is extensive and challenging; there are few facets of DFT as intellectually stimulating as the quixotic quest for the kinetic energy functional.

Starting around 1980, there was a surge in new approaches to the kinetic energy density functional. Much progress has been made; modern functionals are much more accurate than anything available to Kohn and Sham. A breakthrough is still needed, however: no orbital-free density functional method has ever been shown to achieve high accuracy (e.g., chemical reaction energies and reaction barriers to within 5 kcal/mol). It seems doubtful whether any known orbital-free kinetic energy functional even achieves errors of 50 kcal/mol for reaction-thermochemistry and kinetics.

Most of the better approximate functionals give reasonable, albeit unspectacular, results for the kinetic energy when accurate atomic and molecular

densities are used. However, when the functionals are used in the variational principle for the electron density, the results deteriorate catastrophically, giving kinetic energies, total energies, and electron densities that are qualitatively incorrect. These failings may be attributed to the N -representability problem for density functionals: the kinetic energy functional does not correspond to an acceptable N -electron system.

We have been pursuing a method that addresses this failing directly. The idea is that the Pauli principle is partly encapsulated by the requirement that each electron excludes another electron with the same spin from its immediate vicinity. Mathematically, this condition is manifest in the normalization of the exchange hole,

$$-1 = \int \rho^\sigma(\mathbf{r}') h_x^{\sigma\sigma}(\mathbf{r}, \mathbf{r}') d\mathbf{r}' \quad (151)$$

Invoking the link between the exchange hole and the 1-matrix,

$$\left(\gamma^{\sigma\sigma}(\mathbf{r}, \mathbf{r}') \right)^2 = -\rho^\sigma(\mathbf{r}) h_x^{\sigma\sigma}(\mathbf{r}, \mathbf{r}') \rho^\sigma(\mathbf{r}'). \quad (152)$$

and the link between the kinetic energy and the 1-matrix, every possible model for the exchange hole implies a corresponding model for the kinetic energy. Our attempts to apply this approach using the uniform electron gas model for the

exchange hole gave encouraging results, though the results are still far from sufficient for chemical applications. Further details can be found in chapter 5.

Instead of modeling the exchange hole directly, one can use the exact exchange-correlation hole. Alternatively, one can use the pair density (2-density),

$$\rho_2^{\sigma_1\sigma_2}(\mathbf{r}_1, \mathbf{r}_2) = \rho^{\sigma_1}(\mathbf{r}_1)\rho^{\sigma_2}(\mathbf{r}_2)(1 + h_{xc}^{\sigma_1\sigma_2}(\mathbf{r}_1, \mathbf{r}_2)) \quad (153)$$

as the fundamental descriptor for the electronic system; one then variationally minimizes the energy with respect to the 2-density (rather than the electron density). This orbital free theory is afflicted by the N -representability problem for both the 2-density and for the kinetic energy functional of the 2-density. We derived (chapter 2) and tested (chapters 3 and 4) several kinetic energy functionals of the 2-density. The results are extremely disappointing. In particular, the generalized Weizsäcker functional for the 2-density is not much more accurate than the conventional Weizsäcker density functional. The March-Santamaria functional is more accurate and gives exact results for Slater determinant pair densities, but it incorrectly predicts that the kinetic energy decreases, instead of increases, with increasing electron correlation.

One might expect that moving to the still higher-order electron distribution functions would remedy the situation. It seems not to. The generalized Weizsäcker kinetic energy formula (which is arguably the most logical starting

point) is still extremely inaccurate for the 3-density, and our preliminary investigations of the 4-density were not very encouraging either. It seems that explicit, orbital-free, approaches using the k -density are just as challenging as the orbital-free density-functional theory.

I. G Overview of the Thesis

The focus of my thesis research was on development and testing of kinetic-energy functionals for higher-order electron distribution functions. This is the primary topic of chapters 2, 3, and 4. Discouraged by the difficulty of obtaining good results with these approaches, I then turned my attention to kinetic energy functionals in conventional DFT. The idea of that work, contained in chapter 5, was to use knowledge about the pair-density to design new kinetic energy functionals. Later, the similarity of this approach to the traditional weighted density approximation emerged: both the weighted density approximation and the method I propose use the electron density to model the pair-distribution function, which is then used to estimate the kinetic energy.

In Chapter 2, I propose a new derivation of the generalized Weizsäcker kinetic energy functionals. This derivation clarifies the link between the Weizsäcker kinetic energy functionals and the Fisher information; it also proposes a

momentum density and a quasi-probability distribution function that are consistent with the Weizsäcker kinetic energy. Using this formulation, it was possible to extend the Weizsäcker kinetic energy formula; unfortunately the extended functionals are actually less accurate than the conventional Weizsäcker kinetic energy.

Chapter 3 presents numerical tests of the spin-free and spin-resolved generalized Weizsäcker functionals for the electron density (1-density), 2-density, and 3-density. The results are disappointing, but they can be understood based on the non- N -representability of the model density matrix. This chapter presents the first systematic test of a kinetic energy functional for the 2-density and the only results in the literature for kinetic energy functionals of the 3-density.

Chapter 4 investigates the March-Santamaria functional for the 2-density. The March-Santamaria functional is exact for Slater determinantal 2-densities, so this work investigated the ability of 2-density methods to recover the kinetic energy contribution to the correlation energy. Unfortunately, the March-Santamaria functional predicts that the kinetic energy decreases with increasing electron correlation, which is qualitatively incorrect.

Chapter 5 abandons the idea of using the 2-density as the fundamental variational parameter and instead constructs a *model* for the 2-density based on the

uniform electron gas. This model can then be used to evaluate the kinetic energy. This approach is in the spirit of the weighted density approximation.⁸⁷ The results are comparable to semi-local kinetic energy functionals but, like all other functionals, are not accurate enough to be useful for chemical calculations. The algorithms that are used in this section, however, together with the insights gleaned from kinetic energy functionals of the 2-density, will facilitate further developments in this field.

In addition to my work on kinetic-energy functionals, I engaged in several other projects. In the field of chemical reactivity theory, I published one paper on higher-order chemical reactivity indicators and have prepared a manuscript showing how the Berlin binding function can be used to characterize the reaction force profile. I have also submitted a paper showing that the exchange hole determines the electron density exactly. Combined with the Hohenberg-Kohn theorem, this justifies using the exchange hole as the fundamental descriptor for an electronic system. A corollary of this mathematical theorem is that the exchange holes used in the weighted density approximation must have at least one node: otherwise the hole is not N -representable. This restricts the form of the model exchange hole in weighted density approximations (as in chapter 5). I have also been involved in work on numerical methods in density functional theory

(e.g., algorithms for implementing the weighted density approximation) and on joint projects related to the exchange-correlation density functional.

All of the preceding projects fall under the umbrella of (generalized) density-functional theory. I have worked on developing new methods for fitting diatomic potential energy curves. Those approaches, based on coordinate transformation, are designed to automatically reproduce the united-atom and separated-atom limits.

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Chapter II

Derivation of Generalized von Weizsäcker Kinetic Energies from Quasi-probability Distribution Functions

II.A. Introduction:

As discussed in the previous chapter, one of the biggest challenges in density-functional theory (DFT) and its many-electron generalizations is formulating an approximate kinetic energy functional. In this chapter, we investigate the relationship between the phase space distribution function and the Weizsäcker family of kinetic energy functionals. The Weizsäcker family of functionals¹⁻³ is particularly useful, at least at a theoretical level, because the form of the functional,

$$T_w[p] \propto \int \frac{\nabla p(\boldsymbol{\tau}) \cdot \nabla p(\boldsymbol{\tau})}{8p(\boldsymbol{\tau})} d\boldsymbol{\tau} \quad (1)$$

is preserved, whether $p(\boldsymbol{\tau})$ is a one-electron, two-electron, or many-electron distribution function. Moreover, for the N -electron distribution function, $p(\boldsymbol{\tau}) = |\Psi(\boldsymbol{\tau})|^2$, the Weizsäcker functional form is exact.^{4,5} In this chapter, we are also going to elucidate some properties of the Weizsäcker kinetic energy form, elucidating its link to information theory (Fisher information) and the momentum-space equation for the kinetic energy.

II.B. Fisher Information:

The Fisher information, $I[p]$, of a probability distribution function, $p(\mathbf{x})$, measures the local inhomogeneity of the system.⁶ In fact, Fisher

information is the measure of the variance in quantum fluctuation in any local observable.⁷⁹ For a unimodal distribution, it is a measure of the compactness of $p(\mathbf{x})$. For a multimodal distribution, $I[p]$ is a measure of “peakiness.” As stressed by Frieden, nature seems to favour extreme values of the Fisher information, and many of the laws and governing equations of physics can be obtained by minimizing/maximizing the Fisher information subject to appropriate physical constraints.⁷ An early derivation of the Schrödinger equation by minimizing the Fisher information was given by Sears, Parr, and Dinur.⁵ A recent review by Nalewajski features the many ways Fisher information is used in quantum chemistry and, more generally, molecular electronic structure theory.⁸

Suppose that a probability distribution function depends parametrically on parameters θ . Denote the probability of observing data value \mathbf{x} given that the parameters have values θ as $p(\mathbf{x}|\theta)$. In general, θ is a vector containing multiple parameters. The Fisher information indicates how much information we gain about the value of the parameters by measuring \mathbf{x} . For one data value and one parameter, the Fisher information is simply,

$$\begin{aligned}
 I[p] &= \int p(\mathbf{x}|\theta) \left(\frac{\partial \ln(p(\mathbf{x}|\theta))}{\partial \theta} \right)^2 d\mathbf{x} \\
 &= \int \frac{1}{p(\mathbf{x}|\theta)} \left(\frac{\partial p(\mathbf{x}|\theta)}{\partial \theta} \right)^2 d\mathbf{x}
 \end{aligned} \tag{2}$$

For multiple parameters, this expression generalizes to

$$I[p] = \int \frac{\nabla_{\theta} p(\mathbf{x}|\theta) \cdot \nabla_{\theta} p(\mathbf{x}|\theta)}{p(\mathbf{x}|\theta)} d\mathbf{x} \tag{3}$$

Owing to the Heisenberg momentum-position uncertainty principle, in quantum mechanics we cannot measure the position of particles exactly. What can we say about the true position of a particle if we observe it at the point \mathbf{x} ? Let θ be the position of the particle; this is the quantity we are trying to estimate. The fluctuation of the observed position of the particle from its true position must be translationally invariant. This means that $p(\mathbf{x}|\theta) = p(\mathbf{x} - \theta)$.⁷ Inserting this expression into Eq. (3) and making the substitution $\mathbf{y} = \mathbf{x} - \theta$ gives

$$\begin{aligned}
 I[p] &= \int \frac{\nabla p(\mathbf{y}) \cdot \nabla p(\mathbf{y})}{p(\mathbf{y})} d\mathbf{y} \\
 &= \int p(\mathbf{y}) \left| \nabla (\ln p(\mathbf{y})) \right|^2 d\mathbf{y}
 \end{aligned} \tag{4}$$

This particular manifestation of the Fisher information is sometimes called the Fisher information of locality, because it captures the inherent delocalization of quantum mechanical particles.⁴

The preceding derivation may be criticized in the context of molecular electronic structure theory because when one makes the Born-Oppenheimer approximation, the electronic coordinates \mathbf{x} are no longer translationally invariant because the nuclei are at fixed positions in space. We will not worry about the epistemological issue in this paper, because Eq. (4) may be interpreted even if one questions the appropriateness of this derivation in electronic structure theory.

In his prescient work, Fisher introduced the probability amplitude, $|\psi(\mathbf{x})|^2 = p(\mathbf{x})$. In terms of the probability amplitude, Eq. (4) takes a form reminiscent of the quantum mechanical kinetic energy,

$$I[\psi] = 4 \int \nabla \psi^*(\mathbf{x}) \cdot \nabla \psi(\mathbf{x}) d\mathbf{x} \sim 8T[\psi] \quad (5)$$

This form is the starting point for the derivation of the Schrödinger equation from the principle of extreme physical information.^{4,5,7} Equation (5) is more general, however, because $\psi(\mathbf{x})$ does not have to be a wavefunction.

Now let us consider the Fourier transform of the probability amplitude,

$$\begin{aligned}\widehat{\psi}(\mathbf{p}) &= \left(\frac{1}{2\pi}\right)^{d/2} \int e^{i\mathbf{p}\cdot\mathbf{x}} \psi(\mathbf{x}) d\mathbf{x} \\ \psi(\mathbf{x}) &= \left(\frac{1}{2\pi}\right)^{d/2} \int e^{-i\mathbf{p}\cdot\mathbf{x}} \widehat{\psi}(\mathbf{p}) d\mathbf{p}\end{aligned}\tag{6}$$

Using identities from Fourier analysis and defining the momentum-space probability distribution function in the obvious way, $p(\mathbf{p}) = |\widehat{\psi}(\mathbf{p})|^2$ we can write

$$I[\psi] = 4 \int \mathbf{p} \cdot \mathbf{p} |\widehat{\psi}(\mathbf{p})|^2 d\mathbf{p} \sim 8T[\psi]\tag{7}$$

The derivation of Eq. (7) will be expounded upon later. For now it suffices to note that a very similar derivation may be found in chapter three of Frieden's book.⁷ Eq. (7) is intuitive: the amount of information that can be obtained about position is proportional to the variance of the momentum. It is appealing that the most common of all measures of uncertainty—the variance—Fourier transforms into the Fisher information.

II.C. Kinetic Energy:

Even though the electronic kinetic energy is readily computed from the N -electron wave-function,

$$\begin{aligned}
 T[\Psi] &= \iint \cdots \int \Psi^*(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \left(\sum_{i=1}^N -\frac{1}{2} \nabla_i^2 \right) \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_N \\
 &= \iint \cdots \int \sum_{i=1}^N \frac{1}{2} \nabla_i \Psi^*(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \cdot \nabla_i \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_N
 \end{aligned} \tag{8}$$

the problem of approximating the kinetic energy directly from the electron density persists. In Equation(8), and throughout the remainder of this chapter, atomic units (where $\hbar = m_e = 1$) are used.

As we reviewed in Chapter I; pursuit of kinetic energy density functionals began with the work of Thomas and Fermi,⁹ followed soon after by von Weizsäcker.¹ Later work led to the semi-local gradient expansion approximation and approaches that incorporate information about the exact linear response function of the uniform electron gas.¹²⁻¹⁵ These latter functionals are among the most successful functionals, at least in the solid state.^{13, 18-21}

We wish to focus on two aspects of kinetic energy functionals in this chapter. First, we will focus on the Weizsäcker functional. Many authors have suggested that the Weizsäcker functional is a good starting point for kinetic energy functionals,^{12,16,22-34} partly because it ensures the correct behavior at the nuclear-electron cusps and also in the asymptotic decaying tails of the electron density. The Weizsäcker functional is, in its spin-resolved form,

$$T_w^{(1)}[\rho_\sigma] = \sum_{\sigma=\alpha,\beta} \int \frac{\nabla \rho_\sigma(\mathbf{r}) \cdot \nabla \rho_\sigma(\mathbf{r})}{8\rho_\sigma(\mathbf{r})} d\mathbf{r} \tag{9}$$

where the spin density is given by the expression

$$\rho_{\sigma}(\mathbf{r}) = \left\langle \Psi \left| \sum_{i=1}^N |\sigma(i)\rangle \delta(\mathbf{r}_i - \mathbf{r}) \langle \sigma(i)| \right| \Psi \right\rangle \quad (10)$$

and is normalized to the number of electrons with the specified spin,

$$N_{\sigma} = \int \rho_{\sigma}(\mathbf{r}) d\mathbf{r} \quad (11)$$

The electron density is nonnegative but because it is not normalized to one, it is not a probability distribution function. For this reason, it is sometimes more convenient to work with the so-called shape functions,³⁵⁻³⁸

$$p_{\sigma}(\mathbf{r}) = \frac{\rho_{\sigma}(\mathbf{r})}{N_{\sigma}}. \quad (12)$$

The Weizsäcker functional is then

$$T_w^{(1)}[p_{\sigma}] = \sum_{\sigma=\alpha,\beta} N_{\sigma} \int \frac{\nabla p_{\sigma}(\mathbf{r}) \cdot \nabla p_{\sigma}(\mathbf{r})}{8 p_{\sigma}(\mathbf{r})} d\mathbf{r}. \quad (13)$$

The shape function is usually denoted $\sigma(\mathbf{r})$, but we will use the nonstandard notation in Eq. (12) to avoid confusion with the spin index.

The second aspect of kinetic energy functionals we wish to focus on is the momentum-space representation. In momentum space, the kinetic energy is a simple and explicit functional of the momentum density,

$$T = \sum_{\sigma=\alpha,\beta} \int \frac{1}{2}(\mathbf{p} \cdot \mathbf{p}) \rho_{\sigma}(\mathbf{p}) d\mathbf{p} \quad (14)$$

The momentum density is defined by an expression just like Eq. (10), but now the Fourier-transformed wave-functions (denoted $\hat{\Psi}$; cf. Eq. (6)) are used,

$$\Pi_{\sigma}(\mathbf{p}) = \left\langle \hat{\Psi} \left| \sum_{i=1}^N |\sigma(i)\rangle \delta(\mathbf{p}_i - \mathbf{p}) \langle \sigma(i)| \right| \hat{\Psi} \right\rangle \quad (15)$$

Notice that the momentum density is not the Fourier transform of the position density; this will be important later in our analysis when we try to approximate the kinetic energy functional.

There is another perspective that is intermediate between the position-space and momentum-space approach; this perspective is based on quasiprobability distribution functions.³⁹⁻⁴¹ In classical mechanics, one can generate a phase-space distribution function, $f(\mathbf{r}, \mathbf{p})$ that represents the probability of observing a particle at the point \mathbf{r} with momentum \mathbf{p} . Recall that the Heisenberg uncertainty principle forbids measuring the position and momentum of a particle simultaneously; there are therefore innumerable many choices for $f(\mathbf{r}, \mathbf{p})$. Given a quasiprobability distribution function, however, the local kinetic energy,⁴²⁻⁴⁵

$$t_{\sigma}(\mathbf{r}) = \int \frac{1}{2}(\mathbf{p} \cdot \mathbf{p}) f_{\sigma}(\mathbf{r}, \mathbf{p}) d\mathbf{p}, \quad (16)$$

and the total kinetic energy,

$$T = \sum_{\sigma=\alpha,\beta} \int t_{\sigma}(\mathbf{r}) d\mathbf{r} \quad (17)$$

are readily evaluated.

The one-electron quasiprobability distribution function can be computed from the one-electron reduced density matrix,^{41,45,46,47}

$$\gamma_{\sigma\sigma}(\mathbf{r}, \mathbf{r}') = N_{\sigma} \iiint \cdots \int \left[\begin{array}{l} \Psi^*(\mathbf{r}'_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \\ \times (|\sigma(1)\rangle \delta(\mathbf{r}'_1 - \mathbf{r}') \delta(\mathbf{r}_1 - \mathbf{r}) \langle \sigma(1)|) \\ \times \Psi^*(\mathbf{r}'_1, \mathbf{r}_2, \dots, \mathbf{r}_N) d\mathbf{r}_1 d\mathbf{r}'_1 d\mathbf{r}_2 \dots d\mathbf{r}_N \end{array} \right] \quad (18)$$

by the equation,

$$f_{\sigma}(\mathbf{r}, \mathbf{p}) = \left(\frac{1}{2\pi} \right)^6 \iiint e^{-i\tau \mathbf{p}} e^{-i\boldsymbol{\theta}(\mathbf{r}-\mathbf{u})} g(\boldsymbol{\theta}, \boldsymbol{\tau}) \gamma_{\sigma\sigma}(\mathbf{u} + \frac{1}{2}\boldsymbol{\tau}, \mathbf{u} - \frac{1}{2}\boldsymbol{\tau}) d\mathbf{u} d\boldsymbol{\theta} d\boldsymbol{\tau} \quad (19)$$

where the function $g(\boldsymbol{\theta}, \boldsymbol{\tau})$ is any function that is well-behaved enough for the integral to exist that satisfies the constraints

$$\begin{aligned} g(\boldsymbol{\theta}, \boldsymbol{\tau} = 0) &= g(\boldsymbol{\theta} = 0, \boldsymbol{\tau}) = 1 \\ (g(\boldsymbol{\theta}, \boldsymbol{\tau}))^* &= g(-\boldsymbol{\theta}, -\boldsymbol{\tau}) \end{aligned} \quad (20)$$

The most popular choice, $g = 1$, corresponds to the Wigner distribution³⁹. Quasiprobability distribution functions for many-electron reduced density matrices are computed from very similar formulas.

Every kinetic energy density functional is based on some choice, whether implicit or explicit, for the momentum density and/or the quasiprobability distribution function.

II.D. Generalized Weizsäcker Forms of the Kinetic Energy:

It should be noted that the Weizsäcker kinetic energy functional, Eq.(13), strongly resembles the form of the Fisher information, Eq. (4). Similarly, the *exact* kinetic energy functional as in Eq.(14), recalls the momentum-space formula for the Fisher information, Eq. (7). Is there some way to, using the link to momentum space, improve the Weizsäcker functional so that it is more accurate? Can formulating a momentum-density or quasiprobability distribution version of the Weizsäcker functional give some insight into the functional?

Since the Weizsäcker functional depends only on the electron density in position space, the corresponding momentum density must also be a density functional. Consider the momentum density of a “piece” of the electron density,

$$\pi_{\sigma}^{(a)}(\mathbf{p}) = \left(\frac{1}{2\pi}\right)^{3/2} \int e^{i\mathbf{p}\cdot\mathbf{r}} (\rho_{\sigma}(\mathbf{r}))^a d\mathbf{r} \quad (21)$$

A reasonable, if highly approximate, formula for the momentum density is then

$$\tilde{\Pi}_{\sigma}^{(a)}(\mathbf{p}) = \frac{1}{2} \left(\pi_{\sigma}^{(a)}(\mathbf{p}) \left[\pi_{\sigma}^{(1-a)}(\mathbf{p}) \right]^* + \left[\pi_{\sigma}^{(a)}(\mathbf{p}) \right]^* \pi_{\sigma}^{(1-a)}(\mathbf{p}) \right) \quad (22)$$

This form is motivated by the idea that the square root of the density has the units of the wave-function. So using the square root of the electron density instead of $\psi(\mathbf{r})$ in Eq. (6) seems analogous to the usual procedure for deriving the momentum density and, moreover, is exact for one-electron systems; we will see that this is equivalent to the Weizsäcker approximation. Eq. (22) is just the generalization of this idea, and we hoped that by optimizing the value of a we could obtain better results.

