

**ADIABATIC CONNECTION AND UNIFORM  
DENSITY SCALING: CORNERSTONES OF A  
DENSITY FUNCTIONAL THEORY**

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## ABSTRACT OF THE DISSERTATION

# Adiabatic Connection and Uniform Density Scaling: Cornerstones of a Density Functional Theory

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Density Functional Theory (DFT) is an effective and popular approach to the quantum many-body problem. DFT is exact but, in practice, the exchange-correlation contribution to the total energy must be approximated. Because of the demand for higher accuracy in applications, the modelling and understanding of this exchange-correlation functional is an important area of research and is the focus of this thesis. First, a DFT is developed for a one-dimensional delta-function interaction. Then, the focus returns to the Coulomb-interacting problem. Uniform density scaling relationships are generalized to spin-scaling relationships. The adiabatic connection is considered at both strong and weak interaction limits. In the strong limit, the strictly-correlated electron hypothesis is tested. In the weak limit, the accuracy of exact-exchange DFT for large gap solids is examined.

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# Chapter 1

## The Need for a Density-Based Electronic Structure Theory

### 1.1 The Importance of Electronic Structure Theory

Electronic structure theory is the attempt to understand and accurately determine the properties of atoms, molecules, surfaces, and solids. The goal, chemical accuracy, would be invaluable in the custom design of materials, the simulation of chemical reactions, and the discovery of new pharmaceuticals.

Even though chemical accuracy has not yet been achieved, exciting results have already been obtained from electronic structure calculations. For example, density functional theory has been used to find a new catalysis for the Haber-Bosch process which is important in the industrial production of ammonia [1]. Computer simulations of how the enzymes in viruses interact are already useful and will someday become a powerful weapon in fighting diseases like HIV [2, 3].

Two main objectives of computational physics are to give a better understanding of what is seen in experiments and to offer information about materials before they are ever studied in the lab. For example, molecular and crystal structures depend on how the electronic ground state energy changes as a function of the position of the atomic nuclei [4]. By analyzing how the total energy changes, we can compute the forces acting on atoms. Results from a calculation like this could be used, for example, to maximize the strength and minimize the rust of alloyed construction girders [5].

This thesis will deal with *ab initio* or first principles methods. First principles calculations are based on the underlying laws of physics and do not require system-specific input based on experiments. These sorts of methods are the most technically demanding and expensive but promise to be most accurate.

*Ab initio* calculations are difficult even though the underlying physical laws are known. The trouble is that the electrons obey complicated and nonintuitive quantum mechanical laws. According to quantum theory, the electrons can only be described probabilistically. This means that the absolute positions and velocities of the electrons cannot be known exactly; rather, the whole system must be described by a mathematical object - the wave-function. Experiments have shown that the wave-function satisfies the Schrödinger equation, but solving this equation to find the wave-function is not generally feasible. One difficulty comes from the fundamental nature of the electron. Electrons are fundamentally identical. This has more than just philosophical implications, it means that the wave-function is unchanged except for its sign when two electrons switch places. The other complication results from terms in the Schrödinger equation that describe how the electrons repel each other. This mutual interaction makes the solution grow exceedingly complex as the number of electrons increases.

## 1.2 An Assortment of Methods

Only a few non-interacting quantum mechanical problems and precious fewer interacting problems have exact analytic solutions. Numerical methods offer the only possibility to find answers for more general situations. Computation alone is not enough. Careful understanding of the underlying physics is required to make computations feasible and reliable.

Several methods have been developed to deal with the electronic structure problem. It is insightful to briefly consider these so that the importance of a

density-based theory becomes obvious. The two most popular classes of methods are *empirical* and *ab initio*.

*Empirical* methods such as force field methods approximate the problem by parameterizing similar well-studied problems [6]. Since these *empirical* methods are designed for certain classes of systems, they are not to be trusted when applied to general situations. These methods can be designed to work at various length scales but are not the best tool to explore new science reliably.

*Ab initio*, Latin for “from the source”, methods start from the underlying physical equations. In principle, these methods are exact. Since they are based on general laws of physics, these methods can be expected to reproduce nature when applied to unstudied systems.

There are two subclasses of *ab initio* methods.

The first subclass relies on finding increasingly better approximations to the wave-function. The simplest approximation is to assume that the many-particle wave-function is just a product of single-particle orbitals. By enforcing the proper quantum mechanical law under particle exchange, we arrive at the Hartree-Fock approximation. For many systems, Hartree-Fock is reasonably accurate but since it involves bold assumptions about the form of the wave-function, it does not provide a complete theory for electronic structure [7, 8, 9]. Configuration interaction methods (CI) improve systematically upon Hartree-Fock and can, in principle, give exact solutions [6]. However, exact CI is too computationally expensive, especially for dozens or more electrons. Another approach is to vary parameters in a carefully chosen approximate wave-function[10]. The integrals involved in this scheme are complicated and often require Monte Carlo integration. This variational approach is also best for small systems where the number of parameters to vary is small [11].

A second subclass of methods considers objects related to but more manageable than the wave-function. These may or may not offer a full description of

the physics. An example is Green's function theory. Like wave-function theory, it can be exact. Its advantage is that the one- or even two-particle Green's function is a much simpler object than a many-electron wave-function. For large systems like solids, Green's function methods allow the descriptions of large numbers of particles in a compact form. The GW approximation to the self-energy is a practical implementation of Green's function theory and is useful for many applications [12, 13]. The G refers to the Green's function for the electrons, and W is the screened electron-electron interaction. Generally, GW results agree well with experiment but the calculations for many systems can only be performed on supercomputers. Yet simpler objects, like the density matrix [14], and even simpler, the density, might form the basis for a theory. Density functional theory is based on one of the simplest of these objects, the electronic density.

### 1.3 The Advantages of a Density Based Theory

A grain of table salt has  $3 \times 10^{19}$  electrons, and many interesting molecules have hundreds, thousands, and even millions of electrons. For typical systems, the many-particle wave-function is unwieldy and hard to find. To get an idea of the problem, imagine that we need to know values of the wave-function at only a few of points in space. Let us record the wave-function at  $M$  points along each spatial direction. In three dimensions, an  $M \times M \times M$  sized array would be large enough to store the sampled wave-function for a one-particle system. Adding another electron raises this size by one power. For a system with  $N$  electrons, we would need  $M^{3N}$  entries in our array. For 10 electrons and only 10 sample points, we would need  $10^{30}$  entries! This is too many entries. Of course, in real calculations, there are more clever ways to describe the system than this, but the basic conclusion is the same. The wave-function is not a practical description for even a moderate number of electrons.

In order to examine larger systems more efficiently, it is enticing to use less grids points. Examples of objects that are easier to handle are the density and density matrix. The density goes as  $M^3$  and the density matrix goes as  $M^6$ . Notice that the density does not take up more memory with the number of electrons. The efficiency of an electronic structure method is often characterized by the way a calculation scales with the number of electrons,  $N$ . Ideally, an electronic structure calculation would scale as  $N$ . DFT typically scales as  $N^3$  but in some cases as  $N$ . Hartree Fock scales as  $N^3$ . Full CI scales as  $Exp(N)$ , with approximate CI methods scaling as gradually as  $N^5$  at best [6]. We can use this information to estimate the relative system sizes that each method can consider.

It would be ideal to have a complete description of the physics without having to calculate the awkward wave-function. The trouble is whether this reduction is formally justified and can in principle be exact. Do we really lose information by not calculating the wave-function? Or could a complete theory be based on the density rather than the wave-function?

A common argument against this reduction is that the density seems to have less information than the wave-function. The wave-function, after-all, has more arguments and knows explicitly about all the electrons.