Now we derive the kinetic energy density functional that is built from the approximate momentum-space density in Eq.(22),

$$\tilde{T}_{\sigma}^{(a)} = \int \frac{1}{2} (\mathbf{p} \cdot \mathbf{p}) \tilde{\Pi}_{\sigma}^{(a)}(\mathbf{p}) d\mathbf{p} \quad (23)$$

Substituting in the definition of the approximate momentum density, this simplifies to

$$\begin{aligned}
 \tilde{T}_\sigma^{(a)} &= \frac{1}{4} \left(\int (\mathbf{p} \cdot \mathbf{p}) \pi_\sigma^{(a)}(\mathbf{p}) \left(\pi_\sigma^{(1-a)}(\mathbf{p}) \right)^* d\mathbf{p} + \text{c.c.} \right) \\
 &= \frac{1}{4} \left(\frac{1}{2\pi} \right)^3 \int (\mathbf{p} \cdot \mathbf{p}) \left[\iint e^{i(\mathbf{p} \cdot \mathbf{r})} (\rho_\sigma(\mathbf{r}))^a e^{-i(\mathbf{p} \cdot \mathbf{r}')} (\rho_\sigma(\mathbf{r}'))^{1-a} d\mathbf{r} d\mathbf{r}' \right] d\mathbf{p} + \text{c.c.}
 \end{aligned}
 \tag{24}$$

Here c.c. denotes the addition of the complex conjugate of the preceding term.

Interchanging the order of integration and using the Fourier transform form of the derivative,

$$(-1)^n \mathcal{D}^{(n)}(x-x') = \frac{1}{2\pi} \int e^{ip(x-x')} (ip)^n dp \tag{25}$$

gives

$$\begin{aligned}
 \tilde{T}_\sigma^{(a)} &= -\frac{1}{4} \iint \mathcal{D}^{(2)}(\mathbf{r}-\mathbf{r}') (\rho_\sigma(\mathbf{r}))^a (\rho_\sigma(\mathbf{r}'))^{1-a} d\mathbf{r} d\mathbf{r}' + \text{c.c.} \\
 &= -\frac{1}{4} \int (\rho_\sigma(\mathbf{r}'))^{1-a} \nabla^2 (\rho_\sigma(\mathbf{r}'))^a d\mathbf{r}' + \text{c.c.} \\
 &= -\frac{1}{2} \int (\rho_\sigma(\mathbf{r}'))^{1-a} \nabla^2 (\rho_\sigma(\mathbf{r}'))^a d\mathbf{r}'
 \end{aligned}
 \tag{26}$$

This formula simplifies to

$$\begin{aligned}
 \tilde{T}_\sigma^{(a)} &= -\frac{a(a-1)}{2} \int (\rho_\sigma(\mathbf{r}'))^{1-a} (\rho_\sigma(\mathbf{r}'))^{a-2} (\nabla \rho_\sigma(\mathbf{r}') \cdot \nabla \rho_\sigma(\mathbf{r}')) d\mathbf{r}' \\
 &\quad - \frac{a}{2} \int \nabla^2 \rho(\mathbf{r}) d\mathbf{r} \\
 &= -\frac{a(a-1)}{2} \int \frac{\nabla \rho_\sigma(\mathbf{r}') \cdot \nabla \rho_\sigma(\mathbf{r}')}{\rho_\sigma(\mathbf{r}')} d\mathbf{r}'
 \end{aligned}
 \tag{27}$$

The Laplacian term in the second line vanishes because of the rapidly decaying nature of the electron density (which is, in turn, forced by the boundary conditions on the electronic wave-function). If we wish to interpret Eqs. (23) and (27) as manifestations of the Fisher information, it is better to write instead

$$\tilde{T}_\sigma^{(a)} = -\frac{a(a-1)}{2} N_\sigma \int \frac{\nabla p_\sigma(\mathbf{r}') \cdot \nabla p_\sigma(\mathbf{r}')}{p_\sigma(\mathbf{r}')} d\mathbf{r}' \quad (28)$$

The approximate kinetic energy functional $\tilde{T}_\sigma^{(a)}$ is a parabola in a with maximum value at $a = 1/2$. The maximum value is precisely the Weizsäcker functional.^{3,49,50} Since the Weizsäcker functional is a lower bound to the true kinetic energy, the most accurate member of this family of generalized Weizsäcker functionals is the conventional Weizsäcker functional itself.

Notice also that $\tilde{T}_\sigma^{(0)} = \tilde{T}_\sigma^{(1)} = 0$. This follows from Eq. (28) and the fact that the following momentum density has zero kinetic energy,

$$\tilde{\Pi}_\sigma^{(0)}(\mathbf{p}) = \tilde{\Pi}_\sigma^{(1)}(\mathbf{p}) = \frac{1}{2} \left(\delta(\mathbf{p}) \int e^{i\mathbf{p}\cdot\mathbf{r}} \rho_\sigma(\mathbf{r}) d\mathbf{r} + \text{c.c.} \right) \quad (29)$$

The reader may wonder why we did not consider the straightforward Fourier transform of the electron density,

$$\bar{\rho}(\mathbf{p}) = \frac{1}{2} \left(\int e^{i\mathbf{p}\cdot\mathbf{r}} \rho_{\sigma}(\mathbf{r}) d\mathbf{r} + \text{c.c.} \right). \quad (30)$$

(Notice: this is *not* the ansatz in Eqs. (21) and (22).) This momentum density gives an entirely different, and seemingly absurd, value for the kinetic energy. Namely,

$$\begin{aligned} \tilde{T}_{\sigma}[\bar{\rho}_{\sigma}] &= \int \frac{1}{2}(\mathbf{p} \cdot \mathbf{p}) \bar{\rho}_{\sigma}(\mathbf{p}) d\mathbf{p} \\ &= \int \frac{1}{2}(\mathbf{p} \cdot \mathbf{p}) \left(\frac{1}{2} \right) \left[\left(\frac{1}{2\pi} \right)^{3/2} \int e^{i\mathbf{p}\cdot\mathbf{r}} \rho_{\sigma}(\mathbf{r}) d\mathbf{r} + \text{c.c.} \right] d\mathbf{p} \\ &= -\frac{1}{2}(2\pi)^{3/2} \int \delta^{(2)}(\mathbf{r} - \mathbf{0}) \rho_{\sigma}(\mathbf{r}) d\mathbf{r} \\ &= -\sqrt{2\pi^3} \nabla^2 \rho_{\sigma}(\mathbf{0}) \end{aligned} \quad (31)$$

For an atom centered at the origin, this kinetic energy actually diverges. Distressingly, this formula for the kinetic energy appears to be origin-dependent (and, therefore, not translationally invariant), but this reveals an oversight in the derivation—the integrand is too ill-conditioned to permit interchange of the order of differentiation in the second step of Eq. (31)—rather than a physical inconsistency. (In general, the Laplacian of the density is evaluated at a point in space that is determined by the electron density itself.)

Returning to the Weizsäcker form, the density matrix corresponding to the Weizsäcker functional is,

$$\tilde{\gamma}_{\sigma\sigma}(\mathbf{r}, \mathbf{r}') = \sqrt{\rho_{\sigma}(\mathbf{r})\rho_{\sigma}(\mathbf{r}')} \quad (32)$$

This density matrix usually violates the Pauli principle (it is not N -representable) because there are N_{σ} electrons in the first natural orbital.⁵⁰ This is why the correction to the Weizsäcker functional is often made using the Pauli potential.^{22, 23, 51, 52}

It is interesting, and disappointing, that even though the Weizsäcker model for the density matrix, Eq. (32), is very simple, the quasi-probability distribution cannot generally be expressed in closed form, even for the simplest $g(\mathbf{0}, \mathbf{r}) = 1$ case (corresponding to the Wigner distribution). To understand this, consider that even for the ground state of the hydrogen atom, the Wigner distribution has a very complicated analytic form.⁵³⁻⁵⁵ Thus, while the naïveté of the Weizsäcker form is obvious from the mathematical form of the reduced density matrix, the momentum distribution function, $\tilde{\Pi}_{\sigma}^{(a)}(\mathbf{p})$, and quasiprobability distribution function have complicated forms that seem to obscure the inappropriateness of this choice and for which, in general, there is no explicit expression.

II.E. Extension to Many-Electron Distribution Functions:

As attempts to find accurate, variationally stable, explicit kinetic energy functionals of the electron density have so far been unsuccessful, it is

reasonable to consider descriptors that contain more information than the electron density. In *ab initio* quantum chemistry, there is a hierarchy of methods, starting with single-particle methods, then electron pair methods, etc. There is also a hierarchy of *k*-density functional theories based on the electron distribution functions,^{3, 56, 57} starting with the electron density (*k*=1) and moving to the pair density (*k*=2) and even higher-order electron distribution functions. The most common of these “extended” density-functional theories is based on electron pair density,⁵⁸⁻⁶⁰

$$\rho_{\sigma\sigma'}^{(2)}(\mathbf{r}, \mathbf{r}') = \left\langle \Psi \left| \sum_{i=1}^N \sum_{\substack{j=1 \\ j \neq i}}^N \sigma(i) \sigma'(j) \right\rangle \delta(\mathbf{r}_i - \mathbf{r}) \delta(\mathbf{r}_j - \mathbf{r}') \left\langle \sigma'(j) \sigma(i) \right| \Psi \right\rangle$$

(33)

The theoretical properties of the kinetic energy functional of the pair density have been thoroughly explored;^{3, 58, 61-63} some practical formulas have also been presented.^{2, 3, 64-72} The most popular functional seems to be the two-electron Weizsäcker function,^{2, 3, 65, 73, 74}

$$\begin{aligned}
 T_w^{(2)}[\rho_{\sigma\sigma'}^{(2)}] &= \sum_{\sigma=\alpha,\beta} \frac{1}{N_\sigma - 1} \iint \frac{\nabla_1 \rho_{\sigma\sigma}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \cdot \nabla_1 \rho_{\sigma\sigma}^{(2)}(\mathbf{r}_1, \mathbf{r}_2)}{8 \rho_{\sigma\sigma}^{(2)}(\mathbf{r}_1, \mathbf{r}_2)} d\mathbf{r} d\mathbf{r}' \\
 &= \sum_{\sigma=\alpha,\beta} N_\sigma \iint \frac{\nabla_1 p_{\sigma\sigma}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \cdot \nabla_1 p_{\sigma\sigma}^{(2)}(\mathbf{r}_1, \mathbf{r}_2)}{8 p_{\sigma\sigma}^{(2)}(\mathbf{r}_1, \mathbf{r}_2)} d\mathbf{r} d\mathbf{r}' \quad (34) \\
 &= \sum_{\sigma=\alpha,\beta} \frac{N_\sigma}{2} \iint \frac{\nabla_\tau p_{\sigma\sigma}^{(2)}(\boldsymbol{\tau}) \cdot \nabla_\tau p_{\sigma\sigma}^{(2)}(\boldsymbol{\tau})}{8 p_{\sigma\sigma}^{(2)}(\boldsymbol{\tau})} d\boldsymbol{\tau}
 \end{aligned}$$

The second equality in Eq. (34) uses the unit-normalized many-electron shape functions,

$$p_{\sigma\sigma'}(\mathbf{r}, \mathbf{r}') = \begin{cases} \frac{\rho_{\sigma\sigma'}(\mathbf{r}, \mathbf{r}')}{N_\sigma N_{\sigma'}} & \sigma \neq \sigma' \\ \frac{\rho_{\sigma\sigma}(\mathbf{r}, \mathbf{r}')}{N_\sigma (N_\sigma - 1)} & \sigma = \sigma' \end{cases} \quad (35)$$

The third equality in Eq.(34) uses the 6-dimensional gradient. This form is especially useful for extending the Weizsäcker functional to the higher-order electron distribution functions needed in general k -density functional theories,

$$T_w^{(k)}[\rho_{\sigma_1 \sigma_2 \dots \sigma_k}^{(k)}] = \sum_{\sigma=\alpha,\beta} \frac{N_\sigma}{k} \iint \frac{\nabla_\tau p_{\sigma\sigma \dots \sigma}^{(k)}(\boldsymbol{\tau}) \cdot \nabla_\tau p_{\sigma\sigma \dots \sigma}^{(k)}(\boldsymbol{\tau})}{8 p_{\sigma\sigma \dots \sigma}^{(k)}(\boldsymbol{\tau})} d\boldsymbol{\tau} \quad (36)$$

The extended Weizsäcker functionals from Eq. (36) form an increasing sequence of lower bounds to the exact kinetic energy,

$$T_w^{(1)} \leq T_w^{(2)} \leq T_w^{(3)} \leq \dots \leq T_w^{(N)} = T_{\text{exact}} \quad (37)$$

with the $k=N$ formula being exact for any N -electron distribution function that arises from a real-valued wave-function.³ Unfortunately, this series of bounds converges slowly.⁷⁵

Comparing Eqs. (28) and (36), it is clear that the entire analysis from the previous section can be extended to many-electron distribution functions. In particular, we can define a k -particle spin-momentum probability distribution function by

$$\begin{aligned}\pi_{\sigma_1\sigma_2\ldots\sigma_k}^{(a,k)}(\mathbf{P}) &= \left(\frac{1}{2\pi}\right)^{3k/2} \int e^{i\mathbf{P}\cdot\boldsymbol{\tau}} \left(p_{\sigma_1\sigma_2\ldots\sigma_k}^{(k)}(\boldsymbol{\tau})\right)^a d\boldsymbol{\tau} \\ \tilde{\Pi}_{\sigma_1\sigma_2\ldots\sigma_k}^{(a,k)}(\mathbf{P}) &= \frac{1}{2} \left(\pi_{\sigma_1\sigma_2\ldots\sigma_k}^{(a,k)}(\mathbf{P}) \left[\pi_{\sigma_1\sigma_2\ldots\sigma_k}^{(1-a,k)}(\mathbf{P}) \right]^* + \left[\pi_{\sigma_1\sigma_2\ldots\sigma_k}^{(a,k)}(\mathbf{P}) \right]^* \pi_{\sigma_1\sigma_2\ldots\sigma_k}^{(1-a,k)}(\mathbf{P}) \right)\end{aligned}\quad (38)$$

One of the many possible expressions for the kinetic energy that can be written using these approximate k -particle momentum distributions is,

$$\tilde{T}^{(k)} \left[\tilde{\Pi}_{\sigma_1\sigma_2\ldots\sigma_k}^{(a,k)} \right] = \sum_{\sigma=\alpha,\beta} \frac{N_\sigma}{k} \int \frac{1}{2} (\mathbf{P} \cdot \mathbf{P}) \tilde{\Pi}_{\sigma\sigma\ldots\sigma}^{(a,k)}(\mathbf{P}) d\mathbf{P}. \quad (39)$$

As before, the most accurate functional is obtained for $a = 1/2$, which is the Fourier-transformed form of the extended Weizsäcker functional in Eq. (36).

The other aspects of the analysis of one-particle Weizsäcker kinetic energy functional also generalize. For example, the k -electron reduced density matrix that is implicit in Eq. (36) is

$$\tilde{\Gamma}_{\sigma \dots \sigma; \sigma \dots \sigma}^{(k)}(\boldsymbol{\tau}, \boldsymbol{\tau}') = \binom{N_{\sigma}}{k} \sqrt{p_{\sigma \sigma \dots \sigma}^{(k)}(\boldsymbol{\tau}) p_{\sigma \sigma \dots \sigma}^{(k)}(\boldsymbol{\tau}')} \quad (40)$$

This density matrix is usually not N -representable because the maximum occupation number of a k -particle state is $\binom{N_{\sigma}}{k} \frac{1}{N_{\sigma} - k + 1}$.⁷⁶⁻⁷⁸ The extended Weizsäcker functionals can be exact only when the number of electrons of a given spin is equal to the number of electrons in the functional, k .

II.F. Summary:

The expression for the Fisher information in coordinate space is similar to the form of the Weizsäcker kinetic energy functional; compare Eqs. (4) and (13). The expression for the Fisher information in reciprocal (momentum) space is reminiscent of the quantum mechanical kinetic energy; compare Eqs. (7) and (14). These similarities motivated us to find a momentum representation for the Weizsäcker functional and to, moreover, attempt to generalize the Weizsäcker functional. The form of momentum distribution in Eqs. (21) and (22) recovers the Weizsäcker functional for $a = 1/2$. Unfortunately, even though this family of momentum densities gives a generalized Weizsäcker function (Eq. (28)), all of the other functionals in this family are less accurate than the Weizsäcker functional.

Is it possible to generalize Eq. (22) still further, so that we can perhaps obtain an improved kinetic energy density functional? We tried to use the more general form,

$$\tilde{\Pi}_{\sigma}^{(a,b,c,d)}(\mathbf{p}) = \frac{1}{2} \left(\left(\pi_{\sigma}^{(a)}(\mathbf{p}) \right)^c \left[\left(\pi_{\sigma}^{(b)}(\mathbf{p}) \right)^d \right]^* + \left[\left(\pi_{\sigma}^{(a)}(\mathbf{p}) \right)^c \right]^* \left(\pi_{\sigma}^{(b)}(\mathbf{p}) \right)^d \right) \quad (41)$$

$$ac + bd = 1$$

We were unable to find the position-space representation of the kinetic energy functional for this form. Perhaps some functionals in the extended family derived from Eq. (41) are more accurate than the usual Weizsäcker form. We note that approximating the momentum density by simply Fourier transforming the spatial electron density gives seemingly absurd, and certainly inaccurate, results.

The same reasoning applies to the extended Weizsäcker functionals that are used in what is often called k -density functional theory, where the fundamental descriptor of an electronic system is the k -electron distribution function. The extended Weizsäcker functionals are also proportional to the Fisher information of the k -electron distribution function, and they also have a compact momentum-space representation that follows directly from the momentum-space representation of the Fisher information density via the probability amplitude. To our knowledge, this is the first time that the

momentum-space representation for the many-electron Weizsäcker family of functionals has been presented. We find it intuitively appealing that the second moment (ergo, the variance, and also the Weizsäcker kinetic energy) of the momentum is closely related to the Fisher information of a many-electron distribution function.

In the following chapter, we are going to show how the one-, two-, and three-electron Weizsäcker functionals deviate from the true kinetic energy for atoms and some selected molecules. We will also discuss the origin of pair-density functional theory and explain why density functionals based on the pair density are important in that context.

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Chapter III

Failure of the Weizsäcker Kinetic Energy Functionals for Higher-Order Electron Distribution Functions

III.A. Motivation:

In the Hohenberg-Kohn-Sham approach to density-functional theory (DFT), properties are computed using an effective one-electron Hamiltonian. The N -electron eigenstates of this Hamiltonian provide an initial approximation to electronic properties of the system, including the energy. The difference between the properties of the non-interacting system and the interacting system is due to exchange and correlation; these effects are approximated using a density functional.

The biggest disadvantage of DFT is the inability to systematically improve results by refining the treatment of exchange and correlation in the system. For example, if a given density functional approximation (e.g., the famous B3LYP¹⁻⁴) fails to work, it is impossible to improve the results systematically without breaking away from the fundamental spirit of DFT and resorting to *ab initio*-flavored approaches to the quantum many-body problem. For example, one can systematically improve the results using Görling-Levy perturbation theory,^{5,6} but by doing so one incurs all of the computational costs and convergence issues associated with Møller-Plesset theory. On the other hand, it is possible to construct hierarchies of density-functional approximations (e.g., the Jacob's ladder of functionals⁷⁻⁹) that improve results *on average*. For a given system,

however, there is no guarantee that the results will improve with the increasing complexity and computational cost of the density-functional approximation. Moreover, if the error of none of the approximations suffices, further improvement of the results seems to require an approach based on many-electron correlated wave-functions.¹⁰⁻¹³ Finally, it is possible that there is not much room for further improvement in density-functional approximations. Recent work on functionals proves that the exact exchange-correlation functional has a discontinuous dependence on the Kohn-Sham orbitals.^{14,15} (Similarly, the correlation functional in first-order density matrix functional theory must also have a discontinuous dependence on the orbitals.) Insofar as it seems very difficult to design explicit exchange-correlation functionals that are discontinuous, but continuous functionals will always produce physically absurd results in some systems, one may question whether how much improvement in density-functional approximations is possible.

In the mid-1990's, Ziesche proposed an alternative to Görling-Levy perturbation functional for improving density functional approximations.^{16,17} Instead of considering a wave-function-based correction strategy for systematically improving density-functional approximations, he considered an approach based on higher-order electron distribution functions and, specifically,

the electron pair density. By including information from higher-order electron distribution functions, one may systematically approach the exact result.^{18,19} At the top of the hierarchy, the N -electron distribution function is merely the square of the exact ground-state wave-function for the system, and the exact functional is known. For the pair density (2-density) and higher-order electron distribution functions (k -densities), the potential-energy portion of the electronic energy can be computed exactly, and the only term that needs to be approximated is the kinetic energy functional. Unlike the situation in density-functional theory and first-order density matrix functional theory, there is no evidence that the approximate functionals in k -density functional theory ($k > 1$) need to be discontinuous.

The development of k -density functional theories and, especially, pair density functional theory is an active area of research.¹⁶⁻⁵⁵ Numerical results are scant, largely because of the theoretical difficulties attendant to this approach. In addition, most of the practical proposals require six-dimensional numerical integration of highly peaked (even singular) integrands, and therefore are not amenable to off-the-shelf black-box implementations.