On the the other hand, there are reasons to believe a density-based theory might be rigorous. For small systems and systems varying slightly from the uniform limit we *can* find the potential from the density. For these systems at least, the reduction is exact. Why shouldn't we be able to find the potential from the density in general?

If we could use the density instead of the wave-function, we would greatly increase the size and scope of the problems we could answer exactly. In fact, we can do this, and the density indeed contains all the same information as the wave-function!

Density functional theory is important for more than just computational expediency; it is a conceptually new approach to quantum mechanics. The Kohn-Sham version of the theory, which we will discuss in more detail later, can be used to give a rigorous meaning to molecular orbitals and to clarify chemical notions of hardness and softness [15].

## 1.4 The History of Density Functional Theory

Investigations into a density-based theory of matter started about the same time as wave-function quantum mechanics. In 1927, Thomas and Fermi attempted a density-based description of atoms [16, 17]. At that time, there was no known formal justification for this method. For most practical applications, Thomas-Fermi theory was inadequate. Nevertheless, the idea of a density-based theory was appealing and work continued. In 1935, Weizsäcker introduced the first gradient density functional [18].

The computer was developed in the forties and was a new tool for physics. If used properly, it could provide a quantitative theory of matter. Slater realized this and pushed for a density-based approximation to quantum theory that would be compatible with computing. His  $X\alpha$  method was found to be good but, like Thomas-Fermi theory, lacked a known formal justification [19].

Justification came in 1964 when Hohenberg and Kohn demonstrated that the density, as well as the potential, uniquely characterizes a ground-state electronic structure problem [20]. This observation suggested the introduction of a non-interacting Kohn-Sham counterpart with the same density as the interacting system [21]. The solutions for the non-interacting problem could be readily calculated and used to get information about the interacting system.

Hohenberg and Kohn determined that the total ground-state energy is a functional of the density, and the only part of the energy which must be approximated

is the exchange-correlation energy. They proposed to approximate this contribution to the energy by that of the uniform electron gas. The scheme became known as the local density approximation (LDA). At the time, simple approximations to the exchange-correlation energy of the uniform gas were known [22, 23, 24]. More accurate and essentially exact parameterizations have since been developed and are in common use today [26, 27, 28].

Throughout the seventies, DFT - mostly within the local density approximation - was widely applied to solids. Rough ideas about its accuracy were found [29, 30]. The LDA reproduced crystal structures well but underestimated band gaps. By the late seventies, people started to understand why LDA worked as well as it did and began trying to go beyond it by proposing gradient expansions [31, 32]. Today, several generalized gradient approximations are available [33, 34, 35, 36].

In 1979, Levy's constrained search proof provided a more intuitive and constructive derivation of the Hohenberg-Kohn theorem [37, 38].

In 1988, a GGA was invented which was well-suited to chemical problems [33, 34]. In the early nineties, DFT methods were implemented into John Pople's electronic structure code, Gaussian [40]. Since then, the number of papers in quantum chemistry using DFT has increased exponentially [41]. The introduction of hybrids functionals further increased the accuracy of DFT [42, 43]. By 1998, DFT had become so ubiquitous, popular, and successful that the Noble prize went to Walter Kohn "for his development of the density-functional theory" and John Pople "for his development of computational methods in quantum chemistry" [44].

Paralleling the development of ground-state theory, DFT has been extended to more general situations. Most notably, Runge and Gross generalized the theory to time-dependent and excited-states [45, 46]. In the nineties, Gaussian and DFT became a standard tool for excited state as well as ground state calculations [47]. Today, understanding and improving the accuracy of predictions for excited states

in DFT is an active area of research.

## 1.5 Successes, Failures, and the Future

Density functional theory provides ground-state structures, energetics, and vibrational properties for interacting-electron systems. One of the greatest advantages of DFT is its generality; all elements are treated with the same functionals excepting the inclusion of relativistic effects for heavier elements. Because of its generality it, DFT can be used for metallic, covalent, and ionic bonds. The theory even performs well for traditionally difficult cases like describing Ozone. DFT is particularly suited to handle organometallic systems.

DFT calculations output the ground-state density, spin-density, and total energy. From these quantities, many experimentally observables can be extracted like dipole moments, polarizabilities, hyper-polarizabilities, magnetic moments, and geometries.

DFT methods typically other methods in accuracy. Strong bonds in solids, in molecules, and at surfaces are typically within 0.02 Angstroms of the experimentally measured quantities. Bond angles and dihedral angles a few percent of experiment. GGA binding energies are with 10 kJ/mol of experiments and are comparable to sophisticated CI approaches. Vibrational frequencies are 10-50  $\text{cm}^{-1}$ . Because DFT is based on the density, the methods is highly efficient, and can handle larger systems than other *ab initio* methods: 100 atoms or 1000 atom clusters by using symmetries of the cluster. Self-consistency typically takes 10-20 iterations for organic and semiconductors. Metals and transition metals are harder to converge. Molecular dynamics methods like Carr-Parinello for 100 atoms are 1000 times slower than empirical methods, but offer the possibility of being first principles.

Density functional theory has been exceptionally successful in solid-state

physics. Because the density of the electrons in a solid is typically close to uniform, the local-density approximation should be expected to work well. In fact, the LDA gives lattice constants for simple crystals within 1% of the experimental values [4]. On average, crystal structures and the dispersion of the energy bands are also well-described. Phase transitions in solids[48] and liquid metals[49, 50] have also been studied. The goal of energy band structure calculations for solids is the understanding of conducting and insulating behavior, understanding the types of crystal bonding, the prediction of electronic excitations like band gaps and photo spectra.???

The introduction of more accurate functionals than the LDA has made DFT useful in atomic and molecular physics. DFT has been used in the study of chemical reactions, the structure of biomolecules, and the nature of active sites on catalysts. Another use for DFT is molecular dynamics where the forces on the nuclei are calculated classically in the electron's field as the simulation proceeds [51]. DFT has even been used in biology and mineralogy [52, 53, 54, 55, 56].

More exotic uses for DFT are to describe super-conductivity [57], atoms in strong laser pulses [58], relativistic effects in heavy elements and nuclei [59], magnetic properties of alloys [60, 61], quantum fluid dynamics [62], and nuclear physics [63].

Density functional theory has a promising future in materials science, solid-state physics, and chemistry. This is because DFT can be used for a wide variety of large and small systems with confidence. Several popular electronic structure codes are available and in wide use: Gaussian, Abinit, Octopus [40, 64, 65]. The accuracy of functionals continues to improve. DFT is necessary for the *ab initio* study of large molecules when other *ab initio* methods are impractically slow. Advances in pseudo-potential theory and order  $N$  techniques allow DFT to be applied accurately to even larger systems.

DFT will be indispensable in future technological engineering tasks like the

calculation of transport properties in molecular wires and the design of nanomachines. However, before density functional methods reach fruition, proper descriptions of van der Waals effects, scattering properties, and excited states [66] will be important.