The k -electron distribution function (k -density) can be defined in either the spin-averaged,

$$\rho_k(\mathbf{R}_1, \dots, \mathbf{R}_k) = \left\langle \Psi \left| \sum_{i_1 \neq i_2 \neq \dots \neq i_k} \delta(\mathbf{r}_{i_1} - \mathbf{R}_1) \dots \delta(\mathbf{r}_{i_k} - \mathbf{R}_k) \right| \Psi \right\rangle \quad (1)$$

or spin-resolved

$$\rho_k^{\sigma_1 \dots \sigma_k}(\mathbf{R}_1, \dots, \mathbf{R}_k) = \left\langle \Psi \left| \sum_{i_1 \neq i_2 \neq \dots \neq i_k} |\sigma_1(i_1) \dots \sigma_k(i_k)\rangle \delta(\mathbf{r}_{i_1} - \mathbf{R}_1) \dots \delta(\mathbf{r}_{i_k} - \mathbf{R}_k) \langle \sigma_1(i_1) \dots \sigma_k(i_k) | \right| \Psi \right\rangle \quad (2)$$

form. In both cases, for $k > 1$, the exact interaction energy with the external potential and the exact electron-electron repulsion energy can be computed as a functional of k -particle density and it is only the kinetic energy that needs to be approximated. According to generalized Hohenberg-Kohn theorem, the kinetic energy is a universal functional of the k -density. For a given approximate kinetic energy functional, $\tilde{T}[\rho_k]$, the ground-state energy is then computed by the variational procedure,

$$E_{g.s.} = \min_{\{\rho_k | \rho_k \text{ is } N\text{-representable}\}} (\tilde{T}[\rho_k] + V_{ext}[\rho_k] + V_{ee}[\rho_k]) \quad (3)$$

Notice that the minimization has to be restricted to k -densities that are N -representable. The N -representability problem is a big problem in k -DFT; the necessary and sufficient conditions for N -representability are known on a lattice⁴¹ and in real space,³² but they are not known in a useful form. There has been much

work on necessary conditions for N -representability.^{19,20,27, 28, 38-42, 52, 54} Partly because the N -representability problem seems so intractable, most of the work in k -DFT concentrates on the development of kinetic-energy functionals. (If the kinetic-energy functional is defined appropriately, the N -representability constraints can be shifted from the minimization principle into the functional.^{29,30,56} That is, one can consider “ N -representability of the functional”⁵⁷⁻⁶⁰ instead of “ N -representability of the k -density.”^{28, 32, 41})

Suppose that, in analogy to the one-electron Schrödinger equation for the Kohn-Sham orbitals, one proposes an effective two-electron Schrödinger equation for a model system of geminals($g_{\kappa}(\mathbf{r}_1, \mathbf{r}_2)$),

$$E_{v,N}^{g,s}[\rho_2] = \min_{\substack{\rho_2(\vec{r}_1, \vec{r}_2) = N(N-1) \\ \rho_2(\vec{r}_1, \vec{r}_2) \geq 0}} \left[T[\rho_2] + \iint \rho_2(\vec{r}_1, \vec{r}_2) \frac{[v(\vec{r}_1) + v(\vec{r}_2)]}{2(N-1)} d\vec{r}_1 d\vec{r}_2 + \frac{1}{2} \iint \frac{\rho_2(\vec{r}_1, \vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_1 d\vec{r}_2 \right] \quad (4)$$

$$\left\{ \frac{1}{2(N-1)} [\hat{h}_0(\mathbf{r}_1) + \hat{h}_0(\mathbf{r}_2)] + \frac{1}{2|\mathbf{r}_1 - \mathbf{r}_2|} + v_{xc}[\rho_2; \mathbf{r}_1, \mathbf{r}_2] \right\} g_{\kappa}(\mathbf{r}_1, \mathbf{r}_2) = \varepsilon_{\kappa} g_{\kappa}(\mathbf{r}_1, \mathbf{r}_2) \quad (5)$$

The geminals are orthonormal and, in analogy to the expression for the electron density as the sum of the orbital densities in Kohn-Sham theory, the pair density can be written as the sum of the geminal densities,

$$\rho_2(\mathbf{r}_1, \mathbf{r}_2) = \sum_{\kappa}^{occ} |g_{\kappa}(\mathbf{r}_1, \mathbf{r}_2)|^2 \quad (6)$$

where,

$$g_{\kappa}^0(\vec{r}_1, \vec{r}_2) = \begin{vmatrix} \varphi_{\kappa_1}(\vec{r}_1) & \varphi_{\kappa_2}(\vec{r}_1) \\ \varphi_{\kappa_1}(\vec{r}_2) & \varphi_{\kappa_2}(\vec{r}_2) \end{vmatrix} \quad (7)$$

Clearly, the kinetic energy functional splits into a part that is explicitly dependent on the geminals and an unknown remainder that is a functional of pair density.

$$T[\rho_2] = \frac{1}{2(N-1)} \sum_{\kappa}^{occ} \left\langle g_{\kappa} \left| -\frac{1}{2} \nabla_1^2 - \frac{1}{2} \nabla_2^2 \right| g_{\kappa} \right\rangle + T_{xc}[\rho_2] \quad (8)$$

The functional $T_{xc}[\rho_2]$ is approximated and the associated potential,

$$v_{xc}[\rho_2; \mathbf{r}_1, \mathbf{r}_2] = \frac{\delta T_{xc}[\rho_2]}{\delta \rho_2(\mathbf{r}_1, \mathbf{r}_2)}$$

acts as effective electron-electron interaction. The

ground-state energy can be evaluated as

$$E_{g.s.} = \sum_{\kappa}^{occ} \varepsilon_{\kappa} + T_{xc}[\rho_2] - \iint \rho_2(\mathbf{r}_1, \mathbf{r}_2) v_{xc}[\rho_2; \mathbf{r}_1, \mathbf{r}_2] d\mathbf{r}_1 d\mathbf{r}_2 \quad (9)$$

Many pair density theories fit into this framework. If the geminals are considered to be simple singlet-state Slater determinants of the occupied Kohn-Sham orbitals,

$$g_k^0(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_k^0(\mathbf{r}_1)\alpha(1) & \phi_k^0(\mathbf{r}_1)\beta(1) \\ \phi_k^0(\mathbf{r}_2)\alpha(2) & \phi_k^0(\mathbf{r}_2)\beta(2) \end{vmatrix} \quad (10)$$

then the kinetic energy in this theory is the same as in Kohn-Sham theory. (Note that these geminals do not solve Eq. (4) unless the electron-electron repulsion is replaced by the mean-field representations of the electron-electron repulsion potentials used in Kohn-Sham theory.) If a single geminal is used, one recovers the approach of Nagy,^{25,26} which leads to the popular Weizsäcker functional that we will test in this chapter. If many geminals are used, one has the formulation that was originally proposed by Ziesche, and then developed further by Gonis *et al.*^{16,17,21,22}

Unfortunately, there have been very few calculations testing the accuracy of these, and other, approximations to the kinetic energy functional.^{45,46} There do not seem to be numerical implementations for even the simplest possible functional forms, the Weizsäcker-style functional,^{14,18-20,28,52}

$$T_w^{(k)}[\rho_k] = \frac{(N-k)!}{2(N-1)!} \iint \cdots \int \left| \nabla_{\mathbf{r}_1} \sqrt{\rho_k(\mathbf{r}_1, \dots, \mathbf{r}_k)} \right|^2 d\mathbf{r}_1 \dots d\mathbf{r}_k \quad (11)$$

and its spin-resolved analogues, e.g.,¹⁴

$$\begin{aligned}
 T_{w,s}^{(k)}[\rho_k^{\sigma_1\sigma_2\ldots\sigma_k}] &= \frac{(N_\alpha - k)!}{2(N_\alpha - 1)!} \iint \cdots \int \left| \nabla_{\mathbf{r}_1} \sqrt{\rho_k^{\alpha\alpha\cdots\alpha}(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_k)} \right|^2 d\mathbf{r}_1 d\mathbf{r}_2 \cdots d\mathbf{r}_k \\
 &\quad + \frac{(N_\beta - k)!}{2(N_\beta - 1)!} \iint \cdots \int \left| \nabla_{\mathbf{r}_1} \sqrt{\rho_k^{\beta\beta\cdots\beta}(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_k)} \right|^2 d\mathbf{r}_1 d\mathbf{r}_2 \cdots d\mathbf{r}_k
 \end{aligned} \tag{12}$$

The goal of this chapter is to test the quality of these two simple functionals. Among the various spin-resolved Weizsäcker forms,¹⁸ we chose Eq. (11) because it seems to give the best results.

The Weizsäcker functionals have appealing theoretical properties. All Weizsäcker functionals can be derived from considerations of the Fisher information;^{53,62,63} there is also a derivation based on the quasiprobability distribution functions.⁶⁴ The spin-averaged Weizsäcker functionals (Eq. (11)) are an increasing sequence of lower bounds to the true kinetic energy that becomes exact when $k = N$. The spin-resolved Weizsäcker functionals are an increasing sequence of lower bounds for the kinetic energy; results are exact for σ -spin component of the kinetic energy when $k = N_\sigma$. In wave-function-based theories, a sequence of approximations that is exact for increasing numbers of electrons (e.g., CCSD ($k=2$), CCSDT ($k=3$) ...) rapidly converges towards the exact energy. One might expect, then, that the Weizsäcker kinetic-energy bounds rapidly converge towards the true kinetic energy. The purpose of this chapter is to show that this is

not the case. This is shown in the next section. Following those results, we will speculate about the reasons for our disappointing findings and propose directions for future research.

III.B. Computational Tests of k -Weizsäcker Kinetic Energy Functionals:

We evaluated the k -densities from the reoptimized Clementi-Roetti Hartree-Fock wave-functions of Koga et al.^{65,66} We then evaluated the Weizsäcker kinetic energy functionals in Eqs. (11) and (12) using numerical integration methods; in problematic cases we used several different numerical integration algorithms to obtain an estimate on the integration error. Our results are accurate to 5 or 6 digits in most cases. For the higher-dimensional integrals ($k = 3$) of the larger atoms we are less confident in our results because different numerical integration techniques sometimes gave differing results. The number of digits in Tables 1 and 2 reflects our estimated uncertainties in the integration errors. Especially for large atoms and the $k = 3$ functionals, our estimates may be too optimistic. We are confident that the trends we report are correct.

The underlying reason for these numerical difficulties is that the integrands in Eq. (11) have singularities and near-singularities; this is most clear when they are rewritten as

$$T_w^{(3)}[\rho_3] = \frac{1}{2(N-1)(N-2)} \iiint \frac{|\nabla_{\mathbf{r}_1} \rho_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)|^2}{4\rho_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)} d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 \quad (13)$$

For such strongly peaked functions, numerical integration methods converge poorly. Even in the worst cases, our conclusions are not altered: because the errors are small compared to the total kinetic energy, they do not affect the qualitative trends.

Table 1 presents the atomic kinetic energies computed using the Weizsäcker functionals for the He-Ne and higher-atomic number elements from the first three columns of the periodic table (Groups 1, 2, and 13). In agreement with theoretical predictions, the Weizsäcker functionals are lower bounds to the true kinetic energy and they are exact when the order of the functional is equal to the total number of electrons (spin-averaged functional) or the number of electrons of a given spin (spin-resolved functional). The spin-resolved functionals are much tighter lower bounds, but they are not very accurate. The errors are massive (several Hartrees) and they deteriorate rapidly with increasing electron number. The general trend is clear from Fig. 1 (first-row atoms) and Fig. 2 (alkaline earths). The failure of the Weizsäcker bounds to converge rapidly to the true kinetic energy can be characterized as follows: the percentage of the Hartree-

Fock energy that is recovered does not diminish as k increases. That is, we have a problem of non-decreasing returns: the correction we obtain from increasing k does not decrease (significantly, if at all) as k increases. This is not what is usually observed in quantum chemistry, where a law of diminishing returns indicates that increasing k (e.g., from CCSD to CCSDT to CCSDTQ) provides successively smaller corrections to the energy. Because of this, we do not believe the Weizsäcker bounds are likely to be practically useful. Examination of the smaller atoms in Table 1 reveals that the final correction (from $k = N - 1$ to $k = N$) is not at all negligible. Since evaluating the Weizsäcker functional for $k > 4$ is highly impractical, this limits the utility of this functional to systems with very few electrons.

We also investigated the Be, B, Mg, and Al iso-electronic series, as shown in Table 2. Not only does the absolute accuracy of the Weizsäcker functionals deteriorate rapidly with increasing Z , the relative accuracy (see Figure 3) decreases. For the isoelectronic series, we used the Hartree-Fock wave-functions of Clementi and Roetti.⁶⁷

Table 1: Results from the generalized Weizsäcker kinetic energy functionals, in Hartree, for selected atoms. The k -densities of the reoptimized Clementi-Roetti wave-functions of Koga et al.⁶⁵ are used to evaluate the spin-averaged Weizsäcker functionals, $T_w^{(k)}[\rho_k]$, (Eq.(11)) and the spin-resolved Weizsäcker functionals, $T_{w,s}^{(k)}[\rho_k^{\sigma_1 \dots \sigma_k}]$ (Eq.(12)). The --- entries refer to cases where the functional is undefined. In all these cases, generalizing the functional definition would reproduce the Hartree-Fock value in the last column.

Atoms	$T_w^{(1)}$	$T_w^{(2)}$	$T_w^{(3)}$	$T_{w,s}^{(1)}$	$T_{w,s}^{(2)}$	$T_{w,s}^{(3)}$	Hartree-Fock
He	2.86168	2.86168	---	2.86168	2.86168	---	2.8616799
Li	7.1948	7.23861	7.38568	7.23984	7.43273	---	7.4327257
Be	13.662	13.7127	13.898	13.662	14.573	---	14.5730211
B	21.985	22.0787	22.2825	22.0572	23.4816	24.5292	24.5290583
C	31.9701	32.1067	32.3414	32.2604	34.3106	35.3447	37.6886164
N	43.8028	44.0282	44.3807	44.1732	46.9322	48.0525	54.4009314
O	57.6913	57.9683	58.3223	58.1464	61.1564	66.1228	74.8093948
F	73.1752	73.5121	73.9637	73.6478	77.0231	81.9227	99.4093436
Ne	90.6143	90.6643	91.4291	90.6143	92.3258	99.7039	128.5470893
Na	110.509	111.046	111.797	110.562	115.024	121.241	161.8589059
Mg	132.599	133.224	134.085	132.599	137.608	143.724	199.6146304

Al	156.791	157.508	158.297	156.818	162.574	169.636	241.8766997
K	345.148	346.486	347.507	345.186	355.197	365.724	599.1646995
Ca	384.08	385.53	387.534	384.08	394.778	406.0000	676.7580985
Ga	939.62	942.479	945.97	939.653	959.922	982.668	1923.260944

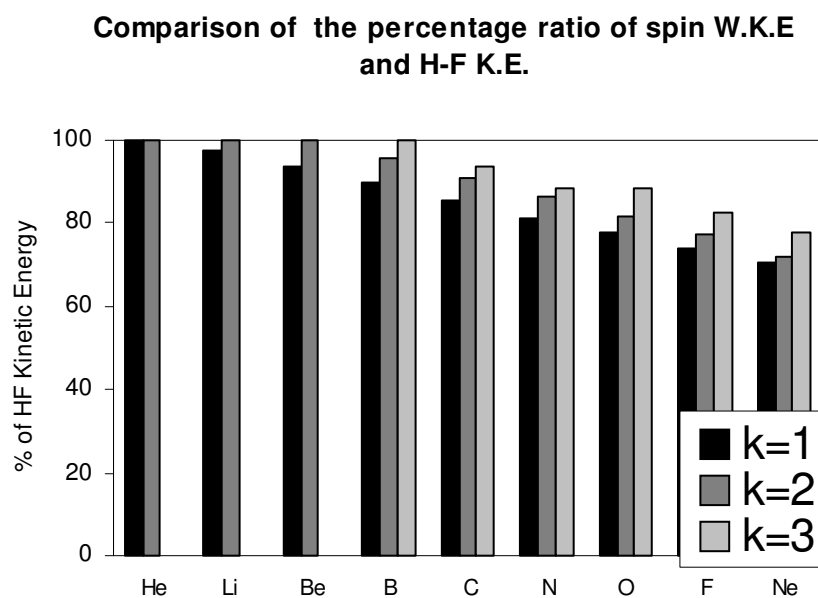


Figure 1.

The percentage of the Hartree-Fock kinetic energy that is obtained from the spin-resolved Weizsäcker kinetic-energy functionals, $T_{w,s}^{(k)}[\rho_k^{\sigma_1 \cdots \sigma_k}]$ (Eq. (12)) in the atoms from the first two rows of the periodic table.

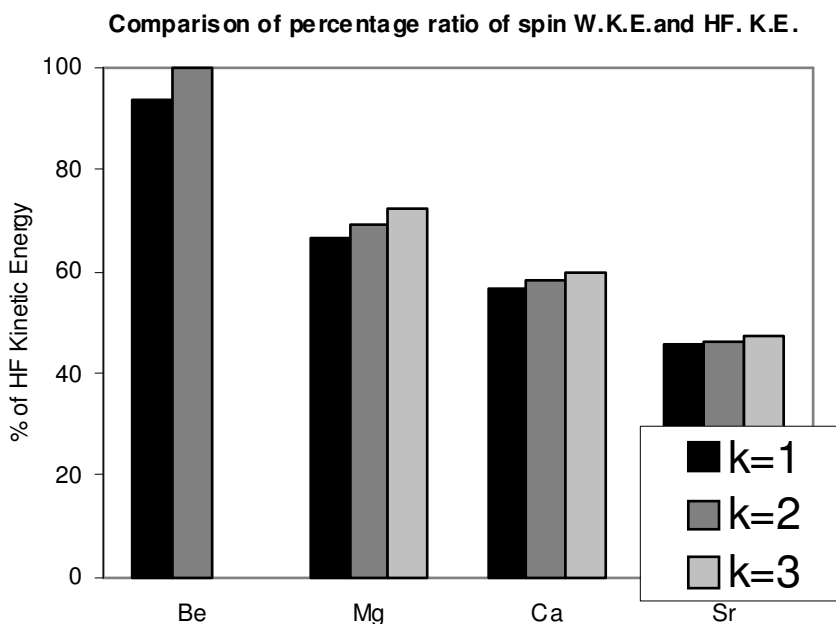


Figure 2.

The percentage of the Hartree-Fock kinetic energy that is obtained from the spin-resolved Weizsäcker kinetic-energy functionals, $T_{w,s}^{(k)}[\rho_k^{\sigma_1 \cdots \sigma_k}]$ (Eq. (12)) in the alkaline earth atoms.

Table 2: Results from the generalized Weizsäcker kinetic energy functionals, in Hartree, for selected isoelectronic atomic series. The k -densities of the Clementi-Roetti Hartree-Fock wave-functions⁵⁵ are used to evaluate the spin-averaged Weizsäcker functionals, $T_w^{(k)}[\rho_k]$, (Eq. (11)) and the spin-resolved Weizsäcker functionals, $T_{w,s}^{(k)}[\rho_k^{\sigma_1 \dots \sigma_k}]$ (Eq. (12)). The --- entries refer to cases where the functional is undefined.