## Chapter 2

# A Formal Introduction to Density Functional Theory

### 2.1 The Schrödinger Equation

The resolution of the electronic structure problem is to understand the solutions of the Schrödinger equation,

$$\left( -\frac{\hbar^2}{2m_e} \frac{1}{2} \sum_{i=1}^N \nabla_i^2 + \frac{1}{2} \sum_{\substack{i,j=1 \\ j \neq i}}^N \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{i=1}^N v_{ext}(\mathbf{r}_i) \right) \Psi(x_1 \dots x_N) = E \Psi(x_1 \dots x_N), \quad (2.1)$$

for different potentials,  $v_{ext}(\mathbf{r})$ , where  $x_i = \{\mathbf{r}_i, \sigma_i\}$  represents a set of both position and spin values and  $N$  is the number of electrons. Sometimes the Schrödinger equation is written in operator form,

$$(\hat{T} + \hat{V}_{ee} + \hat{V}_{ext}) \Psi(x_1 \dots x_N) = E \Psi(x_1 \dots x_N), \quad (2.2)$$

where

$$\hat{T} = -\frac{\hbar^2}{2m_e} \sum_{i=1}^N \nabla_i^2 \quad (2.3)$$

is the kinetic energy operator,

$$\hat{V}_{ee} = \frac{1}{2} \sum_{i,j=1, j \neq i}^N \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \quad (2.4)$$

is the electron-electron interaction, and

$$\hat{V}_{ext} = \sum_{i=1}^N v_{ext}(\mathbf{r}_i) \quad (2.5)$$

is the external potential. Typically in solid-state physics and chemistry, the external potential is a Coulombic attraction to a set of nuclei,

$$v_{ext}(\mathbf{r}) = \sum_j \frac{Z_j e^2}{|\mathbf{r} - \mathbf{R}_j|}, \quad (2.6)$$

where  $\mathbf{R}_j$  and  $Z_j$  are the locations and charges of the nuclei. Sometimes, the external potential may have a different form as in realistic solid calculations. In this thesis, we use the Born-Oppenheimer approximation and fix the positions of the nuclei. This approximation is accurate because the typical mass of a nuclei is much larger than the mass of an electron.

Because the electrons are fermions, the wave-function,  $\Psi(x_1 \dots x_N)$ , is antisymmetric under particle interchange:

$$\Psi(x_1 \dots x_a \dots x_b \dots x_N) = -\Psi(x_1 \dots x_b \dots x_a \dots x_N). \quad (2.7)$$

This antisymmetry implies that no two fermions can occupy the same quantum state.

In principle, all of electronic physics within the fixed-nuclei approximation, both solid state and chemical systems, can be described accurately from Eqs. (2.1, 2.7, & 2.6). Unfortunately, as mentioned in Chapter 1, exact solutions in all but a few rare cases are unattainable.

In this thesis, we will be most concerned with a density-based theory. The total electron density is defined as

$$n(\mathbf{r}) = N \sum_{\sigma_1, \sigma_2 \dots \sigma_N} \int d\mathbf{r}_2 \dots d\mathbf{r}_N |\Psi(\mathbf{r}, \mathbf{r}_2 \dots \mathbf{r}_N)|^2. \quad (2.8)$$

Henceforth,  $e^2 = \hbar = m_e = 1$  and all energies will be in Hartrees and all lengths in Bohr radii,  $a_0$ , unless explicitly stated. Recall that 1 Hartree = 27.2 eV = 628 kcal/mol and  $a_0 = 52.9 \times 10^{-12} m = 0.529$  Angstroms.

## 2.2 Variational Principle

An important theoretical principle, upon which many calculations rely, is the variational principle. It tells us how to look for ground-state solutions by guessing them. The exact ground-state wave-function minimizes the expectation value of the Hamiltonian [67]:

$$E_{gs} = \min_{\Psi} \langle \Psi | \hat{H} | \Psi \rangle / \langle \Psi | \Psi \rangle. \quad (2.9)$$

A guess approximate normalized wave-function will always give a greater expectation value for the total energy unless of course the guess is exact! A rough derivation of the variational principle is as follows. Imagine we expand a trial solution in the complete basis of exact solutions for a chosen Hamiltonian:

$$|\Psi_{trial}\rangle = \sum_i c_i |\psi_i\rangle. \quad (2.10)$$

We require that the trial wave-function be normalized:

$$\langle \Psi_{trial} | \Psi_{trial} \rangle = \sum_i |c_i|^2 = 1. \quad (2.11)$$

Now, we write the energy expectation value using the trial wave-function,

$$E_{trial} = \langle \Psi_{trial} | \hat{H} | \Psi_{trial} \rangle = \sum_i |c_i|^2 E_i. \quad (2.12)$$

If the eigenvalues,  $E_i$ 's, are ordered then  $E_0$  has the lowest value. We can only achieve the minimum if we have the maximum contribution of  $E_0$ ; that is when  $|c_0|^2 = 1$ .

Two popular electronic structure methods, Hartree-Fock and configuration-interaction (CI), rely directly on this principle. Hartree-Fock theory is based on the minimization of Eq. (2.9) using one anti-symmetrized product of  $N$  single-particle orbitals or a Slater determinant [19]:

$$\Phi(x_1 \dots x_N) = \begin{vmatrix} \phi_1(x_1) & \dots & \phi_N(x_1) \\ \vdots & & \vdots \\ \phi_1(x_N) & \dots & \phi_N(x_N) \end{vmatrix}. \quad (2.13)$$

The latter, CI, involves minimization over a sum of different N-particle Slater determinants. The space of many-particle wave-functions is spanned by a series of Slater determinants, and the exact wave-function can be expressed exactly this way. But since the number of Slater determinants can often be large, this scheme is only useful for small systems.

DFT relies on the variational principle, but in a different way as we will see in the next section.

### 2.3 The Hohenberg-Kohn Theorem

The traditional way to solve the ground-state electronic structure problem goes as follows. Start with an external potential and solve Eq. (2.1) to get the wave-function. Then, use the wave-function to find the electron density or other interesting properties. Schematically, this is as follows:

$$V_{ext} \rightarrow \Psi_{Many-body} \rightarrow n. \quad (2.14)$$

The problem is that the many-body wave-function is hard to get and difficult to handle for even small numbers of electrons.

Density functional theory starts with the observation that the wave-function and all physical properties derived from it are uniquely characterized by the ground-state density. The map between external potential and the electron density is both unique and one-to-one:

$$n \leftrightarrow V_{ext}. \quad (2.15)$$

There are some caveats about systems with degenerate ground-states, and we will assume in what follows that the ground-state is non-degenerate. As before in Eq (2.14), the potential still determines the wave-function; but since the potential is determined by the density, it follows that all derived quantities can be written as

functionals of the density. In practice, writing everything in terms of the density might not be so simple to do, but theoretically it is possible.

The proof is by *reductio ab absurdum* [20]. Suppose that we have two different external potentials that each yield the same ground-state density. By different, we mean that the potentials differ by more than a constant. The two potentials will have different ground-state wave-functions. Now, we use the variational principle. If we use the ground-state wave-function for one of the potentials as a trial wave-function for the other, we find the inequality,

$$\langle \Psi_2 | \hat{T} + \hat{V}_{ee} + \hat{V}_{ext,1} | \Psi_2 \rangle > \langle \Psi_1 | \hat{T} + \hat{V}_{ee} + \hat{V}_{ext,1} | \Psi_1 \rangle. \quad (2.16)$$

Notice that this is an inequality. The equality can only be satisfied if both wave-functions are the same, and we had assumed this not to be true. The last term on both sides of Eq. (2.16) is equal since we assume that both wave-functions have the same density;

$$\langle \Psi_{1,2} | \hat{V}_{ext} | \Psi_{1,2} \rangle = \int d^3r n(\mathbf{r}) v_{ext}(\mathbf{r}) \quad (2.17)$$

If we cancel the terms like Eq. (2.17) in Eq. (2.16), we find

$$\langle \Psi_2 | \hat{T} + \hat{V}_{ee} | \Psi_2 \rangle > \langle \Psi_1 | \hat{T} + \hat{V}_{ee} | \Psi_1 \rangle. \quad (2.18)$$

Next, we repeat this but use the other wave-function as a trial wave-function for the first potential. We find

$$\langle \Psi_2 | \hat{T} + \hat{V}_{ee} | \Psi_2 \rangle < \langle \Psi_1 | \hat{T} + \hat{V}_{ee} | \Psi_1 \rangle. \quad (2.19)$$

Both 2.18 and 2.19 cannot be satisfied simultaneously. That means that no two different potentials can yield the same density. One potential is uniquely related to one density, and conversely, the potential is uniquely determined by the density.

## 2.4 Levy-Constrained Search Proof

Another and perhaps more intuitive proof that the density uniquely characterizes a system comes from the Levy constrained search proof [37]. We rewrite the

variation principle, Eq. (2.9), for the total energy in two steps,

$$E[n] = \min_n \left[ F[n] + \int d\mathbf{r} \hat{v}(\mathbf{r}) n(\mathbf{r}) \right] \quad (2.20)$$

where the minimization is over all  $N$ -particle density-distributions, and

$$F[n] = \min_{\Psi \rightarrow n} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle \quad (2.21)$$

where the minimization is over all many-body wave-functions,  $\Psi$ , that yield the density,  $n$ .  $F[n]$  does not depend on the form of the external potential. It is a universal functional of the density! That means that one well-chosen approximation for  $F[n]$  should give accurate results for a large class of external potentials.

We can explicitly recover the potential from the density by minimizing Eq. (2.20) with the constraint that the density integrates up to a fixed number of electrons.

$$\delta \left\{ F[n] + \int d^3r n(\mathbf{r}) v_{\text{ext}}(\mathbf{r}) - \mu \int d^3r n(\mathbf{r}) \right\} = 0. \quad (2.22)$$

The result is

$$v_{\text{ext}}(\mathbf{r}) = \mu - \frac{\delta F[n]}{\delta n(\mathbf{r})}, \quad (2.23)$$

the external potential as a functional of the density.

Solving this Eq. (2.22) would be equivalent to solving the many-particle Schrödinger equation if we have an accurate approximation for  $F[n]$ . Note that this, unlike Eq. (2.1), is an equation in one variable with only three components!

In DFT, the total energy is expressed as a functional of the density:

$$E[n] = T[n] + V_{ee}[n] + \int d\mathbf{r} v_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) \quad (2.24)$$

where we split  $F[n]$  into kinetic,  $T[n]$ , and interaction parts,  $V_{ee}[n]$ .

## 2.5 Thomas-Fermi Theory

The first and simplest DFT was conceived in the early days of modern quantum mechanics. Thomas and Fermi wrote the total energy of an electron system as a pure functional of the density [16, 17],

$$E[n] = T_{TF}[n] + U_H[n] + \int d^3r n(\mathbf{r}) v_{\text{ext}}(\mathbf{r}) \quad (2.25)$$

with

$$T_{TF}[n] = \frac{3}{10}(2\pi^2)^{\frac{2}{3}} \int d^3r n^{\frac{5}{3}}(\mathbf{r}) \quad (2.26)$$

taken from the kinetic energy of a uniform non-interacting electron gas and with the next term being the classical Hartree term,

$$U_H[n] = \frac{1}{2} \int d^3\mathbf{r} \int d^3\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \quad (2.27)$$

Eq. (2.25) for the total energy can be minimized with respect to the density and solved for a variety of external potentials. For most applications, this approximation is not accurate enough because it fails to describe most quantum mechanical effects accurately. The majority of this inaccuracy comes from the way the kinetic energy is treated fully locally.

## 2.6 The Non-Interacting Kohn-Sham System

In practice, most DFT calculations rely on the analysis of a non-interacting counterpart to the interacting system [21]. The main idea is, instead of using the kinetic energy of a uniform electron gas, Eq (2.26), to use

$$T_s[n] = \min_{\phi_s \rightarrow n} \langle \phi_s | \hat{T} | \phi_s \rangle. \quad (2.28)$$

where  $\phi_s$  is a Slater determinant of single-particle orbitals, and the minimization is over all determinants that give the density  $n$ . This is the exact kinetic energy of a system of non-interacting electrons with a certain density.

The remainder of  $F[n]$  is the classical Hartree contribution and  $E_{\text{xc}}[n]$  which is everything left over. The total energy is

$$E[n] = T_{\text{s}}[n] + U[n] + E_{\text{xc}}[n] + \int d^3\mathbf{r} v_{\text{ext}}(\mathbf{r})n(\mathbf{r}). \quad (2.29)$$

Performing the Euler-Lagrange variation and constraining the particle number gives the Kohn-Sham equation,

$$v_{\text{KS}}(\mathbf{r}) = \mu - \frac{\delta T_{\text{s}}[n]}{\delta n(\mathbf{r})}. \quad (2.30)$$

Solving Eq. (2.30) is equivalent to solving

$$\left(-\frac{1}{2}\nabla^2 + v_{\text{KS}}([n]; \mathbf{r})\right) \phi_{i,\sigma}(\mathbf{r}) = \epsilon_{i,\sigma} \phi_{i,\sigma}(\mathbf{r}). \quad (2.31)$$

for the Kohn-Sham (KS) orbitals in the local multiplicative KS potential,

$$v_{\text{KS}}(\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + \frac{\delta U[n]}{\delta n(\mathbf{r})} + \frac{\delta E_{\text{xc}}[n]}{\delta n(\mathbf{r})}. \quad (2.32)$$

To get the density, we simply sum the contributions from the occupied KS orbitals,

$$n(\mathbf{r}) = \sum_i \theta(\mu - \epsilon_i) |\phi_i(\mathbf{r})|^2 \quad (2.33)$$

If the  $E_{\text{xc}}$  used in the calculation is exact, this density that comes out is also exact.

The Kohn-Sham equation, Eq. (2.31), must be solved using a self-consistent scheme. That is an initial guess for the density is made and a KS potential is constructed from it. The resulting KS equation is solved for the KS orbitals, and the orbitals are then used to find a new density. The new density gives a new potential and we calculate again. This procedure is reiterated until the density changes less than some chosen criteria.

Analysis of this KS system can then be used to give information about the interacting system. For example, the total energy is related to the density and the KS eigenvalues through

$$E[n] = \sum_{\text{occ.}} \epsilon_{\text{KS}} + U[n] + E_{\text{xc}}[n] - \int d^3\mathbf{r} v_{\text{H}}(\mathbf{r}) n(\mathbf{r}) - \int d^3\mathbf{r} v_{\text{xc}}(\mathbf{r}) n(\mathbf{r}). \quad (2.34)$$

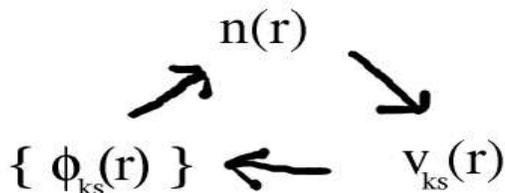


Figure 2.1: Kohn-Sham Self-Consistent Cycle shown Schematically

In this KS approach, a large portion of the total energy, the kinetic contribution, is treated exactly for a system of non-interacting electrons. It is important to note that the KS wave-function is not an approximation to the exact wave-function. In KS theory, only  $E_{\text{xc}}$  must be approximated, and this turns out to be amenable to local and semi-local approximations.

Is it true that for every interacting ground-state problem we can find this non-interacting counterpart? Two formal problems are the questions of N- and V-representability. A density is N-representable if it can be obtained from some N particle wave-function [68, 69]. A density is V-representable if it can be obtained from the ground-state wave-function for a local external potential. The former problem has been solved [37, 70, 71, 72], but the latter remains unsolved [37].

The problem of inverting the KS equation and finding the potential from the density, Eq. (2.30), has also been considered [73, 74, 75].