Atoms	$T_w^{(1)}$	$T_w^{(2)}$	$T_w^{(3)}$	$T_{w,s}^{(1)}$	$T_{w,s}^{(2)}$	$T_{w,s}^{(3)}$	Hartree-Fock
Be	13.6601	13.7106	13.8959	13.6601	14.573	---	14.5730211
B ⁺	22.2872	22.3957	22.7771	22.2872	24.2377	---	24.237358
C ²⁺	33.0613	33.2478	33.8879	33.0613	36.4089	---	36.408167
N ³⁺	45.9816	46.2655	47.2273	45.9816	51.0828	---	51.081823
O ⁴⁺	61.0466	61.4476	62.7937	61.0466	68.2579	---	68.257209
F ⁵⁺	78.2581	78.7956	80.5888	78.2581	87.9345	---	87.934406
Ne ⁶⁺	97.6095	98.3046	100.612	97.6095	110.111	---	110.11053
Si ¹⁰⁺	196.467	197.9880	202.961	196.467	223.826	---	223.82185
K ¹⁵⁺	368.256	371.252	380.979	368.256	422.212	---	422.21645
Cr ²⁰⁺	593.661	598.628	614.679	593.661	683.107	---	683.1065
Cu ²⁵⁺	872.641	880.063	904.007	872.641	1006.49	---	1006.5046
B	21.9846	22.0784	22.2819	22.0569	23.4814	24.5288	24.5290583

C ⁺	32.5439	32.7184	33.0817	32.7055	35.2783	37.2954	37.292134
N ²⁺	45.239	45.4840	46.0095	45.5178	49.5057	52.7429	52.815497
O ³⁺	60.0679	60.4588	61.2438	60.4912	66.2951	71.0701	71.094284
F ⁴⁺	77.0323	77.5797	78.6521	77.6275	85.546	92.1264	92.126286
Ne ⁵⁺	96.1258	96.8369	98.2549	96.9202	107.248	115.901	115.91027
P ¹⁰⁺	223.607	225.496	229.078	225.806	252.933	276.098	276.09476
Ca ¹⁵⁺	404.397	408.005	414.778	408.681	460.472	505.033	505.03896
Mn ²⁰⁺	638.507	644.396	655.379	645.556	729.95	802.764	802.73882
Zn ²⁵⁺	925.894	934.596	950.774	936.387	1061.14	1169.17	1169.19
Mg	132.584	133.208	133.697	132.584	137.624	143.856	199.6133
Al ⁺	156.908	157.69	158.565	156.908	163.164	170.362	241.67309
Si ⁺²	183.418	184.374	185.528	183.418	191.047	200.572	287.9984
P ⁺³	212.092	213.244	214.486	212.092	221.216	231.817	338.56931
S ⁺⁴	242.95	244.312	245.885	242.95	253.716	266.992	393.3776
Cl ⁺⁵	275.982	277.577	279.041	275.982	288.516	303.688	452.42601
Ar ⁺⁶	311.1660	313.006	315.31	311.166	325.595	343.71	515.68668
Ti ⁺¹⁰	473.657	476.676	480.553	473.657	497.036	527.066	811.05743
Co ⁺¹⁵	725.513	730.396	736.208	725.513	763.137	810.724	1275.3289
Ge ⁺²⁰	1031.51	1038.69	1047.2	1031.51	1086.82	1157.7	1845.201
Al	156.78	157.496	158.39	156.808	162.551	169.322	241.86967
Si ⁺	183.203	184.084	184.967	183.255	190.264	197.408	288.56642
P ⁺²	211.786	212.845	213.804	211.868	220.252	229.919	339.6366

S^{+3}	242.537	243.795	245.046	242.652	252.557	264.476	395.07063
Cl^{+4}	275.451	276.923	278.528	275.6050	287.141	300.258	454.8561
Ar^{+5}	310.52	312.226	314.22	310.718	324.043	340.326	518.998851
V^{+10}	518.283	521.411	524.973	518.773	542.876	572.986	904.7713
Ni^{+15}	780.088	785.051	790.99	780.989	819.021	866.408	1398.9843
As^{+20}	1095.95	1103.19	1111.39	1097.38	1152.71	1222.06	2001.5808

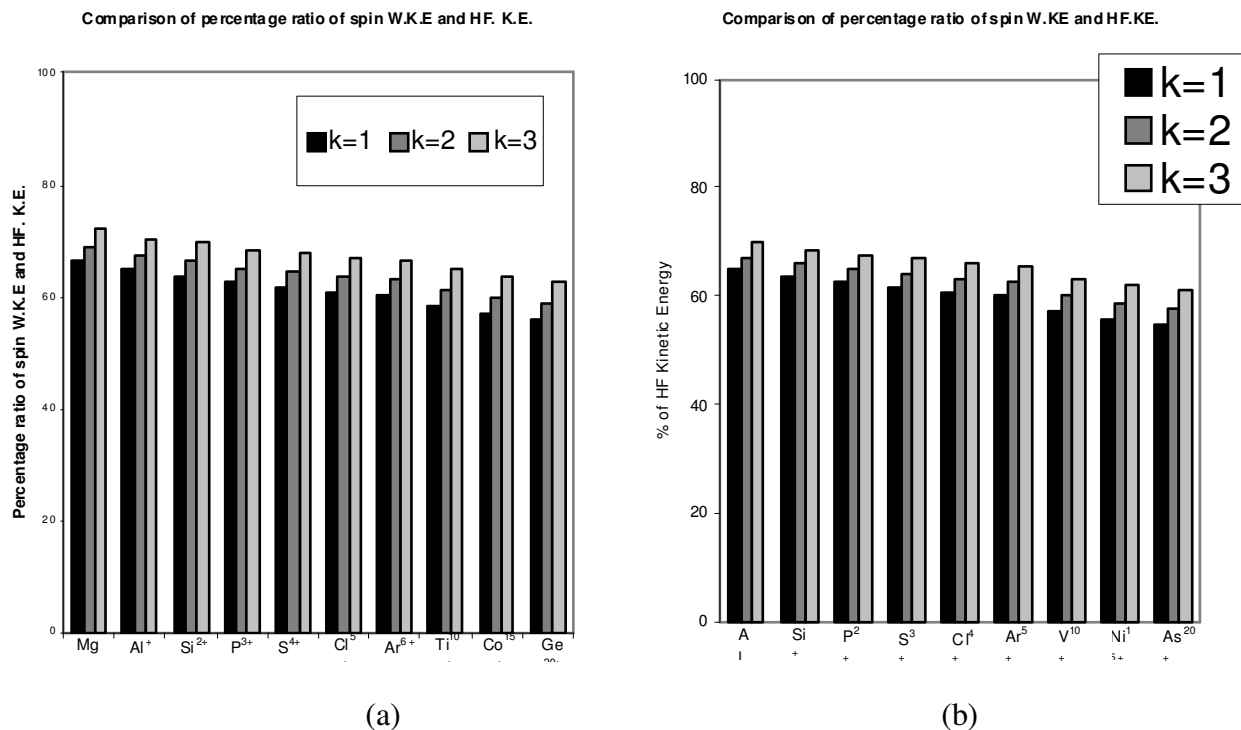


Figure 3.

The percentage of the Hartree-Fock kinetic energy that is obtained from the spin-resolved Weizsäcker kinetic-energy functionals, $T_{w,s}^{(k)}[\rho_k^{\sigma_1 \dots \sigma_k}]$ in the (a) Boron and (b) Aluminum isoelectronic series. The results for the Beryllium isoelectronic series are qualitatively similar to the Boron case, but the results are exact for $k=2$ (instead of $k=3$). The results for the Magnesium isoelectronic series strongly resemble the results for Aluminum series. Notice the deterioration of results as the atomic number increases.

III. C. Discussion

Can we dismiss these results as inappropriate tests of the Weizsäcker functionals for the k -density? For example, it is known to be dangerous to test conventional density functionals ($k = 1$) for the noninteracting kinetic energy and exchange energy using data from Hartree-Fock because of the small, yet subtle, differences between the definitions of the various energy terms in Hartree-Fock and conventional DFT. The same is true here: the values of the exact kinetic energy functionals for a Slater-determinantal k -density^{29, 30} might differ from the Hartree-Fock kinetic energy. (E.g., among all wave-functions with a given 2-density, there might be one with a lower kinetic energy than the Hartree-Fock kinetic energy.³⁰) The variational principle for the energy dictates that the difference between the value of the exact kinetic energy functional and the Hartree-Fock kinetic energy is less than the quantum chemical electron correlation energy.¹ Since the errors in the Weizsäcker functionals are enormously larger than the possible error in the Hartree-Fock approximation to the k -DFT kinetic energy, this theoretical subtlety does not affect the interpretation of our results.

Why are the Weizsäcker kinetic-energy functionals so poor? Consider that Eqs. (11) and (12) are derived, implicitly, from a reconstruction of the k -

electron reduced density matrix from the k -density. For example, Eq. (11) may be derived by assuming that the k -electron reduced density matrix is¹⁸

$$\Gamma_k(\mathbf{r}_1, \dots, \mathbf{r}_k; \mathbf{r}'_1, \dots, \mathbf{r}'_k) = \left(\sqrt{\rho_k(\mathbf{r}_1, \dots, \mathbf{r}_k)} \right) \left(\sqrt{\rho_k(\mathbf{r}'_1, \dots, \mathbf{r}'_k)} \right) \quad (13)$$

The exact k -electron reduced density matrix can be written in terms of the natural k -bitals as^{68,69}

$$\Gamma_k(\mathbf{r}_1, \dots, \mathbf{r}_k; \mathbf{r}'_1, \dots, \mathbf{r}'_k) = \sum_i n_i^{(k)} \phi_i^{(k)}(\mathbf{r}_1, \dots, \mathbf{r}_k) \left(\phi_i^{(k)}(\mathbf{r}'_1, \dots, \mathbf{r}'_k) \right)^* \quad (14)$$

An N -representability constraint on Γ_k restricts the occupation numbers of the natural k -bitals

$$0 \leq n_i^{(k)} \leq \frac{1}{N - k + 1}. \quad (15)$$

For $k < N$, there must be more than one occupied k -bital. The expression in Eq. (13) is not an N -representable Γ_k , and so it does not give an acceptable kinetic energy functional. In particular, for $k < N$, the density matrix ansatz in Eq. (13) strongly violates Fermi statistics (though it is perfectly satisfactory for bosonic systems). As is usually the case, failure to impose adequate N -representability conditions on the k -electron density matrix results in a very weak lower bound on the energy. Because the violation of N -representability in Eq.(15) reduces very

slowly with increasing k , and is still “large” even for $k = N - 1$, the k - Weizsäcker family of functionals converges very slowly to the correct result.

Where do we go from here? The negative result suggests that while the Weizsäcker family of kinetic energy bounds may have theoretical utility, they are not useful for practical computations. Other functionals should be pursued. For Slater determinantal k -densities like those used here, March and Santamaria derived an exact functional,⁷⁰ which is, in spin-resolved form,¹⁸

$$T_{\text{MS}}^{(2)}[\rho_2^{\sigma_1\sigma_2}] = -\iint \frac{|\nabla_{\mathbf{r}_1}(\rho_2^{\alpha\alpha}(\mathbf{r}_1, \mathbf{r}_2) - \rho_1^\alpha(\mathbf{r}_1)\rho_1^\alpha(\mathbf{r}_2))|^2}{8(\rho_2^{\alpha\alpha}(\mathbf{r}_1, \mathbf{r}_2) - \rho_1^\alpha(\mathbf{r}_1)\rho_1^\alpha(\mathbf{r}_2))} d\mathbf{r}_1 d\mathbf{r}_2 \\ - \iint \frac{|\nabla_{\mathbf{r}_1}(\rho_2^{\beta\beta}(\mathbf{r}_1, \mathbf{r}_2) - \rho_1^\beta(\mathbf{r}_1)\rho_1^\beta(\mathbf{r}_2))|^2}{8(\rho_2^{\beta\beta}(\mathbf{r}_1, \mathbf{r}_2) - \rho_1^\beta(\mathbf{r}_1)\rho_1^\beta(\mathbf{r}_2))} d\mathbf{r}_1 d\mathbf{r}_2 \quad (16)$$

This functional would give exact results for all the systems considered in this chapter. The problem with the functional is that the integrand is often singular in real systems, leading to extreme numerical difficulties and possible lack of convergence. The March-Santamaria functional can be extended, with some difficulty, to $k > 2$ ¹⁸. Because the March-Santamaria functional is exact for a single Slater determinant, to test it we should use correlated wavefunctions. Those tests are reported separately in the next chapter.⁷¹

An alternative approach, first proposed by Ayers and Levy, is more closely aligned with the spirit of a hierarchy of k -density functional theories³¹. In that approach, one starts with the non-interacting kinetic energy from Kohn-Sham DFT, $T_s[\rho]$, and corrects it based on the differences between the pair density from the Kohn-Sham Slater determinant, $\rho_{2,s}(\mathbf{r}_1, \mathbf{r}_2)$, and the true pair density, obtaining a functional of the form³¹

$$T_{\text{AL}}^{(2)}[\rho_2] = T_s[\rho[\rho_2]] + T_c[\rho_{2,s}; \rho_2]. \quad (17)$$

This could be extended to $k = 3$ by replacing the Kohn-Sham calculation with Gonis-type theory for the pair density.^{21,22} Given the difficulties we encountered with the Weizsäcker family of functionals, we are skeptical that any truly explicit form for the kinetic energy functional will give satisfactory results. Based on this hunch, we are currently writing a computer program that will allow us to explore approaches based on Eq. (17).

It would also be interesting to test the Weizsäcker functional for bosonic systems. For bosons, a pair-density approach using the Weizsäcker functional might give results that are significantly better than density functional theory, without prohibitive computational cost.

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Chapter IV

March-Santamaria Kinetic Energy Functional

IV.A. Motivation:

One way to construct a hierarchy of density-functional theories, that is analogous to the Hartree-Fock, configuration interaction-singles CIS, CISD, CISDT hierarchy of traditional wave-function-based *ab initio* theory is to consider the k -electron density as the fundamental descriptor of electronic system.^{1,2} In the limit as k approaches the number of electrons, exact results are obtained; this is reminiscent of the convergence of wave-function-based *ab initio* methods to the exact result in the full-CI limit (where N -electron excitations are included). We call methods based on the k -electron distribution function k -density functional theories.

Most work in k -density functional theory (k -DFT) has been focused on the electron pair density,^{3,4} but most of the work has been formal in nature, with few practical theoretical results. There seem to be two major obstacles to practical k -DFT approaches. The first is N -representability problem: for $k > 1$, some seemingly reasonable k -electron distribution function is unattainable by any N -fermion system.⁵ While exact and approximate N -representability constraints are known, imposing these constraints on the variational principle is not easy.^{2,6-10} For more information about the N -representability problem, the reader is referred to the review article by Davidson.¹¹

The other problem is that there is no simple, explicit, and accurate formula for the kinetic energy in terms of the k -electron density for $k < N$. Much of the previous work has been focused on the generalized Weizsäcker functionals^{1, 12-16} but, as shown in the previous chapter, the accuracy of this functional is inadequate.¹⁷ Just as with the N -representability problem, exact approaches to the kinetic-energy functional problem are known at a formal level,^{1,4,18,19} but these results are not practically useful. It is interesting that appropriately constructed kinetic-energy functionals can include the N -representability constraints.¹⁸⁻²⁰ Therefore, if a sufficiently accurate kinetic energy functional were known, the N -representability problem might be avoided.

Even before the rise of 2-density functional theory, March and Santamaria proposed a functional for the kinetic energy in terms of the same-spin electron pair density,²¹

$$\rho_2^{\sigma\sigma}(\mathbf{R}_1, \mathbf{R}_2) = \left\langle \Psi \left| \sum_{i_1 \neq i_2} \sigma(i_1) \sigma(i_2) \right| \delta(\mathbf{r}_{i_1} - \mathbf{R}_1) \delta(\mathbf{r}_{i_2} - \mathbf{R}_2) \right\rangle \left\langle \sigma_2(i_2) \cdots \sigma(i_1) \right| \Psi \right\rangle \quad (1)$$

namely,

$$T_{\text{MS}} = \sum_{\sigma=\alpha,\beta} \frac{-1}{8} \iint \frac{|\nabla_1 (\rho_2^{\sigma\sigma}(\mathbf{r}_1, \mathbf{r}_2) - \rho^\sigma(\mathbf{r}_1) \rho^\sigma(\mathbf{r}_2))|^2}{(\rho_2^{\sigma\sigma}(\mathbf{r}_1, \mathbf{r}_2) - \rho^\sigma(\mathbf{r}_1) \rho^\sigma(\mathbf{r}_2))} d\mathbf{r}_1 d\mathbf{r}_2 \quad (2)$$

Here $\rho^\sigma(\mathbf{r})$ is the usual spin-resolved electron density. The March-Santamaria function was derived for pair densities that arise from Slater determinants,

$$\begin{aligned}\rho_2^{\sigma\sigma}(\mathbf{r}_1, \mathbf{r}_2) &= \gamma^\sigma(\mathbf{r}_1, \mathbf{r}_2) \wedge \gamma^\sigma(\mathbf{r}_1, \mathbf{r}_2) \\ &= \gamma^{\sigma\sigma}(\mathbf{r}_1, \mathbf{r}_1) \gamma^{\sigma\sigma}(\mathbf{r}_2, \mathbf{r}_2) - \gamma^{\sigma\sigma}(\mathbf{r}_1, \mathbf{r}_2) \gamma^{\sigma\sigma}(\mathbf{r}_2, \mathbf{r}_1) \quad (3) \\ &= \rho^\sigma(\mathbf{r}_1) \rho^\sigma(\mathbf{r}_2) - \gamma^{\sigma\sigma}(\mathbf{r}_1, \mathbf{r}_2) \gamma^{\sigma\sigma}(\mathbf{r}_2, \mathbf{r}_1)\end{aligned}$$

and is exact in that case. Slater determinants present the simplest possible uncorrelated wave-function for a pair density, but for a real system, the correlation between electrons makes a chemically significant contribution to the total energy. As shown in the appendix, the March-Santamaria functional may be derived as the lowest-order approximate kinetic energy functional that can be constructed from the cumulant expansion of the reduced density matrix;¹ in this sense it is conceptually similar to coupled-cluster theory.²²⁻²⁴ Since the cumulant expresses the corrections to the independent particle approximation, it is thus questionable whether the March-Santamaria functional can capture the effects of electron correlation.

The purpose of this article is to assess the accuracy of the March-Santamaria functional for spin-resolved pair densities. Because the March-Santamaria functional is based on the ansatz in Eq.(2), we use this approximation to the pair density, but we use correlated density matrices. Presuming that the cumulant contribution—which is assumed to be zero in the derivation of the

March-Santamaria functional—is negligible, these results can reveal how good, or bad, the March-Santamaria functional is. Our basic finding in section III is that the quality of the March-Santamaria functionals rapidly deteriorates as the quality of the pair density improves. Indeed, as electron correlation is introduced into a system, the kinetic energy should rise, but the March-Santamaria functional predicts the opposite trend.

IV.B. Computational Methods:

The spin-resolved 2-densities (Eq (1)) were computed using the GAMESS program.^{25,26} Hartree-Fock and complete active space self-consistent field (CASSCF) calculations were performed for different active spaces, approaching the full-CI limit. In order to keep the computational cost modest (accurately evaluating the integral in Eq. (2) is difficult), we used a small (3-21G) basis set. Our results are reported in Tables 1 and 2.

Table 1: Results from the March-Santamaria kinetic functional, \tilde{T}_{MS} for atoms and various active spaces (cf. Eq. (2)).

Atom	Active spaces of CASSCF ($K_{\text{core}}, N_{\text{active}}, K_{\text{active}}$)	E_c	T	\tilde{T}_{MS}	Absolute error
He	HF	--	2.836	--	--
	(0,2,2)	-0.0149	2.859	2.821	0.0377
Li	HF	--	7.371	--	--
	(0,3,9)	-0.0003	7.369	7.369	0.0003
Be	HF	--	14.478	--	--
	(0,4,3)	-0.0024	14.478	14.472	0.0060
	(0,4,4)	-0.0189	14.486	14.392	0.0941
	(0,4,6)	-0.0327	14.494	14.349	0.1454
	(0,4,9)	-0.0446	14.500	14.321	0.1791
	(1,2,2)	-0.0023	14.478	14.472	0.0061
	(1,2,4)	-0.0188	14.488	14.395	0.0926
B	HF	--	24.315	--	--
	(0,5,3)	0	24.315	24.315	0
	(0,5,4)	-0.0177	24.329	24.217	0.1113

	(0,5,5)	-0.0329	24.341	24.154	0.1871
	(1,3,3)	-0.0176	24.328	24.217	0.1116
	(1,3,4)	-0.0328	24.341	24.154	0.1871
C	HF	--	37.351	--	--
	(0,6,4)	0	37.351	37.351	0
	(0,6,5)	-0.0181	37.364	37.239	0.1256
	(1,4,4)	-0.0181	37.364	37.239	0.1256
	(1,4,6)	-0.0217	37.369	37.228	0.1401
N	HF	--	53.918	--	--
	(0,7,5)	0	53.918	53.918	0
	(0,7,6)	-0.0011	53.919	53.917	0.0014
	(0,7,7)	-0.0048	53.923	53.906	0.0165
	(1,5,5)	-0.0009	53.919	53.918	0.0015
	(2,3,5)	-0.0037	53.922	53.907	0.0151
O	HF	--	74.149	--	--
	(0,8,5)	0	74.149	74.149	0
	(0,8,6)	-0.0004	74.151	74.149	0.0015
	(0,8,7)	-0.0095	74.161	74.123	0.0389
	(0,8,8)	-0.0170	74.173	74.107	0.0651

	(1,6,6)	-0.0096	74.162	74.162	0.0389
	(2,4,4)	-0.0092	74.161	74.121	0.0395
	(2,5,4)	-0.0179	74.172	74.101	0.0713
F	HF	--	98.537	--	--
	(0,9,5)	0	98.537	98.537	0
	(0,9,7)	-0.0186	98.559	98.485	0.0751
	(0,9,9)	-0.0319	98.576	98.463	0.1133
	(1,7,5)	-0.0013	98.539	98.537	0.0031
	(1,7,6)	-0.0101	98.549	98.507	0.0423
	(1,7,7)	-0.0328	98.576	98.457	0.1196
	(2,5,4)	-0.0097	98.551	98.509	0.0425
	(2,5,5)	-0.0188	98.561	98.485	0.0754
Ne	HF	--	127.418	--	--
	(0,10,6)	-0.0105	127.429	127.385	0.0442
	(0,10,7)	-0.0376	127.457	127.310	0.1472
	(0,10,8)	-0.0772	127.494	127.216	0.2777
	(0,10,9)	-0.1152	127.518	127.128	0.3902
	(1,8,5)	-0.0104	127.429	127.386	0.0435
	(1,8,6)	-0.0375	127.458	127.311	0.1468

	(1,8,7)	-0.0770	127.495	127.217	0.2776
	(1,8,8)	-0.1136	127.526	127.135	0.391
	(2,6,4)	-0.0100	127.429	127.386	0.0437
	(2,6,5)	-0.0367	127.458	127.301	0.1571
	(2,6,6)	-0.0758	127.495	127.219	0.2761
	(2,6,7)	-0.0774	127.498	127.217	0.2811

Active spaces are denoted as $(K_{\text{core}}, N_{\text{active}}, K_{\text{active}})$, where K_{core} is the number of occupied core orbitals, N_{active} is the number of electrons in the active space, and K_{active} is the number of orbitals in the active space. The correlation energy is denoted $E_c = E_{(K_{\text{core}}, N_{\text{active}}, K_{\text{active}})} - E_{\text{HF}}$ and the kinetic energy is denoted T . All energies are reported in Hartree. The March-Santamaria functional is exact for the Hartree-Fock calculations.

Table 2: Results from the March-Santamaria kinetic functional, \tilde{T}_{MS} for the Beryllium isoelectronic series.

Atom	Active spaces of CASSCF ($K_{\text{core}}, N_{\text{active}}, K_{\text{active}}$)	E_c	T	\tilde{T}_{MS}	Absolute error
Be	HF	--	14.478	--	--
	(0,4,3)	-0.0024	14.478	14.472	0.0060
	(0,4,4)	-0.0189	14.486	14.392	0.0941
	(0,4,6)	-0.0327	14.494	14.349	0.1454
	(0,4,9)	-0.0446	14.500	14.321	0.1791
	(1,2,2)	-0.0023	14.478	14.472	0.0061
	(1,2,4)	-0.0188	14.488	14.395	0.0926
B ⁺	HF	--	23.879	--	--
	(0,4,3)	-0.0025	23.874	23.867	0.0069
	(0,4,4)	-0.0234	23.901	23.738	0.1625
	(0,4,6)	-0.0413	23.922	23.661	0.2604
	(0,4,9)	-0.0569	23.938	23.610	0.3282
	(1,2,3)	-0.0234	23.902	23.739	0.1628
C ²⁺	HF	--	35.721	--	--

	(0,4,3)	-0.0023	35.715	35.709	0.0066
	(0,4,4)	-0.0284	35.755	35.496	0.2597
	(0,4,6)	-0.0506	35.786	35.365	0.4217
	(0,4,9)	-0.0702	35.811	35.276	0.5347
	(1,2,3)	-0.0282	35.749	35.483	0.2671
N ³⁺	HF	--	49.991	--	--
	(0,4,3)	-0.0022	49.984	49.978	0.0064
	(0,4,4)	-0.0335	50.038	49.654	0.3847
	(0,4,6)	-0.06	50.079	49.449	0.6303
	(0,4,9)	-0.0836	50.112	49.313	0.7990
	(1,2,3)	-0.0325	50.009	49.673	0.3360
	(1,2,4)	-0.0334	50.046	49.603	0.4429
O ⁴⁺	HF	--	66.799	--	--
	(0,4,3)	-0.0022	66.792	66.786	0.0059
	(0,4,4)	-0.0037	66.798	66.256	0.5420
	(0,4,9)	-0.0975	66.952	65.816	1.1357
	(1,2,3)	-0.0022	66.792	66.785	0.0068
F ⁵⁺	HF	--	86.020	--	--
	(0,4,3)	-0.0021	86.011	86.005	0.0066

	(0,4,4)	-0.0444	86.091	85.351	0.7405
	(0,4,6)	-0.0801	86.154	84.940	1.2133
	(0,4,9)	-0.1116	86.202	84.663	1.5395
	(1,2,3)	-0.0002	86.018	86.018	0
Ne ⁶⁺	HF	--	107.669	--	--
	(0,4,3)	-0.0021	107.660	107.653	0.0072
	(0,4,4)	-0.0501	107.752	106.782	0.9705
	(0,4,6)	-0.0907	107.823	106.237	1.5865
	(0,4,9)	-0.1262	107.880	105.867	2.0133
	(1,2,3)	-0.0003	107.667	107.667	-0.0001
Mg ⁸⁺	HF	--	152.082	--	--
	(0,4,3)	-0.0354	152.072	151.562	0.5100
	(0,4,6)	-0.0968	152.061	150.837	1.2244
	(1,2,3)	-0.0354	152.072	152.019	0.0530
	(1,2,4)	-0.0967	152.105	150.837	1.2242
Si ¹⁰⁺	HF	--	212.077	--	--
	(0,4,3)	0	212.077	212.077	0
	(0,4,6)	-0.1278	212.065	209.915	2.1504
	(1,2,3)	-0.0209	212.105	212.056	0.0494

	(1,2,4)	-0.1276	212.066	209.912	2.1537
	(1,2,8)	-0.1276	212.057	209.900	2.1570

The column headings have the same meaning as in Table 1.

IV.C. Assessing the March-Santamaria Functional:

Table 1 reports the results for the March-Santamaria functional for Helium and the second-row atoms, Li-Ne, for a variety of different active spaces. Exact results are obtained for Hartree-Fock (and are not reported); as the amount of electron correlation energy recovered increases, the true kinetic energy tends to increase, but the March-Santamaria approximation to the kinetic energy tends to decrease. The trend is wrong, but the results are much more accurate than we observed for the generalized Weizsäcker functionals in the previous chapter.¹⁷ Nonetheless, errors of tens, and even hundreds, of milli-Hartree are routinely observed. This is much more accurate than many orbital-free kinetic energy density functionals, but still woefully inadequate for chemical applications.

The exact kinetic energy would always increase if the virial theorem held exactly because reducing the energy by including electron correlation increases

the kinetic energy, but the virial theorem is far from satisfied in this small basis. Still, the trend is clearly explained by the virial theorem.

Why is the March-Santamaria kinetic energy below the true kinetic energy? Why does it become worse when the amount of electron correlation decreases? Consider the cumulant expansion of the 2-electron reduced density matrix,

$$\Gamma_2 = \gamma \wedge \gamma + \Delta_2 \quad (4)$$

where Γ_2 is the 2-electron reduced density matrix and Δ_2 is the 2-electron reduced density cumulant. The second term is neglected in this paper and in the derivation of the March-Santamaria functional. The present approximation, as in Eq. (2), then, reduces to

$$\tilde{T}_{\text{MS}} = \frac{1}{2} \iint \nabla_1 \gamma(\mathbf{r}_1, \mathbf{r}_2) \cdot \nabla_1 \gamma(\mathbf{r}_2, \mathbf{r}_1) d\mathbf{r}_1 d\mathbf{r}_2 \approx T_{\text{MS}} \quad (5)$$

Inserting the natural orbital expansion of the 1-electron reduced density matrix,

$$\begin{aligned} \gamma(\mathbf{r}_1, \mathbf{r}_2) &= \sum_i n_i \chi_i(\mathbf{r}_1) \chi_i^*(\mathbf{r}_2) \\ 0 &\leq n_i \leq 1 \end{aligned} \quad (6)$$

into the right-hand-side of this equation gives

$$\begin{aligned}
 \tilde{T}_{\text{MS}} &= \frac{1}{2} \sum_i \sum_j n_i n_j \left(\int \nabla \chi_i(\mathbf{r}_1) \cdot \nabla \chi_j^*(\mathbf{r}_1) d\mathbf{r}_1 \right) \left(\int \chi_i^*(\mathbf{r}_2) \chi_j(\mathbf{r}_2) d\mathbf{r}_2 \right) \\
 &= \frac{1}{2} \sum_i \sum_j n_i n_j \left(\int \nabla \chi_i(\mathbf{r}_1) \cdot \nabla \chi_j^*(\mathbf{r}_1) d\mathbf{r}_1 \right) \delta_{ij} \\
 &= \sum_i n_i^2 \left(\frac{1}{2} \int \nabla \chi_i(\mathbf{r}_1) \cdot \nabla \chi_i^*(\mathbf{r}_1) d\mathbf{r}_1 \right)
 \end{aligned} \tag{7}$$

This can be compared to the exact result,

$$\tilde{T} = \sum_i n_i \left(\frac{1}{2} \int \nabla \chi_i(\mathbf{r}_1) \cdot \nabla \chi_i^*(\mathbf{r}_1) d\mathbf{r}_1 \right) \tag{8}$$

which differs only in that the natural orbital occupation numbers are not squared.

Since the occupation numbers are between zero and one, $n_i^2 \leq n_i$ with equality only when $n_i = 0$ or $n_i = 1$. So the March-Santamaria functional is exact for an idempotent density matrix corresponding to a Slater determinant, but in other cases the first contribution in Eq. (7) is below the true energy. The cumulant term should be negligible for the calculations used here: the dominant kinetic-energy contribution from the cumulant should be from the electron-electron cusp, which is poorly resolved in small basis sets like the ones used here.

To verify this reasoning, we considered the Beryllium isoelectronic series (Table 2). As the atomic number increases, the 2p and 2s orbitals become nearly degenerate, and the natural orbital occupation numbers for the 2p and 2s orbitals deviate further from their Hartree - Fock values of zero and one, respectively. If

the preceding explanation of the flaws in the March - Santamaria functional is correct, then we expect the quality of the approximation to deteriorate with increasing nuclear charge in Table 2. This is what is observed.

IV.D. Summary:

The March - Santamaria functional is exact for Hartree - Fock theory but it gives results that are sometimes a few tenths of one Hartree too small when the pair density is approximated using correlated one-electron density matrices instead of the idempotent density matrices associated with Slater determinants. These results can be explained by noting that the contribution of a single natural orbital to the kinetic energy is multiplied by the natural orbital occupation number in the exact theory, but by the square of the occupation number in the March-Santamaria approximation. We predict, based on this result, that the March-Santamaria functional may be useful for systems where the exact wave-function is very close to Hartree - Fock (so that there is very little electron correlation), but such systems are unlikely to be especially important from a chemical point of view, so we did not pursue that line of reasoning further. The fact that the March-Santamaria functional tends to give kinetic energies that decrease with increasing electron correlation, while the true kinetic energy increases with increasing

electron correlation, strongly suggests that a different approach to the pair-density kinetic-energy functional problem is needed.

Where do we go from here? The negative result in this paper and the previous one¹⁷ suggests that it may be very difficult to derive a simple and explicit form of the kinetic energy functional for the pair density. The approach of Ayers and Levy, where the 2-density is only used to compute the correlation component of the kinetic energy, can ensure that the kinetic energy increases as electron correlation increases.²⁷ This approach would, at least, solve the largest shortcoming of the March-Santamaria functional. Another possibility is to explicitly use a more sophisticated approximation to the underlying wavefunction in pair-density functional theorem thereby providing a better model for the treatment of non-integer occupation numbers. This is the approach of Higuchi and Higuchi.^{28,29} Finally, it would be interesting to validate this paper's assessment of the March-Santamaria functional using more accurate computations.

IV.E. Appendix:

This appendix derives the March-Santamaria functional.

The key concept is the cumulant from statistics. For random variables, x and y , and a probability distribution $p(x,y)$, the second-order cumulant is defined as,

$$\kappa_2(x, y) = \iint xyp(x, y) dx dy - \left(\iint xp(x, y) dx dy \right) \left(\iint yp(x, y) dx dy \right) \quad (9)$$

which we can also denote

$$\kappa_2(x, y) = \langle xy \rangle - \langle x \rangle \langle y \rangle \quad (10)$$

The cumulant, which is in this case just the covariance, measures the extent to which the joint probability of observing x and y cannot be captured by the probability of observing them, independently. In other words, the cumulant measures the extent of correlation between the random variables.

The cumulant of the 2-electron distribution function measures the extent to which the probability of simultaneously observing electrons at \mathbf{r} and \mathbf{r}' with spins σ and σ' cannot be expressed as the products of the probabilities of observing electrons at these points, separately,

$$\begin{aligned}
 \kappa_2(\mathbf{r}\sigma; \mathbf{r}'\sigma') &= \left\langle \Psi \left| \sum_{i=1}^N \sum_{j=1}^N (|\sigma_i\rangle \delta(\mathbf{r}_i - \mathbf{r}) \langle \sigma_i|) (|\sigma'_j\rangle \delta(\mathbf{r}_j - \mathbf{r}') \langle \sigma'_j|) \right| \Psi \right\rangle \\
 &\quad - \left\langle \Psi \left| \sum_{i=1}^N (|\sigma_i\rangle \delta(\mathbf{r}_i - \mathbf{r}) \langle \sigma_i|) \right| \Psi \right\rangle \left\langle \Psi \left| \sum_{j=1}^N (|\sigma'_j\rangle \delta(\mathbf{r}_j - \mathbf{r}') \langle \sigma'_j|) \right| \Psi \right\rangle \\
 &= \rho_2^{\sigma\sigma'}(\mathbf{r}, \mathbf{r}') - \rho^\sigma(\mathbf{r}) \rho^{\sigma'}(\mathbf{r}')
 \end{aligned}
 \tag{11}$$

That is, the density cumulant is the correction to the independent-particle model (from Hartree theory) for the pair probability.

The cumulant of the two-electron density matrix (2-matrix) is the correction to the independent-fermion model (from Hartree-Fock theory) for the 2-matrix,

$$\Gamma_2(\mathbf{r}_1\sigma_1, \mathbf{r}_2\sigma_2; \mathbf{r}'_1\sigma'_1, \mathbf{r}'_2\sigma'_2) = \left\langle \Psi \left| \hat{\psi}^+(\mathbf{r}'_1\sigma'_1) \hat{\psi}^+(\mathbf{r}'_2\sigma'_2) \hat{\psi}(\mathbf{r}_2\sigma_2) \hat{\psi}(\mathbf{r}_1\sigma_1) \right| \Psi \right\rangle
 \tag{12}$$

where, $\hat{\psi}^+(\mathbf{r}\sigma)$ and $\hat{\psi}(\mathbf{r}\sigma)$ denote the field operators for creating or annihilating a σ -spin electron at the point \mathbf{r} , respectively. In analogy to the above, the density matrix cumulant is

$$\begin{aligned}
 \Delta_2(\mathbf{r}_1\sigma_1, \mathbf{r}_2\sigma_2; \mathbf{r}'_1\sigma'_1, \mathbf{r}'_2\sigma'_2) &= \left\langle \Psi \left| \hat{\psi}^+(\mathbf{r}'_1\sigma'_1) \hat{\psi}^+(\mathbf{r}'_2\sigma'_2) \hat{\psi}(\mathbf{r}_2\sigma_2) \hat{\psi}(\mathbf{r}_1\sigma_1) \right| \Psi \right\rangle \\
 &\quad - \left\langle \Psi \left| \hat{\psi}^+(\mathbf{r}'_1\sigma'_1) \hat{\psi}(\mathbf{r}_1\sigma_1) \right| \Psi \right\rangle \wedge \left\langle \Psi \left| \hat{\psi}^+(\mathbf{r}'_2\sigma'_2) \hat{\psi}(\mathbf{r}_2\sigma_2) \right| \Psi \right\rangle \\
 &= \Gamma_2(\mathbf{r}_1\sigma_1, \mathbf{r}_2\sigma_2; \mathbf{r}'_1\sigma'_1, \mathbf{r}'_2\sigma'_2) - \gamma(\mathbf{r}_1\sigma_1; \mathbf{r}'_1\sigma'_1) \wedge \gamma(\mathbf{r}_2\sigma_2; \mathbf{r}'_2\sigma'_2)
 \end{aligned}
 \tag{13}$$

Setting the primed and unprimed variables equal in the preceding equation (Eq. (5)) provides a relationship between the pair density (the quantity of interest) and the one-electron reduced density matrix (1-matrix),

$$\begin{aligned}\rho_2^{\sigma_1\sigma_2}(\mathbf{r}_1, \mathbf{r}_2) &= \Gamma_2(\mathbf{r}_1\sigma_1, \mathbf{r}_2\sigma_2; \mathbf{r}_1\sigma_1, \mathbf{r}_2\sigma_2) \\ &= \gamma(\mathbf{r}_1\sigma_1; \mathbf{r}_1\sigma_1)\gamma(\mathbf{r}_2\sigma_2; \mathbf{r}_2\sigma_2) - \gamma(\mathbf{r}_1\sigma_1; \mathbf{r}_2\sigma_2)\gamma(\mathbf{r}_2\sigma_2; \mathbf{r}_1\sigma_1) + \Delta_2(\mathbf{r}_1\sigma_1, \mathbf{r}_2\sigma_2; \mathbf{r}_1\sigma_1, \mathbf{r}_2\sigma_2) \\ &= \rho^{\sigma_1}(\mathbf{r}_1)\rho^{\sigma_2}(\mathbf{r}_2) - \gamma(\mathbf{r}_1\sigma_1; \mathbf{r}_2\sigma_2)\gamma(\mathbf{r}_2\sigma_2; \mathbf{r}_1\sigma_1) + \Delta_2(\mathbf{r}_1\sigma_1, \mathbf{r}_2\sigma_2; \mathbf{r}_1\sigma_1, \mathbf{r}_2\sigma_2)\end{aligned}\quad (14)$$

This means that the density cumulant can be written as

$$\begin{aligned}\kappa_2(\mathbf{r}\sigma; \mathbf{r}'\sigma') &= \rho_2^{\sigma\sigma'}(\mathbf{r}, \mathbf{r}') - \rho^\sigma(\mathbf{r})\rho^{\sigma'}(\mathbf{r}') \\ &= -\gamma(\mathbf{r}\sigma; \mathbf{r}'\sigma')\gamma(\mathbf{r}'\sigma'; \mathbf{r}\sigma) + \Delta_2(\mathbf{r}\sigma, \mathbf{r}'\sigma'; \mathbf{r}\sigma, \mathbf{r}'\sigma')\end{aligned}\quad (15)$$

It should be noted that $\gamma(\mathbf{r}, \sigma; \mathbf{r}'\sigma')$ equals zero unless $\sigma = \sigma'$.

If we assume that the independent-fermion approximation to the density cumulant is acceptable (i.e., $\Delta_2 = 0$), then this equation provides a link between the 2-density and the 1- matrix. This is useful because the kinetic energy can be computed directly from the 1-matrix,

$$T = \sum_{\sigma=\alpha, \beta} \frac{-1}{2} \iint [\delta(\mathbf{r}-\mathbf{r}') \nabla^2 \gamma(\mathbf{r}\sigma; \mathbf{r}'\sigma)] d\mathbf{r} d\mathbf{r}' \quad (16)$$

When $\Delta_2 = 0$, the density cumulant will only have the correct normalization,

$$\begin{aligned} -\rho^\sigma(\mathbf{r}) &= \int \kappa_2(\mathbf{r}\sigma; \mathbf{r}'\sigma') d\mathbf{r}' & \sigma' = \sigma \\ 0 &= \int \kappa_2(\mathbf{r}\sigma; \mathbf{r}'\sigma') d\mathbf{r}' & \sigma' \neq \sigma \end{aligned} \quad (17)$$

if the 1- matrix is idempotent,

$$-\rho^\sigma(\mathbf{r}) = -\gamma(\mathbf{r}\sigma; \mathbf{r}\sigma) = \int -\gamma(\mathbf{r}\sigma; \mathbf{r}'\sigma) \gamma(\mathbf{r}'\sigma; \mathbf{r}\sigma) d\mathbf{r}' \quad (18)$$

This is useful, because the cumulant expansion relates the 2-density to the square of the density matrix, but evaluating the kinetic energy requires knowledge of the density matrix itself. However, for idempotent 1-matrices, one has an alternative expression for the kinetic energy,

$$T = \sum_{\sigma=\alpha,\beta} \iint \frac{|\nabla_r \gamma^2(\mathbf{r}, \sigma, \mathbf{r}'\sigma)|^2}{8\gamma^2(\mathbf{r}, \sigma, \mathbf{r}'\sigma)} d\mathbf{r} d\mathbf{r}' \quad (19)$$

Substituting the expression for the density cumulant into this equation gives the March-Santamaria functional.

Why not simply evaluate the 1-matrix from the pair density,

$$\gamma(\mathbf{r}\sigma, \mathbf{r}'\sigma) \approx \sqrt{\rho_2^{\sigma\sigma}(\mathbf{r}, \mathbf{r}') - \rho^\sigma(\mathbf{r})\rho^\sigma(\mathbf{r}')} ?$$

The problem is that the argument of the square root is not always positive (though it is positive for independent electron systems); the kinetic energy evaluated using this equation would be a complex number. It is possible to define an approximate kinetic energy functional as,

$$\begin{aligned}
 T &\approx \text{Re} \left[\sum_{\sigma=\alpha,\beta} \frac{-1}{2} \iint \left[\delta(\mathbf{r}-\mathbf{r}') \nabla^2 \left(\rho_2^{\sigma\sigma}(\mathbf{r},\mathbf{r}') - \rho^\sigma(\mathbf{r}) \rho^\sigma(\mathbf{r}') \right)^{1/2} \right] d\mathbf{r} d\mathbf{r}' \right] \\
 &= \text{Re} \left[\sum_{\sigma=\alpha,\beta} \frac{1}{2} \iint \left[\delta(\mathbf{r}-\mathbf{r}') \nabla \cdot \nabla' \left(\rho_2^{\sigma\sigma}(\mathbf{r},\mathbf{r}') - \rho^\sigma(\mathbf{r}) \rho^\sigma(\mathbf{r}') \right)^{1/2} \right] d\mathbf{r} d\mathbf{r}' \right] \\
 &= \text{Re} \left[\sum_{\sigma=\alpha,\beta} \left(\int \frac{\left\{ \int \delta(\mathbf{r}-\mathbf{r}') \nabla \cdot \nabla' \rho_2^{\sigma\sigma}(\mathbf{r},\mathbf{r}') d\mathbf{r}' \right\} - |\nabla \rho^\sigma(\mathbf{r})|^2}{4 \left(\rho_2^{\sigma\sigma}(\mathbf{r},\mathbf{r}) - \rho^\sigma(\mathbf{r}) \rho^\sigma(\mathbf{r}) \right)^{1/2}} d\mathbf{r} \right. \right. \\
 &\quad \left. \left. - \int \frac{\left\{ \int \delta(\mathbf{r}-\mathbf{r}') |\nabla \rho_2^{\sigma\sigma}(\mathbf{r},\mathbf{r}') - \rho^\sigma(\mathbf{r}') \nabla \rho^\sigma(\mathbf{r})|^2 d\mathbf{r}' \right\}}{8 \left(\rho_2^{\sigma\sigma}(\mathbf{r},\mathbf{r}) - \rho^\sigma(\mathbf{r}) \rho^\sigma(\mathbf{r}) \right)^{3/2}} d\mathbf{r} \right) \right]
 \end{aligned} \tag{20}$$

The presence of zeros in the denominators of this expression might make it extremely difficult to evaluate numerically, however.

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Chapter V

Two-Point Weighted Density Approximations for the Kinetic Energy Density Functional

V. A. Motivation

Most modern density-functional theory (DFT) calculations use the Kohn-Sham method, in which the Kohn-Sham spin-orbitals are introduced as auxiliary functions for evaluating the kinetic energy.¹ Because the Kohn-Sham orbital occupation numbers are restricted to the interval $[0, 1]$, the Pauli principle is satisfied; this prevents collapse of the system into an unphysical, non-fermionic, state.²⁻⁶ However, computing the Kohn-Sham spin-orbitals requires solving a system of coupled, nonlinear, one-electron Schrödinger equations,

$$\left(-\frac{1}{2}\nabla^2 + v(\mathbf{r}) + v_J[\rho^\alpha, \rho^\beta; \mathbf{r}] + v_{xc}^\sigma[\rho^\alpha, \rho^\beta; \mathbf{r}]\right)\phi_i^\sigma(\mathbf{r}) = \epsilon_i^\sigma \phi_i^\sigma(\mathbf{r}) \quad (1)$$

$$\begin{aligned} \rho^\sigma(\mathbf{r}) &= \sum_i n_i^\sigma |\phi_i^\sigma(\mathbf{r})|^2 \\ 0 &\leq n_i^\sigma \leq 1 \end{aligned} \quad (2)$$

The number of equations to be solved grows linearly with the number of electrons.