Incidentally, DFT is valid beyond fixed-nuclei approximation. A quantum mechanical description of the physics beyond the fixed-nuclei approximation is given by multi-component DFT [76].

## 2.7 The Exchange Correlation Energy, Nature's Glue

The exchange-correlation energy is sometimes referred to as *nature's glue* [77] because it is responsible for keeping much of matter together by counter-acting some of the Coulomb repulsion. If nature only kept the classical interaction energy, the

System	$E_{tot}$	$T_s$	$V_{ext}$	$U_H$	$E_x$	$E_C$
H	-0.500	0.500	-0.687	0.313	-0.313	0.000
He	-2.904	2.000	-2.867	2.049	-1.025	-0.042
Be	-14.664	14.588	-33.703	7.217	-2.673	-0.093
Ne	-128.926	128.63	-311.15	66.086	-12.49	-0.002?
Hooke's Atom, k=1/4	2.000	0.635	0.8881	0.5160?	-0.515	-0.039

Table 2.1: Components of the total energy for atoms. The results are from a combination of calculations and comparisons to experimental data [143, 128, 73, 130].  $E_{tot}$  is the total ground-state energy of the system,  $T_s$  is the non-interacting kinetic energy contribution,  $V_{ext}$  is the contribution from the external potential,  $U_H$  is the Hartree contribution,  $E_x$  is the exchange contribution, and  $E_C$  is the correlation contribution.

Hartree term, then chemical bonds would be weaker and longer. The exchange-correlation contribution reduces the interaction energy because it accounts for the tendency of electrons not to collide.

As mentioned earlier, the total energy is often expressed as a functional of the density Eq. (2.24). To give a rough idea of the relative magnitudes of the various components of the energy, we present Table 2.1. The listed values are not all highly accurate and are shown just to give the reader an idea of the orders of magnitude of the energy contributions.

Because of the demand for ever-increasing accuracy in industry and the unmet demands of thermo-chemistry, finding more accurate approximations to this exchange-correlation energy is an important area of research.

## 2.8 Jacob's Ladder of Approximations

John Perdew has classified the ever increasing detail, accuracy, and cost of density functionals according to a biblical analogy. Most popular functionals fall one way or another into this scheme. This is Jacob's ladder of approximations. Chemical accuracy is on top. [78]. Each rung preserves the formal, exact properties of the

lower rungs.

- The local density approximation (LDA).

The lowest rung of the ladder is LDA,

$$E_{\text{xc}}^{\text{LSD}}[n_{\uparrow}, n_{\downarrow}] = \int d^3r n(\mathbf{r}) \epsilon_{\text{xc}}(n_{\uparrow}(\mathbf{r}), n_{\downarrow}(\mathbf{r})). \quad (2.35)$$

The idea is that at each point in a molecule or solid, an electron experiences the same effect from the surrounding electrons as if the electronic density were uniform and equal to the density where the affected electron is. The total interaction energy would then be an integral over all local contributions. The local energy per particle comes from the exact, known, and parameterized exchange-correlation energy of a uniform gas for the exchange correlation energy density at each point in space [21].

The LDA is correct for at least one physical system, the uniform gas, and satisfies many exact constraints [79, 80]. It is accurate for uniform and slowly varying densities and is useful in solid-state physics. Because of its simplicity, this functional is perhaps the most reliable.

A sketch of how the LDA is constructed starts with the exact ground-state energy of a uniform system. Jellium is this system. The exact ground-state energy of the uniform Fermion gas in three dimensions as a function of the electronic density in the high-density limit is [24]

$$\lim_{r_s \rightarrow 0} \left( \frac{E}{N} \right) = \left[ \frac{2.21}{r_s^2} - \frac{0.916}{r_s} + 0.0622 \ln r_s - 0.096 + \mathcal{O}(r_s) \right] \quad (2.36)$$

with

$$r_s = \left( \frac{3}{4\pi n} \right)^{\frac{1}{3}}. \quad (2.37)$$

The first term is the kinetic contribution. The next is the exchange contribution. And the remainder is the correlation contribution. The idea of the LDA is to take the last terms to get the exchange-correlation energy per particle and to use this in the functional, Eq. (2.35).

The ground-state energy of Jellium is known through analytic forms for the high and low density limits and Monte Carlo calculations for intermediate densities [25]. Accurate parameterizations of the entire energy versus density curve have been constructed and are in use [35].

LDA tends to over-emphasize metallic character. In LDA, weak bonds like hydrogen bonds are over-estimated.

- The generalized gradient approximation (GGA).

A naïve gradient expansion about the local-density approximation is problematic [21, 20], but careful considerations lead to the generalized gradient approximations [32, 81, 36],

$$E_{\text{xc}}^{\text{GGA}}[n_{\uparrow}, n_{\downarrow}] = \int d^3r n(\mathbf{r}) \epsilon_{\text{xc}}(n_{\uparrow}, n_{\downarrow}, \nabla n_{\uparrow}, \nabla n_{\downarrow}). \quad (2.38)$$

GGA's preserve many of the exact features of LDA and provide results which are good for chemistry as well as solid-state physics.

- The meta generalized gradient approximation (meta-GGA).

The next rung is the meta-GGA [82],

$$E_{\text{xc}}^{\text{Meta-GGA}}[n_{\uparrow}, n_{\downarrow}] = \int d^3r n(\mathbf{r}) \epsilon_{\text{xc}}(n_{\uparrow}, n_{\downarrow}, \nabla n_{\uparrow}, \nabla n_{\downarrow}, \tau_{\uparrow}, \tau_{\downarrow}), \quad (2.39)$$

which depends on the KS kinetic energy density,

$$\tau = \sum_{\epsilon_i < \mu} \frac{1}{2} |\nabla \phi_i(\mathbf{r})|^2. \quad (2.40)$$

The Meta-GGA is more accurate than the GGA for slowly varying or one-electron densities. Meta-GGA's are becoming implementable in quantum chemistry.

For the first two rungs, the functional derivative yielding the exchange-correlation potential,

$$v_{\text{xc}}(n; \mathbf{r}) = \frac{\delta E_{\text{xc}}[n]}{\delta n(\mathbf{r})}, \quad (2.41)$$

can be done analytically and before the calculation. It is less obvious how to take the functional derivatives with respect to  $\tau$ . However, there are ways around this problem [83, 84].

- Orbital functions of the occupied KS orbitals, Hyper-GGA's.

Each step up Jacob's ladder brings more accuracy but also more computational cost. The next rung, orbital functionals of the first type,

$$E_{\text{xc}}^{\text{Orb.I}}[n_{\uparrow}, n_{\downarrow}] = E_{\text{xc}}^{\text{Orb.I}}[\phi_{\text{KS}\uparrow}^{\text{Occ.}}\{n_{\uparrow}\}, \phi_{\text{KS}\downarrow}^{\text{Occ.}}\{n_{\downarrow}\}], \quad (2.42)$$

depend on the occupied KS orbitals [86]. Orbitals are implicit functions of the density so that these functionals are still density functionals. Orbital functionals are considerably more expensive to implement self-consistently; however, the non-interacting kinetic energy is a functional of the occupied KS orbitals, and the approximate KS orbitals result from any self-consistent lower-rung calculation. Consequently, using this rung as an augment to a lower rung calculation does not consume significantly more computer time and resources.

A side step from this rung is the idea of a hybrid functional [42, 85, 59],

$$E_{\text{xc}}^{\text{Hybrid}}[n_{\uparrow}, n_{\downarrow}] = (1 - b)E_{\text{xc}}^{\text{GGA}}[n_{\uparrow}, n_{\downarrow}] + bE_{\text{xc}}^{\text{Orb}}[\phi_{\text{KS}\uparrow}, \phi_{\text{KS}\downarrow}]. \quad (2.43)$$

These are popular in chemistry for their accuracy and are appearing in solid-state physics [39]. The understanding of why they work is related to the adiabatic connection which we will discuss later [87].