In principle, DFT calculations should only require that one determine one three-dimensional function (the electron density), not N three-dimensional functions (the Kohn-Sham spin-orbitals). This promise is realized in the orbital-free DFT approach.⁷⁻¹¹ The advantage of orbital-free DFT is especially clear when

one writes the orbital-free equation for the electron (spin)-density in the form proposed by Levy, Perdew, and Sahni,¹²

$$\left(-\frac{1}{2}\nabla^2 + v(\mathbf{r}) + v_J[\rho^\alpha, \rho^\beta; \mathbf{r}] + v_{xc}^\sigma[\rho^\alpha, \rho^\beta; \mathbf{r}] + v_\theta^\sigma[\rho^\sigma; \mathbf{r}]\right)\phi^\sigma(\mathbf{r}) = \epsilon^\sigma \phi^\sigma(\mathbf{r}) \quad (3)$$

$$\rho^\sigma(\mathbf{r}) = N^\sigma |\phi^\sigma(\mathbf{r})|^2 \quad (4)$$

In orbital-free DFT, one need only solve one nonlinear Schrödinger equation.¹³⁻¹⁸ (Or, in the spin-resolved DFT case, two coupled nonlinear Schrödinger equations.) The number of equations to be solved is independent of the number of electrons.

The major problem in orbital-free DFT is violations of the Pauli principle. This is clear from Eq.(3); if the Pauli potential $v_\theta^\sigma(\mathbf{r})$ is omitted, the solution to Eq. (3) corresponds to a non-interacting system of bosons, where all the particles are in a single orbital. It is only the presence of the Pauli potential,

$$v_\theta^\sigma[\rho^\sigma; \mathbf{r}] = \frac{\delta T_\theta[\rho^\sigma]}{\delta \rho^\sigma(\mathbf{r})} = \frac{\delta T_s^\sigma[\rho^\sigma]}{\delta \rho^\sigma(\mathbf{r})} - \frac{\delta T_w^\sigma[\rho^\sigma]}{\delta \rho^\sigma(\mathbf{r})}, \quad (5)$$

that allows Eq. (3) to be consistent with Fermi statistics. In Eq. (5),

$$T_s^\sigma[\rho^\sigma] = \sum_i n_i^\sigma \left\langle \phi_i^\sigma \left| -\frac{1}{2}\nabla^2 \right| \phi_i^\sigma \right\rangle \quad (6)$$

and

$$T_w^\sigma[\rho^\sigma] = \left\langle \sqrt{\rho^\sigma(\mathbf{r})} \left| -\frac{1}{2} \nabla^2 \right| \sqrt{\rho^\sigma(\mathbf{r})} \right\rangle = N^\sigma \left\langle \varphi^\sigma(\mathbf{r}) \left| -\frac{1}{2} \nabla^2 \right| \varphi^\sigma(\mathbf{r}) \right\rangle \quad (7)$$

denote the Kohn-Sham and the Pauli kinetic energies, respectively. The primary research topic in orbital-free DFT, then, is approximating the kinetic energy.^{7,9,10,19-24} It is particularly important that the contribution of the Pauli principle to the kinetic energy be captured precisely. The failure of orbital-free DFT functionals to respect the Pauli principle leads to qualitative problems. For example, many approximate orbital-free kinetic energy functionals give reasonable kinetic energies for the true Kohn-Sham density, but upon variational optimization of the energy, the shell structure of the electron density vanishes and the energy decreases. This decrease in energy indicates that there is some electron density, $\rho^\sigma(\mathbf{r}) \neq \rho_{\text{exact}}^\sigma(\mathbf{r})$, for which

$$\tilde{T}_s^\sigma[\rho^\sigma] < \sum_i n_i^\sigma \mathcal{E}_i^\sigma - \int \rho^\sigma(\mathbf{r}) v_s^\sigma(\mathbf{r}) d\mathbf{r} = T_s^\sigma[\rho^\sigma], \quad (8)$$

where $\tilde{T}_s^\sigma[\rho^\sigma]$ denotes the approximate kinetic energy functional and $v_s^\sigma(\mathbf{r})$ is the Kohn-Sham potential. Expression (8) indicates that the kinetic-energy functional does not satisfy the Pauli principle.³ That is, expression (8) indicates that $\tilde{T}_s^\sigma[\rho^\sigma]$ is not N -representable in the sense that there exists no fermion

wave-function or ensemble with the electron density $\rho^\sigma(\mathbf{r})$ and the kinetic energy \tilde{T}_s^σ .

It is essential that orbital-free kinetic energy functionals come very close to modeling the Pauli principle exactly. Even a tiny error in the occupation number of a core orbital or a high-lying virtual orbital will cause a massive error in Eq. (6).^{2,3}

The goal of this work is to explore a family of weighted density approximation functionals²⁵⁻²⁷ that are designed to directly address the N -representability problem. The hope is that by imposing necessary conditions associated with the Pauli principle, we can find a functional that is accurate and robust. In the next section, the weighted density approximations we will use are discussed. Numerical methods are revealed in section III and results are presented in section IV. Section V discusses our findings and concludes.

V. B. Weighted Density Approximation (WDA) for the 1-Electron Reduced Density Matrix (1-matrix)

1. The Kohn-Sham 1-matrix

In Kohn-Sham DFT, one explicitly constructs an N -representable 1-electron reduced density matrix (1-matrix) from the electron density. This can be achieved, for example, using the Levy constrained search,²⁸⁻³⁰

$$T_s^\sigma[\rho] = \min_{\left\{ \gamma^\sigma \left| \begin{array}{l} \rho^\sigma(\mathbf{r}) = \gamma^\sigma(\mathbf{r}, \mathbf{r}) \\ \gamma^\sigma = (\gamma^\sigma)^2 \end{array} \right. \right\}} \iint \delta(\mathbf{r} - \mathbf{r}') \left(-\frac{1}{2} \nabla_{\mathbf{r}}^2 \gamma^\sigma(\mathbf{r}, \mathbf{r}') \right) d\mathbf{r} d\mathbf{r}' \quad (9)$$

$$\gamma_s^\sigma[\rho^\sigma; \mathbf{r}, \mathbf{r}'] = \arg \min_{\left\{ \gamma^\sigma \left| \begin{array}{l} \rho^\sigma(\mathbf{r}) = \gamma^\sigma(\mathbf{r}, \mathbf{r}) \\ \gamma^\sigma = (\gamma^\sigma)^2 \end{array} \right. \right\}} \iint \delta(\mathbf{r} - \mathbf{r}') \left(-\frac{1}{2} \nabla_{\mathbf{r}}^2 \gamma^\sigma(\mathbf{r}, \mathbf{r}') \right) d\mathbf{r} d\mathbf{r}' \quad (10)$$

Among all idempotent 1-matrices with the correct electron density, Eq. (10) selects the one with the lowest kinetic energy. (There are alternative approaches; if one minimized the Hartree-Fock energy functional (instead of the kinetic energy), then one would obtain a different $\rho^\sigma(\mathbf{r}) \rightarrow \gamma^\sigma(\mathbf{r}, \mathbf{r}')$ mapping.^{31,32}) as is clear from Eq.(10), the mapping between the electron density and the 1-matrix in Kohn-Sham DFT is implicit.

2. A General Model for the 1-matrix

Every *explicit*, and therefore approximate, mapping between the electron density and the 1-matrix induces an orbital-free kinetic energy functional,

$$\tilde{T}_s^\sigma[\rho] = \iint \delta(\mathbf{r} - \mathbf{r}') \left(-\frac{1}{2} \nabla_{\mathbf{r}}^2 \tilde{\gamma}^\sigma[\rho^\sigma; \mathbf{r}, \mathbf{r}'] \right) d\mathbf{r} d\mathbf{r}' \quad (11)$$

In this paper, we decorate the symbols for approximate functionals with \sim . This is the approach we pursue in this paper. We note, in passing, that any density-to-1-matrix mapping also implies an approximate exchange-energy functional,

$$\tilde{E}_x^\sigma[\rho] = \frac{-1}{2} \iint \frac{|\tilde{\gamma}^\sigma[\rho^\sigma; \mathbf{r}, \mathbf{r}']|^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'. \quad (12)$$

To use Eq.(11), one first needs to select a functional form for the 1-matrix. This 1-matrix needs to be easy to compute. Equation (11) has no utility unless it is much easier to determine the model 1-matrix than it is to solve for the exact Kohn-Sham 1-matrix using Eq. (10). The form we consider is

$$\tilde{\gamma}^\sigma[\rho^\sigma; \mathbf{r}, \mathbf{r}'] = \sqrt{\rho^\sigma(\mathbf{r}) \rho^\sigma(\mathbf{r}')} \tilde{g}(k_F^\sigma |\mathbf{r} - \mathbf{r}'|) \quad (13)$$

where the function $\tilde{g}(x)$ must satisfy

$$\begin{aligned} \tilde{g}(0) &= 1 \\ \tilde{g}'(0) &= 0 \\ \tilde{g}''(0) &< 0 \end{aligned} \quad (14)$$

In addition, for all physically achievable values of the argument, $x \geq 0$, we must have

$$-1 < \tilde{g}(x) \leq 1. \quad (15)$$

The 1-matrix form in Eq. (13) will not give idempotent density matrices for systems with more than two electrons unless $\tilde{g}(x) < 0$ for some values of x .³³

This 1-matrix form is potentially exact because one can choose the Fermi wave-vector as the 6-dimensional function,

$$k_F^\sigma(\mathbf{r}, \mathbf{r}') \equiv \frac{\tilde{g}^{-1} \left(\frac{\gamma_s^\sigma[\rho^\sigma; \mathbf{r}, \mathbf{r}']}{\sqrt{\rho^\sigma(\mathbf{r}) \rho^\sigma(\mathbf{r}')}} \right)}{|\mathbf{r} - \mathbf{r}'|}. \quad (16)$$

Equation (16) usually has many solutions because $\tilde{g}(x)$ is not invertible.

3. The 1-point Model for the 1-matrix

In order for Eq. (13) to be useful as a density functional, one needs to write the Fermi wave-vector, k_F^σ , as a functional of the electron density. In the local density approximation, one chooses the value of the Fermi wave-vector in the uniform electron gas,

$$\tilde{k}_{\text{LDA}}^{\sigma}[\rho^{\sigma}; \mathbf{r}] = \left(6\pi^2 \rho^{\sigma}(\mathbf{r})\right)^{1/3}. \quad (17)$$

Inserting Eq. (17) into Eq. (13) gives a model 1-matrix that depends on the value of the k_F at one point,

$$\tilde{\gamma}_{\text{1pt-LDA}}^{\sigma}(\mathbf{r}, \mathbf{r}') = \sqrt{\rho^{\sigma}(\mathbf{r})\rho^{\sigma}(\mathbf{r}')} \tilde{g}\left(\tilde{k}_{\text{LDA}}^{\sigma}(\mathbf{r})|\mathbf{r}-\mathbf{r}'|\right). \quad (18)$$

4. The 2-point Model for the 1-matrix

This 1-point model gives a 1-matrix that is not Hermitian; $\tilde{\gamma}_{\text{1pt-LDA}}^{\sigma}(\mathbf{r}, \mathbf{r}') \neq \left(\tilde{\gamma}_{\text{1pt-LDA}}^{\sigma}(\mathbf{r}', \mathbf{r})\right)^*$. We can symmetrize this expression using the p -mean,³⁴

$$\tilde{\kappa}_F^{\sigma}(\mathbf{r}, \mathbf{r}') = \left(\frac{\left(k_F^{\sigma}(\mathbf{r})\right)^p + \left(k_F^{\sigma}(\mathbf{r}')\right)^p}{2}\right)^{1/p} \quad (19)$$

This nonlocal symmetrized expression is effective^{10,34-41} when one uses methods like the Chacon-Alvarellos-Tarazona⁴² approach to construct models^{11,24,34-37,39,40,42-50} for the kinetic energy consistent with the Lindhard response.^{51,52} Using Eq. (19) gives a symmetric model for the 1-matrix that depends on the value of k_F at two points,

$$\tilde{\gamma}_{\text{2pt-LDA}}^{\sigma}(\mathbf{r}, \mathbf{r}') = \sqrt{\rho^{\sigma}(\mathbf{r})\rho^{\sigma}(\mathbf{r}')} \tilde{g}\left(\tilde{\kappa}_{\text{LDA}}^{\sigma}(\mathbf{r}, \mathbf{r}')|\mathbf{r}-\mathbf{r}'|\right). \quad (20)$$

For $p > 0$, the value of the k_F is dominated by the larger of $k_F(\mathbf{r})$ and $k_F(\mathbf{r}')$.

For $p < 0$, the value of the k_F is dominated by the smaller of $k_F(\mathbf{r})$ and $k_F(\mathbf{r}')$.

Specific interesting cases are,

$\max(k_F(\mathbf{r}), k_F(\mathbf{r}'))$	ℓ_∞ -mean	$p \rightarrow \infty$
$\sqrt{\frac{k_F^2(\mathbf{r}) + k_F^2(\mathbf{r}')}{2}}$	root-mean-square	$p = 2$
$\frac{k_F(\mathbf{r}) + k_F(\mathbf{r}')}{2}$	arithmetic mean	$p = 1$
$\sqrt{k_F(\mathbf{r})k_F(\mathbf{r}')}$	geometric mean	$p \rightarrow 0$
$\frac{2k_F(\mathbf{r})k_F(\mathbf{r}')}{k_F(\mathbf{r}) + k_F(\mathbf{r}')}$	harmonic mean	$p = -1$
$\min(k_F(\mathbf{r}), k_F(\mathbf{r}'))$	minimum	$p \rightarrow -\infty$

(21)

There are other ways to symmetrize the 1-matrix. (E.g., one can add the 1-matrix to its Hermitian transpose.) We chose Eq. (20) because the resulting form of the 1-matrix more nearly coincides with our intuition, and because the other symmetrized forms that have been proposed do not seem to have ever been tested numerically.^{53,54}

5. Kinetic Energy from the 1-matrix Models

If one substitutes

$$\tilde{\gamma}_{1\text{pt}}^{\sigma}(\mathbf{r}, \mathbf{r}') = \sqrt{\rho^{\sigma}(\mathbf{r})\rho^{\sigma}(\mathbf{r}')} \tilde{g}(k_F^{\sigma}(\mathbf{r})|\mathbf{r}-\mathbf{r}'|) \quad (22)$$

and

$$\tilde{\gamma}_{2\text{pt}}^{\sigma}(\mathbf{r}, \mathbf{r}') = \sqrt{\rho^{\sigma}(\mathbf{r})\rho^{\sigma}(\mathbf{r}')} \tilde{g} \left(\left[\frac{(k_F^{\sigma}(\mathbf{r}))^p + (k_F^{\sigma}(\mathbf{r}'))^p}{2} \right]^{\frac{1}{p}} |\mathbf{r}-\mathbf{r}'| \right) \quad (23)$$

into Eq. (11) and evaluates the kinetic energy, one obtains

$$\tilde{T}_s^{\sigma}[\rho^{\sigma}] = \int \frac{\nabla \rho^{\sigma}(\mathbf{r}) \cdot \nabla \rho^{\sigma}(\mathbf{r})}{8\rho^{\sigma}(\mathbf{r})} d\mathbf{r} - \frac{3\tilde{g}''(0)}{2} \int \rho^{\sigma}(\mathbf{r}) (k_F^{\sigma}(\mathbf{r}))^2 d\mathbf{r}. \quad (24)$$

This expression does not depend on whether one uses the 1-point or the 2-point model. Equation (24) only depends on the model one chooses for $\tilde{g}(x)$ and the way one chooses a value for $k_F(\mathbf{r})$. It should be noted that this result is peculiar to the kinetic energy; the corresponding exchange-energy functional gives different values depending on whether one uses $\tilde{\gamma}_{1\text{pt}}^{\sigma}(\mathbf{r}, \mathbf{r}')$ or $\tilde{\gamma}_{2\text{pt}}^{\sigma}(\mathbf{r}, \mathbf{r}')$.

6. Uniform Electron Gas Model for $\tilde{g}(k_F|\mathbf{r}-\mathbf{r}'|)$

There are many possible choices for $\tilde{g}(k_F|\mathbf{r}-\mathbf{r}'|)$ that are consistent with the mild constraints mentioned in section II.B. The exact form of $\tilde{g}(x)$ is known for the uniform electron gas,

$$\tilde{g}_{\text{UEG}}(x) = 3 \left(\frac{\sin(x) - x \cos(x)}{x^3} \right). \quad (25)$$

In this model,

$$\tilde{g}_{\text{UEG}}''(0) = -\frac{1}{5}. \quad (26)$$

By using this form, we ensure that all our kinetic energy functionals will be exact in the uniform-electron-gas limit.

7. Weighted Density Approximations for the Fermi Wave-Vector, k_F

The simplest approximation for k_F is the aforementioned LDA, Eq. (17). If one substitutes $\tilde{k}_{\text{LDA}}^\sigma$ into Eq.(24), then one derives,

$$\tilde{T}_{\text{LDA}}^\sigma[\rho^\sigma] = \int \frac{\nabla \rho^\sigma(\mathbf{r}) \cdot \nabla \rho^\sigma(\mathbf{r})}{8\rho^\sigma(\mathbf{r})} d\mathbf{r} + \int \frac{3(6\pi^2)^{2/3}}{10} (\rho^\sigma(\mathbf{r}))^{5/3} d\mathbf{r} \quad (27)$$

This gives the Thomas-Fermi plus *full* Weizsäcker functional,^{27,55}

$$\tilde{T}_{\text{LDA}}[\rho^\alpha, \rho^\beta] = \tilde{T}_{\text{TF+W}}[\rho^\alpha, \rho^\beta] = \sum_{\sigma=\alpha, \beta} T_{\text{TF}}^\sigma[\rho^\sigma] + T_w^\sigma[\rho^\sigma]. \quad (28)$$

For atomic and molecular electron densities, this functional gives kinetic energies far above the true values.^{27,50,56}

The local density approximation for k_F should be reliable for nearly-uniform electron densities, but atomic and molecular densities are far from uniform. It would be better to determine an “effective” value for k_F . Recall that the N -representability error in the kinetic-energy functional is associated with the fact that the model 1-matrix is not idempotent. This suggests that we choose the “effective” value for k_F so that the model 1-matrix is idempotent. For example, the idempotency condition on the 1-point model,

$$\int \tilde{\gamma}_{\text{1pt}}^\sigma(\mathbf{r}, \mathbf{r}') \tilde{\gamma}_{\text{1pt}}^\sigma(\mathbf{r}', \mathbf{r}'') d\mathbf{r}' = \tilde{\gamma}_{\text{1pt}}^\sigma(\mathbf{r}, \mathbf{r}'') \quad (29)$$

This is an overdetermined system of equations, with one equation for each pair of points, $(\mathbf{r}, \mathbf{r}'')$, and one unknown for each point, $k_F^\sigma(\mathbf{r})$.⁵⁷ To avoid this difficulty we consider only the diagonal part of the idempotency condition, $\mathbf{r} = \mathbf{r}''$. Then one has

$$\int \tilde{\gamma}_{\text{1pt}}^\sigma(\mathbf{r}, \mathbf{r}') \tilde{\gamma}_{\text{1pt}}^\sigma(\mathbf{r}', \mathbf{r}) d\mathbf{r}' = \rho^\sigma(\mathbf{r}). \quad (30)$$

This is equivalent to the requirement that the exchange hole,

$$h_x^{\sigma\sigma}(\mathbf{r}, \mathbf{r}') = -\frac{\gamma^{\sigma\sigma}(\mathbf{r}, \mathbf{r}')\gamma^{\sigma\sigma}(\mathbf{r}', \mathbf{r})}{\rho^\sigma(\mathbf{r})\rho^\sigma(\mathbf{r}')} \quad (31)$$

be properly normalized,

$$\int \rho^\sigma(\mathbf{r}') h_x^{\sigma\sigma}(\mathbf{r}, \mathbf{r}') d\mathbf{r}' = -1 \quad (32)$$

By forcing Eq.(32), one ensures that the functional is self-interaction free. That is, each σ -spin electron hollows-out a 1-electron hole in its immediate vicinity, so that it interacts with only $N^\sigma - 1$ other σ -spin electrons. This requirement is in the spirit of the Pauli principle, though it is obviously weaker than the Pauli principle (since Eq. (30) does not imply Eq. (29)).

If one substitutes the form of the 1-point model 1-matrix into the diagonal idempotency condition, one obtains a set of uncoupled nonlinear equations for $k_F^\sigma(\mathbf{r})$, with one equation for each point,

$$\rho^\sigma(\mathbf{r}) \int \rho^\sigma(\mathbf{r}') \left(\tilde{g} \left(\tilde{k}_{\text{1pt-WDA}}^\sigma(\mathbf{r}) |\mathbf{r} - \mathbf{r}'| \right) \right)^2 d\mathbf{r}' = \rho^\sigma(\mathbf{r}) \quad (33)$$

Substituting $k_{\text{1pt-WDA}}^\sigma(\mathbf{r})$ into Eqs. (22) and (24) gives the 1-point weighted density approximation (1WDA)²⁵⁻²⁷ to the 1-matrix and the kinetic energy,

$$\tilde{T}_{\text{1pt-WDA}}^\sigma[\rho^\sigma] = \int \frac{\nabla \rho^\sigma(\mathbf{r}) \cdot \nabla \rho^\sigma(\mathbf{r})}{8\rho^\sigma(\mathbf{r})} d\mathbf{r} - \frac{3\tilde{g}''(0)}{2} \int \rho^\sigma(\mathbf{r}) \left(\tilde{k}_{\text{1pt-WDA}}^\sigma(\mathbf{r}) \right)^2 d\mathbf{r} \quad (34)$$

If one substitutes the form of the 2-point model 1-matrix into the diagonal idempotency condition, one obtains a system of *coupled* nonlinear equations for $k_F^\sigma(\mathbf{r})$.

$$\rho^\sigma(\mathbf{r}) \int \rho^\sigma(\mathbf{r}') \left(\tilde{g} \left[\left(\frac{(\tilde{k}_{2\text{pt-WDA}}^\sigma(\mathbf{r}))^p + (\tilde{k}_{2\text{pt-WDA}}^\sigma(\mathbf{r}'))^p}{2} \right)^{1/p} |\mathbf{r} - \mathbf{r}'| \right] \right)^2 d\mathbf{r}' = \rho^\sigma(\mathbf{r}) \quad (35)$$

Substituting $\tilde{k}_{2\text{pt-WDA}}^\sigma(\mathbf{r})$ into Eq. (24) gives the 2-point weighted density approximation (2WDA). The model exchange hole from the 2WDA is both self-interaction free and symmetric; we might hope, then, that the resulting functionals are nearly N -representable.