- Orbital functions of the unoccupied KS orbitals.

The second generation of orbital functionals,

$$E_{\text{xc}}^{\text{Orb.II}}[n_{\uparrow}, n_{\downarrow}] = E_{\text{xc}}^{\text{Orb.II}}[\phi_{\text{KS}\uparrow}\{n_{\uparrow}\}, \phi_{\text{KS}\downarrow}\{n_{\downarrow}\}], \quad (2.44)$$

includes the unoccupied non-interacting KS orbitals [88]. This rung can describe  $E_{\text{xc}}$  exactly in principle but is extremely difficult to implement

since there are an infinite number of unoccupied orbitals. As an example of a second generation orbital functional, we present the Interaction Strength Interpolation (ISI) functional. This function will be discussed in more detail in Chapter 5.

There are other approaches outside the ladder of approximations. One example is self-interaction corrected DFT which ensures that DFT correctly describes one-electron systems and the long-range physics. Another, weighted density theory, uses the density only explicitly and approximates the pair correlation.

Rung	$E_x$	$E_C$	Atom.En.	Bonds	Structures	Energy Barriers
LSD	5%	0.5%	1.5 eV	1% short	Close Packing	100%
GGA	100%	5%	0.4 eV	1% long	Correct	30%

Table 2.2: Typical errors for two different rungs of functionals as transcribed from John Perdew’s lecture notes from the DFT Summer School at Caramulo, Portugal, 2001. Atom. En. refers to atomization energies, which is the energy required to split a molecule to the individual atoms. Bonds refers to bond lengths. Structures refers to the most stable lattice structure. Energy barriers refer to the energy of a transition state.

## 2.9 Exact Constraints on the Exchange-Correlation Functional

The systematic way to climb Jacob’s Ladder and to improve approximations is by imposing exact constraints on approximate functionals. One of the most basic exact constraints is that

$$E_{xc}[n] \leq 0. \tag{2.45}$$

Other examples of exact constraints include the Lieb-Oxford bound [89], electron hole properties [90, 91, 92], sum rules [81], satisfaction of the virial theorem [93], and proper behavior under uniform scaling laws [93]. An example of how exact

constraints have been used to find better functionals has been the imposition of the exchange sum rule on gradient expansion functionals to give the more accurate generalized gradient functionals.

A review of several known constraints and which functionals obey them is available [94]. We will consider the last of these in more detail in Chapter 4.

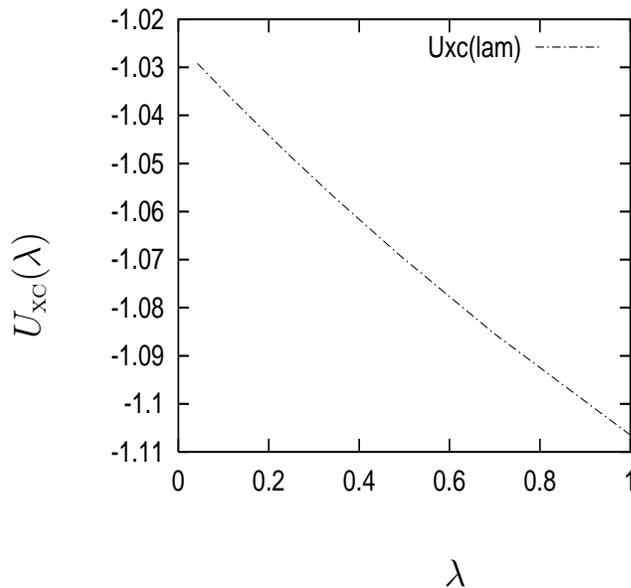


Figure 2.2: The Adiabatic Connection for Helium

Another useful construct is the adiabatic connection. Formally, we can express the unknown exchange-correlation functional as

$$E_{xc}[n] = \int_0^1 d\lambda \left( \langle \Psi_n^{min,\lambda} | \hat{V}_{ee} | \Psi_n^{min,\lambda} \rangle - U[n] \right) = \int_0^1 d\lambda U_{xc}(\lambda), \quad (2.46)$$

where  $\Psi_n^{min,\lambda}$  is the wave-function that minimizes  $\langle \Psi | \hat{T}_s + \lambda \hat{V}_{ee} | \Psi \rangle$  and gives electron density,  $n$ , and  $U_{xc}(\lambda)$  is exchange-correlation potential contribution.

Figure 2.2 shows the adiabatic connection curve for He. The area between the curve and the y-axis is the exchange-correlation energy. The weak interaction limit of the curve is the exchange contribution to this functional. Analysis for the shape of this curve has given insights into the accuracy of approximate functionals.

We will examine this in more detail in Chapter 5.

## 2.10 Cornerstones of a Density Functional Theory

We have seen so far the importance of density functional theory and the need to understand and approximate the exchange-correlation energy in accurate but practical ways. The body of this thesis will be dedicated to understanding the exchange correlation energy functional at a fundamental level. This thesis is entitled, *Adiabatic Connection and Uniform Density Scaling: Cornerstones of a Density Functional Theory*, because it will emphasize how important scaling laws and the adiabatic connection formula are to the understanding of DFT.

We will start by introducing and analyzing a contact interaction in Chapter 3. In developing a density functional theory for this interaction, we will show what kind of general considerations go into functional construction. In particular, we will see that a fairly accurate representation of the local density functional can be obtained by simply applying scaling arguments to a uniform system. We will explore the analogs of some Coulomb-interacting theorems but to get an idea of what exact constraints are useful in functional construction. In particular, we will argue that a good parametrization to the LDA can be improved by ensuring that the high density limit is properly satisfied.

In chapter 4, we focus on the chemically interesting three-dimensional problem. We recall how uniform density scaling laws can be used to check and to improve approximations. We note that many of these scaling laws can be generalized to the case of spin DFT. Perhaps, requiring that functionals obey many of these spin scaling laws will allow for more accurate treatment of magnetic systems.

Scaling is intimately tied with the adiabatic connection. Chapter 5 gives a detailed analysis of how the Adiabatic Connection can lead to more accurate functionals. In particular, we explore what happens when the electron-electron

interaction becomes infinitely strong. We use a model system and a clever manipulation of scaling laws to test several hypotheses about this limit. This chapter ties in with the general theme of the thesis through the use of the adiabatic connection to create new functionals and to test theoretical models.

Another way to construct functionals from the adiabatic connection is to start with just the small  $\lambda$  limit. Considering DFT from this limit provides a systematic way to understand functional development in DFT. For example, analysis of this limit explains why hybrid functionals are so accurate. We choose to start from this limit to consider another fundamental question in DFT. Should DFT describe the fundamental band gap for a solid.

## Chapter 3

# A Simple Example: Density Functional Theory for a One-Dimensional Contact Interaction

Three-dimensional electronic structure calculations are enormously complicated endeavors. It is helpful and insightful to focus on the underlying ideas of a density functional theory with as few complications as possible. To get an idea of what DFT is, how it works, and what considerations go into approximate functional development, we will introduce a one-dimensional analogue of the Coulomb interaction. We will find a local-density functional for the exchange and correlation energies and explore some one-dimensional systems like the analogue of Helium and the Hooke's atom.