V. C. Numerical Methods

We computed the electron densities for small atoms (Hydrogen through Argon) and small molecules by performing all-electron calculations at the unrestricted Hartree-Fock level using the 6-311++G** basis set and the *Gaussian* program.⁵⁸ Then, using these densities, we computed the Thomas-Fermi kinetic energy functional,^{59,60}

$$\tilde{T}_{\text{TF}}[\rho^\alpha, \rho^\beta] = \sum_{\sigma=\alpha, \beta} \int \frac{3(6\pi^2)^{2/3}}{10} (\rho^\sigma(\mathbf{r}))^{5/3} d\mathbf{r}, \quad (36)$$

the Weizsäcker kinetic energy functional,⁶¹

$$\tilde{T}_w[\rho^\alpha, \rho^\beta] = \sum_{\sigma=\alpha, \beta} \int \frac{\nabla \rho^\sigma(\mathbf{r}) \cdot \nabla \rho^\sigma(\mathbf{r})}{8\rho^\sigma(\mathbf{r})} d\mathbf{r}, \quad (37)$$

the second-order gradient expansion approximation,⁶²

$$\tilde{T}_{\text{GEA2}}[\rho^\alpha, \rho^\beta] = \tilde{T}_{\text{TF}}[\rho^\alpha, \rho^\beta] + \frac{1}{9} \tilde{T}_w[\rho^\alpha, \rho^\beta] \quad (38)$$

and the TF+1/5W approximation,⁶³

$$\tilde{T}_{\text{TF}+\frac{1}{5}\text{W}}[\rho^\alpha, \rho^\beta] = \tilde{T}_{\text{TF}}[\rho^\alpha, \rho^\beta] + \frac{1}{5} \tilde{T}_w[\rho^\alpha, \rho^\beta]. \quad (39)$$

In addition, we computed the three approximate functionals described in section II.G, each based on the model 1-matrix from the uniform electron gas, Eq. (25). These functionals are the local density approximation (equivalent to $\tilde{T}_{\text{TF+W}}[\rho^\alpha, \rho^\beta]$; cf. Eq. (28)),^{27,55} the 1WDA functional (cf. Eq. (34)), and the 2WDA functional.

All of the derivatives were performed analytically using the expression for the electron density in the Gaussian basis set. Numerical integrations were done using the Becke-Lebedev method;⁶⁴⁻⁶⁸ we carefully adjusted the number of radial

and angular grid points to ensure that the results we report are converged with respect to the integration grid.

In the conventional WDA (1WDA), the value of $\tilde{k}_{\text{1pt-WDA}}^{\sigma}(\mathbf{r})$ at each grid point was determined by solving the nonlinear equation associated with that grid point. To solve the nonlinear equation, we computed the Jacobian exactly, and then used Newton's method, with a trust radius. In the 2-point WDA (2WDA), there is a system of nonlinear equations with the dimensionality of the integration grid. The Jacobian is extremely diagonally dominant and the equations can be solved, for modest values of p in Eq.(19), by assuming the Jacobian is diagonal and then using Newton's method, again with a trust radius. Our best algorithm inverted the diagonal approximation to the Jacobian and then corrected this model for the inverse-Jacobian using a limited-memory bad-Broyden method. That approach converged rapidly, typically in ten to twenty iterations.

Using the solutions we obtained, we determined the value of p in the generalized p -mean for which the errors in the atomic kinetic energies were the smallest. The best results were obtained for $p = 5$. We used $p = 5$ for all subsequent calculations, even though we could have obtained better kinetic energies for the molecular systems had we used larger p values.

The equations for $k_{2\text{pt-WDA}}^\sigma(\mathbf{r})$ are very ill-conditioned when $p > 1$.

Recalling Eq. (21), when $p > 1$,

$$\tilde{k}^\sigma(\mathbf{r}, \mathbf{r}') = \left(\frac{(\tilde{k}_{2\text{pt-WDA}}^\sigma(\mathbf{r}))^p + (\tilde{k}_{2\text{pt-WDA}}^\sigma(\mathbf{r}'))^p}{2} \right)^{1/p} \quad (40)$$

will be very insensitive to the value of $\tilde{k}_{2\text{pt-WDA}}^\sigma(\mathbf{r}')$ when \mathbf{r}' is far from the molecule. Since the values of $\tilde{k}_{2\text{pt-WDA}}^\sigma(\mathbf{r}')$ in the low-density regions of the molecule have very little effect on the value of the integral in Eq. (35), the 2WDA system of equations is effectively over-determined; it is often impossible to find values for $\tilde{k}_{2\text{pt-WDA}}^\sigma(\mathbf{r}')$ that solve Eq. (35) exactly. To assess the accuracy of the numerical solution, we computed the normalization integral,

$$N = \iint \rho^\sigma(\mathbf{r}) \rho^\sigma(\mathbf{r}') \left(\tilde{g} \left[\left(\frac{(\tilde{k}_F^\sigma(\mathbf{r}))^p + (\tilde{k}_F^\sigma(\mathbf{r}'))^p}{2} \right)^{1/p} |\mathbf{r} - \mathbf{r}'| \right] \right)^2 d\mathbf{r} d\mathbf{r}' \quad (41)$$

for the various choices for the effective Fermi wave-vector, $\tilde{k}_{\text{LDA}}^\sigma$, $\tilde{k}_{\text{1pt-WDA}}^\sigma$, and

$\tilde{k}_{2\text{pt-WDA}}^\sigma$. The first two choices will obviously give poor results but, in cases where

the 2WDA equations, Eq. (35), can be very accurately solved, Eq. (41) should be exact.

V. D. Results

The results for the kinetic energies of atoms and 12 small molecules are reported in Tables 1 and 2, respectively. The most remarkable feature of this data is the extreme inaccuracy of the results obtained when one makes the local density approximation to the 1-matrix, Eq. (27). The assumptions on which this functional is derived are the same as the assumptions on which the Thomas-Fermi functional is based, but it is an order of magnitude less accurate.

Approximating k_F using a weighted density approximation dramatically improves the results. Both the 1WDA and 2WDA functionals give results that are systematically too high; that is consistent with these functionals being almost N -representable. The 2WDA is significantly better than the 1WDA for atoms, but for molecules the two approaches are more comparable. The 2WDA is remarkably accurate for atoms; it is competitive with the best other functional we considered (the 2nd order gradient expansion approximation, Eq. (38)). Neither WDA approach is competitive with the 2nd order gradient expansion for molecules, though WDA2 is still the second-best method we considered.

The 1-matrix is more localized and has a simpler form in atoms, so the simple uniform electron gas model for the 1-matrix might be much less accurate for molecules than it is for atoms. This would explain the disappointing results in Table 2; it also would explain the disappointing results for the errors in the kinetic energy contribution to the atomization energies,

$$\Delta \tilde{T}_s^{\text{atomization}} = \sum_{\alpha \in \text{atoms}} \tilde{T}_s[\rho_\alpha] - \tilde{T}_s[\rho_{\text{molecule}}], \quad (42)$$

reported in Table 3. Except for the Weizsäcker functional, all the functionals we tested give similar results for the atomization energies. The errors, which are of

the order of 1 Hartree (627 kcal/mol), are entirely inadequate for chemical problems.

Errors in the normalization integral, Eqn .(41), are reported in Table 4 (atoms) and Table 5 (molecules). We looked to see whether the errors in the kinetic energy and/or the errors in the atomization kinetic energies could be correlated with the errors here. It is not true that larger errors for the kinetic energy correlate with larger errors in the normalization test. It doesn't seem that the difficulty of solving the nonlinear equations for $\tilde{k}_{2\text{pt-WDA}}^\sigma$ can be invoked as an excuse for the imperfect results reported here. Note that, as expected, the normalization integrals for the LDA approximation to the 1-matrix and the 1WDA are quite poor, though the 1WDA results are systematically better. The last column of Table 5 reports the maximum absolute error in Eq. (35).

Table 1: Atomic kinetic energies obtained from Hartree-Fock (T_{HF}), Thomas-Fermi (\tilde{T}_{TF}), Weizsäcker (\tilde{T}_{w}), 2nd order gradient expansion (\tilde{T}_{GEA2}), TF+1/5W ($\tilde{T}_{\text{TF}+\frac{1}{5}\text{W}}$), the local density approximation to the 1-matrix (\tilde{T}_{LDA}), the one-point weighted density approximation ($\tilde{T}_{\text{1pt-WDA}}$) and the two-point weighted density approximation ($\tilde{T}_{\text{2pt-WDA}}^{p=5}$). All the energies are reported in atomic units (Hartree).

Atom	T_{HF}	\tilde{T}_{TF}	\tilde{T}_{w}	\tilde{T}_{GEA2}	$\tilde{T}_{\text{TF}+\frac{1}{5}\text{W}}$	\tilde{T}_{LDA}	$\tilde{T}_{\text{1pt-WDA}}$	$\tilde{T}_{\text{2pt-WDA}}^{p=5}$	error in $\tilde{T}_{\text{2pt-WDA}}^{p=5}$
H	0.4598	0.2632	0.4599	0.3143	0.3552	0.7231	0.4599	0.4599	3.27E-05
He	2.7339	2.4231	2.7339	2.7269	2.9699	5.1571	2.7340	2.7340	0.0002
Li	7.2010	6.4636	6.9612	7.2371	7.8559	13.4248	7.4108	7.4526	0.2516
Be	14.243	12.82	13.334	14.301	15.486	26.153	14.809	14.846	0.6031
B	24.122	21.61	21.547	24.003	25.919	43.156	25.002	24.98	0.8589
C	37.217	33.4	31.851	36.938	39.769	65.249	38.751	38.549	1.3325
N	53.863	48.095	43.154	52.889	56.725	91.249	55.24	54.7	0.8374
O	74.215	67.532	58.428	74.024	79.217	125.96	78.11	76.933	2.7173
F	98.751	89.456	72.445	97.506	103.95	161.90	102.01	99.981	1.2305
Ne	127.81	116.93	89.626	126.89	134.85	206.55	132.66	129.33	1.5199
Na	160.64	147.54	109.31	159.68	169.4	256.85	166.89	162.17	1.5369
Mg	198.19	182.55	131.24	197.13	208.79	313.79	206.06	199.64	1.4528
Al	240.4	221.89	155.32	239.15	252.96	377.22	249.92	241.5	1.0989
Si	287.24	265.58	181.48	285.75	301.88	447.06	298.50	287.77	0.5233
P	338.96	313.75	209.47	337.02	355.64	523.22	351.96	338.53	-0.4282
S	395.62	367.01	240.10	393.68	415.03	607.11	411.14	394.65	-0.9752
Cl	456.91	424.06	271.89	454.27	478.44	695.95	474.06	454.13	-2.7723
Ar	523.71	486.82	306.28	520.85	548.07	793.1	543.42	519.59	-4.1159
Average Relative Error		-13.005	-60.924	-0.995	8.613	95.086	6.493	0.315	
RMS Relative Error		17.366	91.453	1.332	11.535	127.12	9.025	1.608	

Table 2: Small-molecule kinetic energies obtained from Hartree-Fock (T_{exact}), Thomas-Fermi (\tilde{T}_{TF}), Weizsäcker (\tilde{T}_w), 2nd order gradient expansion (\tilde{T}_{GEA2}), TF+1/5W ($\tilde{T}_{\text{TF}+\frac{1}{5}\text{W}}$), the local density approximation to the 1-matrix (\tilde{T}_{LDA}), the one-point weighted density approximation ($\tilde{T}_{\text{1pt-WDA}}$) and the two-point weighted density approximation ($\tilde{T}_{\text{2pt-WDA}}^{p=5}$). All the energies are reported in atomic units (Hartree).

Molecule	T_{HF}	\tilde{T}_{TF}	\tilde{T}_w	\tilde{T}_{GEA2}	$\tilde{T}_{\text{TF}+\frac{1}{5}\text{W}}$	\tilde{T}_{LDA}	$\tilde{T}_{\text{1pt-WDA}}$	$\tilde{T}_{\text{2pt-WDA}}^{p=5}$	error in $\tilde{T}_{\text{2pt-WDA}}^{p=5}$
BF ₃	320.72	291.96	235.39	318.12	339.04	527.35	332.84	326.69	5.9659
CO	111.69	101.17	86.98	110.83	118.56	188.15	115.99	114.55	2.8553
CO ₂	186.02	168.66	142.27	184.45	197.12	310.93	192.94	190.38	4.3529
H ₂ O	75.39	68.397	56.84	74.712	79.765	125.24	78.369	76.887	1.5003
H ₂ CO	112.75	102.16	87.349	111.86	119.63	189.51	117.3	115.67	2.9145
LiF	105.99	96.333	78.646	105.07	112.06	174.98	110.18	107.94	1.9508
LiH	7.7029	6.9194	7.4134	7.7431	8.4021	14.333	8.2243	8.1962	0.4932
NH ₃	55.566	50.353	43.4116	55.176	59.035	93.764	58.093	57.12	1.5539
C ₂ H ₆	78.044	70.75	63.043	77.755	83.358	133.79	82.201	81.121	3.0776
C ₂ H ₄	76.941	69.687	62.404	76.621	82.168	132.09	80.758	79.828	2.8867
C ₂ H ₂	75.971	68.762	61.649	75.612	81.092	130.41	79.496	78.672	2.7010
C ₆ H ₆	227.74	206.43	183.61	226.83	243.15	390.04	238.27	236.31	8.5642
Average Relative Error		-10.932	-26.798	-0.4892	7.865	83.053	5.614	4.317	
RMS Relative Error		13.151	34.1395	0.7007	9.397	99.548	6.681	5.469	

Table 3: Table comparing the kinetic energy contribution to the atomization energies for a set of 12 molecules, Eq. (42). The methods used are Hartree-Fock (T_{exact}), Thomas-Fermi (\tilde{T}_{TF}), Weizsäcker (\tilde{T}_w), 2nd order gradient expansion (\tilde{T}_{GEA2}), TF+1/5W ($\tilde{T}_{\text{TF}+\frac{1}{5}\text{W}}$), the local density approximation to the 1-matrix (\tilde{T}_{LDA}), the one-point weighted density approximation ($\tilde{T}_{\text{1pt-WDA}}$) and the two-point weighted density approximation ($\tilde{T}_{\text{2pt-WDA}}^{p=5}$). All the energies are reported in atomic units (Hartree).

Molecule	$\Delta T_{\text{HF}}^{\text{atomization}}$	$\Delta \tilde{T}_{\text{TF}}^{\text{atomization}}$	$\Delta \tilde{T}_w^{\text{atomization}}$	$\Delta \tilde{T}_{\text{GEA2}}^{\text{atomization}}$	$\Delta \tilde{T}_{\text{TF}+\frac{1}{5}\text{W}}^{\text{atomization}}$	$\Delta \tilde{T}_{\text{LDA}}^{\text{atomization}}$	$\Delta \tilde{T}_{\text{1pt-WDA}}^{\text{atomization}}$	$\Delta \tilde{T}_{\text{2pt-WDA}}^{\text{atomization}}$
BF ₃	-2.8339	-4.8969	0.4018	-4.8523	-4.8166	-4.4952	-5.7139	-5.539
CO	-1.3178	-1.4329	1.9796	-1.2129	-1.037	0.5467	-0.7375	-0.6135
CO ₂	-2.0196	-2.1498	4.3469	-1.6668	-1.2805	2.1971	-0.5804	-0.4781
H ₂ O	-0.9162	-1.1101	1.7236	-0.9186	-0.7654	0.6135	-0.3617	-0.0138
H ₂ CO	-1.526	-1.9787	2.4195	-1.7098	-1.4948	0.4408	-1.2369	-0.9225
LiF	-0.9615	-1.4748	-0.3654	-1.5154	-1.5479	-1.8402	-2.152	-1.8396
LiH	-0.3174	-0.4655	-0.2707	-0.4955	-0.5196	-0.7362	-0.6817	-0.6037
NH ₃	-0.9624	-2.1782	0.3564	-2.1386	-2.1069	-1.8218	-2.4128	-1.9451
C ₂ H ₆	-2.0184	-3.613	1.9253	-3.399	-3.2279	-1.6877	-3.5948	-2.8798
C ₂ H ₄	-1.7471	-2.992	1.7776	-2.7945	-2.6365	-1.2143	-2.9405	-1.8682
C ₂ H ₂	-1.4796	-2.371	1.709	-2.1811	-2.0292	-0.662	-2.3046	-2.8798
C ₆ H ₆	-4.6163	-7.6011	6.4322	-6.8864	-6.3147	-1.1689	-7.1559	-6.333
Average Relative Error		-0.962	3.596	-0.755	-0.588	0.907	-0.763	-0.391
RMS Relative Error		1.294	4.534	1.104	0.988	1.933	1.466	1.205

Table 4: For atoms, the normalization of different types of model density matrices, including the exact Hartree-Fock density matrix (HF), the local-density approximation (LDA), the 1-point weighted density approximation (1WDA), and the 2-point weighted density approximation with $p = 5$ (2WDA). The last column states the maximum absolute error in normalization at any point during the last step of iteration. The Kohn-Sham results can be used to assess the accuracy of the six-dimensional integration grid.

Atoms	HF	LDA	1WDA	2WDA	Error(2WDA)	Max. abs. error in normalization
H	1.0000	0.2286	0.5000	0.5000	-0.4999	3.89997E-04
He	2.0001	0.6385	2.0001	2.0001	0.0000	3.66047E-08
Li	3.0000	0.9479	2.5491	2.6790	-0.3209	4.00856E-04
Be	3.9999	1.4283	3.1188	3.8524	-0.1476	2.28421E-04
B	4.9999	1.9381	3.6848	4.9149	-0.08507	2.55228E-04
C	5.9999	8.502	8.0445	6.1180	0.1180	5.13794E-05
N	6.9999	3.0743	4.8653	6.9032	-0.0968	2.38088E-04
O	7.9999	3.5729	5.5302	8.0218	0.0218	3.42978E-04
F	8.9999	4.2362	6.0873	8.8816	-0.1184	3.12419E-04
Ne	10.0000	4.8459	6.7196	9.8865	-0.1136	3.07957E-04
Na	10.9999	5.2342	6.9347	10.7444	-0.2556	2.64519E-04
Mg	11.9999	5.7763	7.2295	11.8803	-0.1197	1.69319E-04
Al	13.0000	6.3144	7.5515	12.8991	-0.1009	2.79699E-04
Si	13.9999	6.8823	7.9746	13.9378	-0.06215	3.49458E-04
P	15.0000	7.5063	8.3491	14.8894	-0.1106	2.02306E-04
S	15.9999	8.0685	8.9528	16.0449	0.0449	2.49852E-04
Cl	16.9999	8.7436	9.3449	16.8892	-0.1108	2.62877E-04
Ar	17.9999	9.3996	9.9114	17.9057	-0.0943	2.41629E-04

Table 5: For molecules, the normalization of different types of model density matrices, including the exact Hartree-Fock density matrix (HF), the local-density approximation (LDA), the 1-point weighted density approximation (1WDA), and the 2-point weighted density approximation with $p = 5$ (2WDA). The last column states the maximum absolute error in normalization at any point during the last step of iteration. The Kohn-Sham results can be used to assess the accuracy of the six-dimensional integration grid.

Molecule	HF	LDA	1WDA	2WDA	Error(2WDA)	Max. abs. error in normalization
BF ₃	31.9959	16.1347	22.6334	31.9316	-0.0643	2.36073E-04
CO	13.9999	6.7593	10.0234	13.9129	-0.0869	5.23547E-04
CO ₂	21.9994	11.0348	15.9207	21.932	-0.0673	2.06136E-04
H ₂ O	10.0001	4.7863	6.6806	9.9067	-0.0934	3.78058E-04
HCHO	15.99903	7.8303	11.33698	15.9275	-0.0715	2.51132E-04
LiF	11.9915	5.5715	8.4329	11.8833	-0.1082	5.69642E-04
LiH	3.9986	1.38595	3.49198	3.8717	-0.1269	3.82933E-04
NH ₃	9.9986	4.7514	6.7718	9.9133	-0.0852	5.38250E-04
C ₂ H ₆	18.0018	8.8715	12.8775	17.9334	-0.0685	1.35380E-04
C ₂ H ₄	15.9974	7.7833	11.4812	15.9229	-0.0745	2.87588E-04
C ₂ H ₂	13.9995	6.7069	10.1122	13.9265	-0.07297	2.55714E-04
C ₆ H ₆	42.0013	21.9997	31.4696	41.9514	-0.0499	1.21998E-04

These errors are quite small but because of the large number of points in the numerical integration grids, the sum of the errors can be sizeable.

V. E. Discussion

In this work, we proposed a 2-point weighted density approximation (2WDA) and we tested the conventional weighted-density approximation (1WDA) and the 2WDA for atoms and small molecules. The results are not remarkable, but the 2WDA is a major improvement over the 1WDA.

The strength of the weighted density approximation approach is that one addresses the Pauli principle directly by (partially) imposing a subset of the idempotency conditions on a model 1-matrix. The resulting 1-matrix is self-interaction-free, but it is not idempotent. To test how far the matrix was from idempotent, we computed the natural orbital occupation numbers in the model 1-matrix. For the Argon atom, the maximum and minimum occupations are presented in Table 6; Figure 1 shows the spectrum of most-highly-occupied orbitals. Note that the 1-matrix we considered was resolved on the integration grid: the number of orbital occupation numbers is thus equal to the number of grid points. There are therefore thousands of occupation numbers, most of which are nearly zero.

None of the density matrices is close to idempotent. The primary violation of N -representability is associated with core orbitals that contain significantly more than one electron. Superficially, the violation of the Pauli principle is worse

for the 2WDA 1-matrix than it is for the LDA or the 1WDA model 1-matrix. This may be related to the too-small normalization constants for the LDA and 1WDA 1-matrices in Table 4.

Table 6: Table reporting the maximum and minimum eigenvalues of the model 1-matrix for the Argon atom.