### 3.1 One-Dimensional Delta-Function Models

Density functional theory is typically applied to Coulomb interacting fermions in three dimensions, but the Hohenberg-Kohn theorem holds for other interactions types and in other dimensions. We propose to consider the delta-function interaction in one spatial dimension,

$$v_{ee}(x_i - x_j) = \lambda \delta(x_i - x_j), \quad (3.1)$$

where  $x_i$  and  $x_j$  represent the spatial coordinates of the fermions, which have two spin-labels, and  $\lambda$  is the interaction strength. The exchange-correlation functional will differ from the three-dimensional Coulomb case. The delta-function

interaction scales like the Coulomb one, but is short-ranged. Note that although the interaction itself is short-ranged, the effective interaction need not be. The effective longer range comes from second order interactions.

One-dimensional models are important for several reasons. Perhaps, most obviously, they are useful in mathematical and statistical physics to illustrate problems and concepts that are sometimes hard to conceptualize in three dimensions.

Our motivation, however, is to use this one-dimensional model to understand density functional theory. Although the functional will be different, many of the formal properties of the unknown exchange-correlation functional will still hold. Most of the general problems should persist as well. Solving these problems for delta-function DFT could lead to solutions of the same problems in three-dimensional DFT. For example, this one-dimensional LDA could be used to look at the one-dimensional solid and transport through that solid. Or it could be used to study the analog of stretched  $H_2$ . Delta-function models have already been used to study problems in DFT but without the inclusion of any correlation effects [95]. Using DFT to study non-Coulombic interactions is an exciting area of current research. For example, Capelle et Al. have used DFT to study the Hubbard model [96, 97].

Finally, it has been suggested that delta-function models should give a good representation of the physics of one-dimensional fermions in certain experimental contexts [98, 99, 100, 101]. Examples of such systems are semi-conductor quantum wires, conducting organic materials, and carbon nano-tubes. So, the density functional analysis will be directly useful in modeling one-dimensional physics.

### 3.2 Exact-Exchange Density Functional

In this section, we will see that the Hartree-Fock contribution to the total energy is a local density functional so that delta-interacting Hartree-Fock is actually exact-exchange DFT.

The one-dimensional fermions have two spin labels. Because of the anti-symmetry of the wave-function under particle interchange, particles with like spin-labels will never be found at the same point in space and, consequently, will not experience the delta-function interaction between each other. Only opposite spins will interact directly.

The Hartree term depends only on the total electron density,

$$U_H[n] = \frac{1}{2} \int dx dx' n(x) \lambda \delta(x - x') n(x') = \frac{\lambda}{2} \int dx n(x)^2. \quad (3.2)$$

There is overcounting here because like spins should not interact via the delta function. The exchange term must cancel these spurious like-spin interactions. A simple functional which would do this is

$$E_X[n_\uparrow, n_\downarrow] = -\frac{\lambda}{2} \int dx (n_\uparrow(x)^2 + n_\downarrow(x)^2), \quad (3.3)$$

and this can be derived using the standard rules of many-body perturbation theory [102]. To simplify the notation, let

$$\zeta(x) = \frac{n_\uparrow(x) - n_\downarrow(x)}{n_\downarrow(x) + n_\uparrow(x)}. \quad (3.4)$$

Then, the exact-exchange functional is

$$E_X[n, \zeta] = -\frac{\lambda}{2} \int dx n(x)^2 (1 + \zeta(x)^2)/2. \quad (3.5)$$

For a one-electron system, we have  $E_X[n] = -U_H[n]$ , and exact-exchange is self-interaction free.

### 3.3 Deltium: The One-Dimensional Uniform Fermi Gas

In order to obtain a local density correlation functional, we will consider the exact results for the one-dimensional unpolarized Fermi gas. This Fermi gas will play the role of the uniform electron gas in Coulomb-interacting DFT. The Hamiltonian is

$$\hat{H} = -\frac{1}{2} \sum_i^N \frac{d^2}{dx_i^2} + \lambda \sum_{i < j} \delta(x_i - x_j) \quad (3.6)$$

This system has been considered previously [103, 104, 105, 106]. As noted in the previous section 3.2, the like spins will not be affected by the interaction, and the polarized gas will resemble the non-interacting uniform polarized gas. Thus, we need only find the correlation functional for the unpolarized case.

Let us review the non-interacting case,  $\lambda = 0$ , first. The many-body wavefunction solutions of Eq. (3.6) is a Slater determinant of  $N$  plane-waves with two spin-labels. The allowed momentum for the plane-waves are quantized by periodic boundary conditions. The total energy per particle of the non-interacting gas is purely kinetic,

$$t_s[n] = \frac{\pi^2}{24} n^2. \quad (3.7)$$

When interactions are present, the total energy per particle is

$$\epsilon[n] = t_s[n] + \epsilon_H[n] + \epsilon_X[n] + \epsilon_C[n], \quad (3.8)$$

where  $\epsilon_{\hat{H}}[n]$  is the Hartree energy per particle,  $\epsilon_X[n]$  is the exchange energy per particle, and  $\epsilon_C[n]$  is the correlation energy per particle.

The eigenvalue problem, Eq (3.6) with  $\lambda \neq 0$ , is also exactly solvable via Bethe Ansatz methods [107, 108, 109, 110]. The technique is to guess a wave-function of the form,

$$\Psi(x_1, x_2, \dots, x_N) = \sum_P a_P e^{ik_{P_1}x_1 + \dots + ik_{P_N}x_N}, \quad (3.9)$$

where  $a_P$  is an amplitude that depends on the ordering,  $P$ , of momenta,  $k_i$ 's, for a particular Weyl chamber. A Weyl chamber means an ordering of coordinates:  $0 < x_1 < x_2 < \dots < x_N < L$ . Particle interchange symmetries can be used to construct the wave-function in other Weyl chambers. The wave-function is everywhere continuous, but its derivative is discontinuous at the boundary between Weyl chambers:

$$\left[ \frac{\partial \Psi(x_1, x_2, \dots, x_N)}{\partial x_i} - \frac{\partial \Psi(x_1, x_2, \dots, x_N)}{\partial x_{i+1}} \right]_{x_i=x_{i+1}} = \lambda \Psi(x_i). \quad (3.10)$$

In order to satisfy continuity and derivative discontinuity, the  $a_P$  and the  $k_i$ 's are related via Yang-Baxter relationships [111]. For the uniform Fermi gas, the situation is a bit more difficult because of the two spin-types.

Nevertheless, with some careful book keeping [111], the uniform Fermi gas problem can be recast as a set of integral equations [112]:

$$\tau(x) = \frac{1}{2\pi} + \frac{2}{\pi} \int_{-\infty}^{\infty} d\Lambda \frac{\lambda \sigma(\Lambda)}{\lambda^2 + 4(x - \Lambda)^2} \quad (3.11)$$

and

$$\sigma(\Lambda) = \frac{1}{2\lambda} \int_{-\infty}^{\infty} dx \operatorname{sech}(\pi/\lambda(x - \Lambda)) \tau(x). \quad (3.12)$$

Equations (3.11) and (3.12) must be solved self-consistently for chosen value of  $k_{max}$  to obtain the ground state energy for the delta-function interacting uniform Fermi gas. In order to do this, the integrals are transformed to the interval,  $[-1, 1]$ , and integrated using six-point quadrature rules. Once  $\tau$  is known, we can find the density and energy per particle. The density is

$$n = \int_{-k_{max}}^{k_{max}} dx \tau(x), \quad (3.13)$$

and the energy per particle is

$$\epsilon = \frac{1}{2n} \int_{-k_{max}}^{k_{max}} dx x^2 \tau(x). \quad (3.14)$$

The energy per particle for a wide range of densities could, in the spirit of the three-dimensional, be parameterized in a way that would be useful for actual calculations.

We will consider both the high and low-density limits analytically and numerically. Since we are concerned with parameterizing a functional for correlation, we will subtract out the known kinetic, Hartree, and exchange contributions, and focus on the correlation part.