Maximum Eigenvalue			Minimum Eigenvalue		
LDA	1WDA	2WDA	LDA	1WDA	2WDA
1.2158	1.6413	1.7894	-0.06926	-0.05381	-0.09812

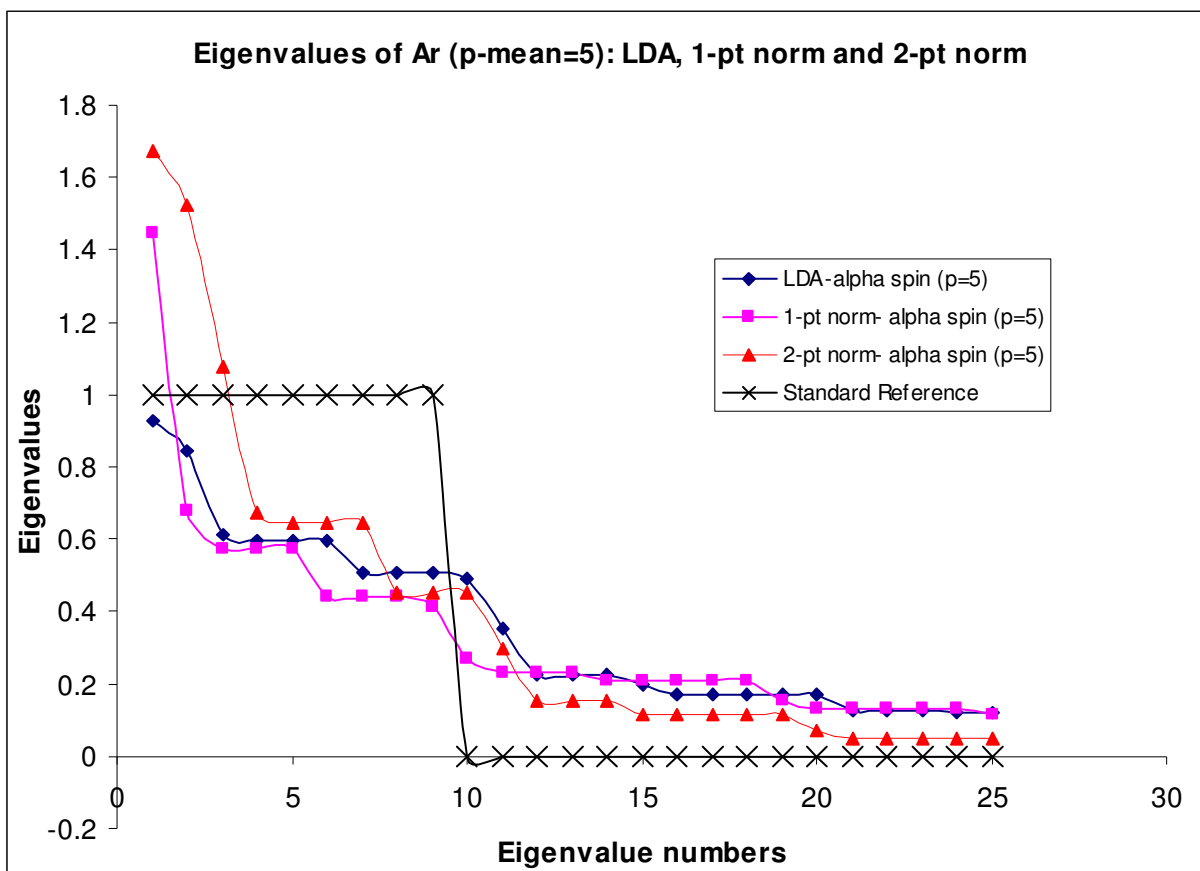


Figure 1: The natural orbital occupation numbers for the model 1-matrix in the LDA, 1-point WDA, and 2-point WDA approximations in the Argon atom. In all cases we symmetrized the 1-matrix (using Eq. (23)) before computing the eigenvalues.

We consider these as preliminary results. As stressed in section V.B., the WDA is a very flexible form, and certain approximations we made here are far from optimal. The most severe approximation we made was to choose the p value that defined the generalized mean to be a constant. By comparing optimal p

values for different atoms, it is clear that it would be better to have a small p value in the tails of the electron density, but a larger p value near the core. (This would also remedy the numerical ill-conditioning mentioned in section III.) Similarly, it is favorable to use a larger p value for molecules, where there is accumulation of density.

We would propose, then, to choose a hierarchy of models for p , in analogy to the “Jacob’s ladder” of functionals in DFT. By including information about the electron density and its derivatives into p , we should be able to improve our model. The simplest choice would be a rational function,

$$p(\mathbf{r}, \mathbf{r}') = \frac{a_0 + a_1 s(\mathbf{r}, \mathbf{r}') + a_2 (s(\mathbf{r}, \mathbf{r}'))^2 + \dots}{1 + b_1 s(\mathbf{r}, \mathbf{r}') + b_2 (s(\mathbf{r}, \mathbf{r}'))^2 + \dots} \quad (43)$$

where

$$s[\rho; \mathbf{r}, \mathbf{r}'] = \frac{1}{2(3\pi^2)^{1/3}} \left(\frac{\left(|\nabla \rho(\mathbf{r})| / \rho^{4/3}(\mathbf{r}) \right)^q + \left(|\nabla \rho(\mathbf{r}')| / \rho^{4/3}(\mathbf{r}') \right)^q}{2} \right)^{1/q} \quad (44)$$

is the generalized- q -mean of the reduced gradients.

In this work we considered only the model 1-matrix taken from the uniform electron gas. The UEG 1-matrix decays very slowly asymptotically,

$$\tilde{g}_{\text{UEG}}(k_F |\mathbf{r} - \mathbf{r}'|) \sim \frac{1}{k_F |\mathbf{r} - \mathbf{r}'|^2} \quad (45)$$

but for atoms, molecules, and insulators, the 1-matrix decays exponentially quickly,

$$\tilde{g}(k_F |\mathbf{r} - \mathbf{r}'|) \sim e^{-bk_F |\mathbf{r} - \mathbf{r}'|}, \quad (46)$$

where the characteristic rate of exponential decay is related to the band gap⁶⁹⁻⁷¹. This suggests that it would be preferable to use an exponential model for the 1-matrix,

$$\begin{aligned} \tilde{g}_{\text{exp}}^{\sigma\sigma}(\tilde{\kappa}_F^{\sigma}(\mathbf{r}, \mathbf{r}'), a^{\sigma}, b^{\sigma}) &= \left(1 - a^{\sigma} \tilde{\kappa}_F^{\sigma}(\mathbf{r}, \mathbf{r}') |\mathbf{r} - \mathbf{r}'|^2\right) \\ &\times \exp \left[\left(\frac{b^{\sigma}}{|\tilde{\kappa}_F^{\sigma}(\mathbf{r}, \mathbf{r}')|} \left(\frac{|\nabla \rho(\mathbf{r})|}{\rho(\mathbf{r})} \right)^2 \right) \left(1 - \sqrt{1 + (\tilde{\kappa}_F^{\sigma}(\mathbf{r}, \mathbf{r}') |\mathbf{r} - \mathbf{r}'|)^2} \right) \right] \end{aligned} \quad (47)$$

where $\kappa(\mathbf{r}, \mathbf{r}')$ is the p -mean of the effective Fermi wave- vectors, Eq. (19). This model decays correctly, but fails to give correct results for the uniform electron gas. That can be mitigated by generalizing the form still further,

$$\begin{aligned} \tilde{g}_{\text{UEG+exp}}^{\sigma\sigma}(\tilde{\kappa}_{\text{UEG}}^{\sigma}(\mathbf{r}, \mathbf{r}'), \tilde{\kappa}_{\text{exp}}^{\sigma}(\mathbf{r}, \mathbf{r}'), a^{\sigma}, b^{\sigma}) &= \tilde{g}_{\text{UEG}}^{\sigma\sigma}(\tilde{\kappa}_{\text{UEG}}^{\sigma}(\mathbf{r}, \mathbf{r}') |\mathbf{r} - \mathbf{r}'|) \\ &\times \exp \left[\left(\frac{b^{\sigma}}{|\tilde{\kappa}_{\text{exp}}^{\sigma}(\mathbf{r}, \mathbf{r}')|} \left(\frac{|\nabla \rho(\mathbf{r})|}{\rho(\mathbf{r})} \right)^2 \right) \left(1 - \sqrt{1 + (\tilde{\kappa}_{\text{exp}}^{\sigma}(\mathbf{r}, \mathbf{r}') |\mathbf{r} - \mathbf{r}'|)^2} \right) \right] \end{aligned} \quad (48)$$

It is clear from Eqs. (43) that as one moves to more sophisticated models for the 1-matrix, there may be large numbers of free parameters to be specified. These parameters could be fit to a data set, but there are also additional constraints that the 1-matrix should satisfy. If one imposes the constraint,

$$\int |\nabla \gamma^\sigma(\mathbf{r}, \mathbf{r}')|^2 d\mathbf{r}' = \left[\nabla \cdot \nabla' \gamma^\sigma(\mathbf{r}, \mathbf{r}') \right]_{\mathbf{r}=\mathbf{r}'}, \quad (49)$$

then this would ensure that the March-Santamaria form of the kinetic energy,^{72,73}

$$T_s = \iint \frac{|\nabla(\gamma^\sigma(\mathbf{r}, \mathbf{r}'))|^2}{8|\gamma^\sigma(\mathbf{r}, \mathbf{r}')|^2} d\mathbf{r} d\mathbf{r}' \quad (50)$$

gave the same results as the conventional form, Eq. (11). Similarly, for an idempotent density matrix,

$$\int \gamma^\sigma(\mathbf{r}, \mathbf{r}') \left[\int \gamma^\sigma(\mathbf{r}', \mathbf{r}'') f(\mathbf{r}'') d\mathbf{r}'' \right] d\mathbf{r}' = \int \gamma^\sigma(\mathbf{r}, \mathbf{r}') f(\mathbf{r}') d\mathbf{r}' \quad (51)$$

for any function $f(\mathbf{r})$. The most logical choice would be $f(\mathbf{r}) = \sqrt{\rho^\sigma(\mathbf{r})}$

because, in that case, the integrals in Eq. (51) take a very simple form.

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Chapter VI

Conclusions and Outlook

VI.A. Summary of the Thesis:

This dissertation has explored different approaches for developing kinetic energy functionals in density-functional theory (DFT) and generalized DFT. It features both formal mathematical results on the kinetic energy functional and numerical tests of approximate kinetic energy functionals. Unfortunately, most of the numerical results are of disappointing quality, emphasizing how difficult it is to develop kinetic energy functionals with sufficient accuracy for chemical modelling.

In DFT, the fundamental descriptor of an electronic system is the electron density, $\rho(\mathbf{r})$. The quest to write the kinetic energy as an explicit functional of the electron density dates back to 1920's, with the work of Thomas and Fermi. Seventy years later, discouraged by the lack of progress in approximating the kinetic energy functional, Ziesche proposed replacing the electron density with the electron pair density, $\rho_2(\mathbf{r}, \mathbf{r}')$, and then using ρ_2 as the fundamental descriptor. Other authors then generalized Ziesche's formalism to higher-order electron distribution functions (k -densities). These generalized DFTs seem promising because the fundamental descriptor (the k -density, with $k \geq 2$) contains much more information than the electron density. One expects, then, that the kinetic energy can be more accurately approximated using the k -densities.

However, the numerical results in this dissertation suggest that little is gained by moving from the electron density to the electron pair density.

In chapter 2, we explored a new approach for deriving kinetic energy functionals in DFT and generalized-DFT. Specifically, we proposed a form for the momentum distribution function, $\Pi(\mathbf{p})$ and showed that the associated kinetic energy expression

$$T = \int \frac{1}{2} p^2 \Pi(\mathbf{p}) d\mathbf{p} , \quad (1)$$

when Fourier transformed into position space, becomes the Fisher information of the electron distribution function. It is intuitively appealing that the second moment of the momentum (i.e., the momentum variance) is closely related to the Fisher information of a many-electron distribution function, which is proportional to Weizsacker kinetic energy functional. This provides a new derivation of the Weizsäcker function in DFT and generalized DFT. More significantly, it is the first time that the momentum distribution and quasi-probability distribution function that correspond to the Weizsäcker functionals have been derived.

Chapters 3 and 4 present numerical tests of kinetic energy functionals for higher-order electron distribution functions. The simplest conceivable functional is the k -electron generalized Weizsäcker functional derived in chapter 2; this functional was tested in chapter 3 for the spin-free and spin-resolved 2-density

and 3-density. The results are usually much worse than Hartree-Fock; we observe that there is a trend of increasing returns: with each additional order of approximation, the amount the functional improves increases. This is in contrast to the law of diminishing returns, wherein higher-order approximations asymptotically approach the exact result, that is almost universally observed in approximate electronic structure theory. The k -electron Weizsäcker functional is inaccurate because the underlying k -electron reduced density matrix is not N -representable, and strongly violates the Pauli exclusion principle. Therefore the k -electron Weizsäcker functional is not N -representable. It is a lower bound to the true kinetic energy, however, which may be useful in some contexts.

Chapter 4 contains numerical tests for the March-Santamaria functional. The March-Santamaria functional was derived from the Hartree-Fock model for the 1-electron reduced density matrix and it is exact for that case. As such, we expect the March-Santamaria functional to violate the Pauli principle less severely than the generalized Weizsäcker functionals. While the March-Santamaria functional is much more accurate than the analogous 2-electron Weizsäcker functional, it makes qualitatively incorrect predictions for the contribution of electron correlation to the kinetic energy: the March-Santamaria functional predicts that the kinetic energy decreases, instead of increases, with increasing electron correlation. While the March-Santamaria functional may be useful for

systems where the Hartree-Fock approximation is very accurate, the March-Santamaria functional is not accurate enough for most chemical applications.

Prior to this thesis, there were many promising theoretical results pertaining to generalized DFT, and especially methods based on the electron pair density. However none of the most frequently proposed kinetic energy functionals had been numerically tested. We tested these functionals and found disappointing results. We also showed that the underlying problem in these functionals is their non- N -representability. This insight can be used to design improved functionals. For example, the Ayers-Levy formulation explicitly constructs an N -representable 1-electron reduced density matrix from the pair density, and thus prevents any severe violations of N -representability.

Chapters 2-4 show how the kinetic energy can be approximated from the electron pair density. Chapter 5 uses this idea but, instead of using the exact pair density, considers a model pair density based on the uniform electron gas. Specifically, this pair density is parameterized so that it is consistent with the Pauli exclusion principle, and the underlying 1-electron reduced density matrix is then used to evaluate the kinetic energy. This results in a generalization of the weighted density approximation (because of the use of the pair density) and the local density approximation (because of the use of the uniform electron gas). Our method is more accurate than both the conventional weighted density

approximation and the local density approximation. However, it is still not accurate enough to be used for chemical applications.

VI.B. Outlook:

In chapter 2, we showed how the electron density can be used to model the momentum density, which can then be used to compute the kinetic energy. This approach to deriving kinetic energy functionals has been used before, but it is still an unconventional approach. Given the disappointing result obtained with other, more conventional, derivation pathways to kinetic energy functionals, it seems worthwhile to pursue this approach further. In the conclusion of chapter 2, we proposed another possible model momentum density, but we were unable to perform the mathematics needed to use it. One could also attempt to combine the ideas in chapters 2 and 5, and derive a weighted density approximation for the momentum density. Such an approach would be entirely novel; it might give favourable results, though scepticism is always warranted when kinetic energy functionals are being considered.

Chapters 3 and 4 wrote the kinetic energy as a functional of the pair density. These results were disappointing. The results in chapter 3 were disappointing because the generalized Weizsäcker functional is far from N -

representable. The results in chapter 4 were disappointing because the March-Santamaria functional erroneously predicts that the correlation contribution to the kinetic energy is negative. First of all, it would be interesting to refine these results by considering more accurate correlated wavefunctions, but we do not expect the results to change qualitatively. Second of all, it would be interesting to design a new approach that solves these problems. A variant of the Ayers-Levy construction could do this. In the Ayers-Levy construction, one first determines the electron density from the pair density,

$$\rho^\sigma(\mathbf{r}) = \frac{1}{N^\sigma - 1} \int \rho_2^{\sigma\sigma}(\mathbf{r}, \mathbf{r}') d\mathbf{r}' \quad (2)$$

and, then inverts the Kohn-Sham equations to determine the Kohn-Sham kinetic energy, $T_s[\rho^\sigma]$ and the Kohn-Sham pair density,

$$\rho_{2,s}^\sigma(\mathbf{r}, \mathbf{r}') = \rho^\sigma(\mathbf{r}) \rho^\sigma(\mathbf{r}') - \sum_i \sum_j \phi_i^\sigma(\mathbf{r}) (\phi_j^\sigma(\mathbf{r}'))^* \phi_j^\sigma(\mathbf{r}) (\phi_i^\sigma(\mathbf{r}'))^* \quad (3)$$

One then needs to find a functional for the correlation kinetic energy, $T_c[\rho_2]$ that is always positive. For example, one might hope that the generalized Weizsäcker functional is accurate for the *correction* to the Kohn-Sham kinetic energy, even though the functional is not accurate for the Kohn-Sham kinetic energy itself. This would give the functional

$$T_c [\rho_2^\sigma] = \sum_{\sigma=\alpha,\beta} \left[\frac{1}{N_\sigma - 1} \iint \frac{|\nabla_{\mathbf{r}} (\rho_2^{\sigma\sigma}(\mathbf{r}, \mathbf{r}') - \rho_{2,s}^{\sigma\sigma}(\mathbf{r}, \mathbf{r}'))|^2}{8(\rho_2^{\sigma\sigma}(\mathbf{r}, \mathbf{r}') - \rho_{2,s}^{\sigma\sigma}(\mathbf{r}, \mathbf{r}'))} d\mathbf{r} d\mathbf{r}' \right. \\ \left. + \frac{1}{N_\sigma} \iint \frac{|\nabla_{\mathbf{r}} (\rho_2^{\sigma\sigma' \neq \sigma}(\mathbf{r}, \mathbf{r}') - \rho^\sigma(\mathbf{r}) \rho^{\sigma' \neq \sigma}(\mathbf{r}'))|^2}{8(\rho_2^{\sigma\sigma' \neq \sigma}(\mathbf{r}, \mathbf{r}') - \rho^\sigma(\mathbf{r}) \rho^{\sigma' \neq \sigma}(\mathbf{r}'))} d\mathbf{r} d\mathbf{r}' \right] \quad (4)$$

Probably there are much more accurate functionals than this one; for example, the proposed dependence of this functional on the opposite-spin density seems especially simplistic. The key is to find a functional that is never negative (because $T_c[\rho_2] \geq 0$); this avoids the problem with the March-Santamaria functional. By using the Kohn-Sham approach to evaluate the uncorrelated portion of the kinetic energy, the N -representability problem for the functional is mostly avoided.

Chapter 5 used a model for the exchange hole or, equivalently, a model for the 1-electron reduced density matrix, to evaluate the kinetic energy. This approach would be exact if the model were exact, so all the errors in this approach can be attributed to the errors in the underlying model for the exchange hole (or density matrix). The method in chapter 5 could be improved, then, by improving the model for the exchange hole. There are several ways to do this. First of all, it is known that the exchange hole in molecules, semiconductors, and insulators

decays exponentially faster than the exchange hole in the uniform electron gas. This suggests that the exchange hole from the uniform electron gas is a poor approximation for atomic and molecular systems; making an improved model hole (ideally one that still gives correct results in the uniform-electron-gas limit) would be helpful. Second, choosing the mixing exponent in the generalized p -mean,

$$k_F(\mathbf{r}, \mathbf{r}') = \left(\frac{k_F^p(\mathbf{r}) + k_F^p(\mathbf{r}')}{2} \right)^{1/p} \quad (5)$$

to be a constant is an oversimplification. Our data shows that it would be ideal to have a functional form where p is large near the nucleus and small far from the nucleus. This suggests that we should write p as a density functional. For example, one might approximate p with a rational function,

$$p = \frac{a + bs[\rho]}{1 + cs[\rho]} \quad (6)$$

where

$$s[\rho] = \frac{\nabla \rho(\mathbf{r})}{(\rho(\mathbf{r}))^{4/3}} \quad (7)$$

is the reduced gradient.

Finally, the results in chapter 5 are based on the conventional form of the kinetic energy,

$$T_s[\rho^\sigma] = \sum_{\sigma=\alpha,\beta} \frac{1}{2} \iint \delta(\mathbf{r}-\mathbf{r}') \nabla \cdot \nabla' \gamma^\sigma(\mathbf{r},\mathbf{r}') d\mathbf{r} d\mathbf{r}' \quad (8)$$

One would get different results using the March-Santamaria form,

$$T_s[\rho^\sigma] = \sum_{\sigma=\alpha,\beta} \iint \frac{|\nabla_{\mathbf{r}}(\gamma^\sigma(\mathbf{r},\mathbf{r}'))|^2}{8(\gamma^\sigma(\mathbf{r},\mathbf{r}'))^2} d\mathbf{r} d\mathbf{r}' \quad (9)$$

It would be interesting to see if results improve using Eq. (9). Alternatively, one could force Eq. (8) to give the same results as Eq. (9) by adding that condition as a constraint when the nonlinear equations for $k_F(\mathbf{r})$ are being solved.

VI.C. Perspective:

Eighty-five years after Thomas developed the first kinetic energy density functional, the quixotic quest for accurate kinetic energy functionals continues. No existing orbital-free kinetic energy functionals can compete with the robustness and accuracy of conventional Kohn-Sham DFT methods. One might sensibly abandon the quest, but kinetic energy functionals are important not only for computational modelling, but also for theoretical reasons. For example, the famous Lee-Yang-Parr correlation-energy functional is built upon a kinetic energy functional. Orbital-free kinetic energy functionals are also useful for density-functional theory embedding calculations, where one uses the kinetic energy

functional to define the “kinetic pressure” that the electrons in a subsystem feel due to its surroundings. Finally, the kinetic energy density is useful for chemical interpretation because it can be used to locate electron-pair regions within a molecular structure. Fortunately, these applications require much less accuracy than computing accurate reaction thermo-chemistry or kinetics. Indeed, it seems possible that there will never be kinetic energy functionals that are competitive, in terms of scope and accuracy, with the chemical reaction energies computed with Kohn-Sham DFT.