The forms in both limits come from a combination of dimensional analysis and examination of the exact Bethe Ansatz results. We find the coefficients by fitting  $e(n)$  to a fourth order polynomial in either  $n$  or  $1/n$  depending on whether we want the low-density or high-density limits and by extracting the appropriate coefficients from the interpolations.

In the high-density limit, the correlation energy per particle is

$$\epsilon_c[n] = -c_H \lambda^2 + \dots \quad (3.15)$$

with  $c_2^H = 0.042$ . As we will see in Chapter 5, there is a relationship between scaling and coupling constant changes. Looking at a system with a high electron density is equivalent to considering a moderate-density system with a small interaction. In fact, in the high-density limit, the interaction energy is of the form of a perturbation in  $\lambda$ .

In the low-density limit, the correlation energy per particle is

$$\epsilon_c[n] = -\frac{\lambda}{4}n + \frac{\pi^2}{8}n^2 - \frac{c_L}{\lambda}n^3 + \dots \quad (3.16)$$

with  $c_2^L = 4.6$ . Notice that the first term in Eq. (3.16) will exactly cancel the Hartree and exchange parts. By the converse argument, the low-density limit is the large  $\lambda$  limit. In this limit, the opposite-spin Fermions repel each other so strongly that the interaction mimics Fermi-anti-symmetrization. Thus, the

interaction energy per particle is kinetic-like and independent of  $\lambda$  in the first term.

### 3.4 A Local-Density Correlation Functional

A simple parameterization of the correlation energy per particle is

$$\epsilon_C^{simple}[n] \approx \frac{-\lambda^2}{2\pi^2} \left( \frac{n^2}{n + \frac{2\lambda}{\pi^2}} \right). \quad (3.17)$$

This approximation gives the first two terms of the low density limit correctly, and the next term approximately. The high density limit is reproduced only approximately. For the parameterization, the first order coefficients are  $c_2^L = \pi^4/16 = 6.088$  in the low density limit and  $c_2^H = 1/2\pi^2 = 0.05$  in the high density limit. Although these terms are not exactly described by the parametrization, the entire curve is well-described. The parametrization has a maximum error of 19 % for  $\epsilon_C$  as  $n \rightarrow \infty$ .

We can write an approximate correlation energy LDA functional for the unpolarized case,

$$E_C^{LDA,simple}[n] \approx -\frac{\lambda^2}{2\pi^2} \int dx \frac{n^2(x)}{n(x) + \frac{2\lambda}{\pi^2}}. \quad (3.18)$$

Regions with more electron density will contribute more to the total energy. Therefore, it is important that the parametrization of the LDA reproduce the high density limit correctly. We can do this in several ways. A simple solution is to add a correction to the parametrization which dies down as the density is smaller. This parametrization of the LDA correlation energy per particle is then

$$\epsilon_C[n] \approx \frac{-\lambda^2}{2\pi^2} \left( \frac{n}{n + \frac{2\lambda}{\pi^2}} \right) \left( 0.829 + (1 - 0.829)e^{-10/\lambda^2 n^2} \right). \quad (3.19)$$

When  $n \rightarrow \infty$ , we find  $\epsilon_C[n] = 0.829\epsilon_C^{simple}[n]$ . The pre-factor,  $c_H/c_H^2 = 0.829$ , ensures that the high-density limit is satisfied. In the low density limit, this

reduces to Eq. (3.17) exponentially fast. The gaussian and factor of 10 are chosen to ensure that the connection between both limits is smooth. A more sophisticated parametrization is possible, but this one is smooth and reproduces between 99-102% of the correlation energy per particle for all densities. This accuracy is sufficient for our purposes. This parametrization can be used in a local density correlation functional,

$$E_C^{LDA}[n] \approx -\frac{\lambda^2}{2\pi^2} \int dx \frac{n^2(x)}{n(x) + \frac{2\lambda}{\pi^2}} \left(0.829 + (1 - 0.829)e^{-10/\lambda^2 n(x)^2}\right). \quad (3.20)$$

In the fully polarized case, there is no interaction contribution to the total energy, and the correlation energy functional is trivially

$$E_C^{LDA}[n] = 0. \quad (3.21)$$

We note here that the local density correlation potential is

$$\begin{aligned} v_C(x) = \frac{\delta E_C^{LDA}[n]}{\delta n(x)} = & -\frac{\lambda^2}{2\pi^2} \frac{n^2(x) + \frac{2\lambda}{\pi^2}}{\left(n(x) + \frac{2\lambda}{\pi^2}\right)^2} \left(0.829 + (1 - 0.829)e^{-10/\lambda^2 n(x)^2}\right) \\ & + 20/\lambda^2 n(x) \frac{\lambda^2}{2\pi^2} \frac{n^2(x)}{n(x) + \frac{2\lambda}{\pi^2}} (1 - 0.829)e^{-10/\lambda^2 n(x)^2}. \end{aligned} \quad (3.22)$$

### 3.5 Diracium, the Delta-Function Interacting Analog of Helium

In order to assess the accuracy of the LDA to handle one-dimensional problems, we will start with perhaps the most difficult test case, a completely non-uniform system, Diracium. This is the one-dimensional analog of Helium with traditional Coulomb terms replaced by delta functions. The system is described by the Hamiltonian:

$$\hat{H} = -\frac{1}{2} \frac{d^2}{dx_1^2} - \frac{1}{2} \frac{d^2}{dx_2^2} - Z\delta(x_1) - Z\delta(x_2) + \lambda\delta(x_1 - x_2) \quad (3.23)$$

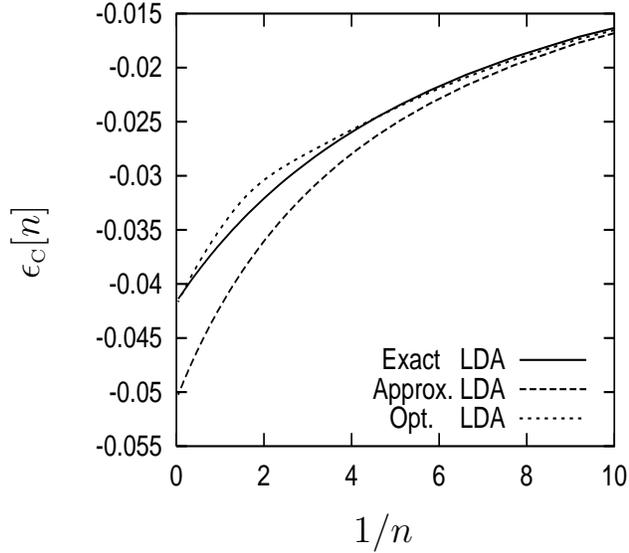


Figure 3.1: Correlation energy per particle for Deltium,  $\lambda = 1$ , the one-dimensional uniform delta-function-interacting Fermi gas. The long dashes are exact results calculated from the Bethe-Ansatz integral equations. The short dashes are a simple parametrization of these results.

and the eigenvalue equation,

$$\hat{H}\Psi_{\sigma\sigma'}(x_1, x_2) = E\Psi_{\sigma\sigma'}(x_1, x_2), \quad (3.24)$$

where  $x_1$  and  $x_2$  are the positions of the electrons,  $\sigma$  and  $\sigma'$  are the spin-like labels of the electrons,  $Z$  is the magnitude of the external potential, and  $\Psi$  is an antisymmetric Fermi wave-function. A similar Hamiltonian, two delta-interacting fermions in a box, was the study of Ref. [113].

The delta function admits only one bound state. If the fermions are polarized, then only one can occupy the well. In order to have a two-particle bound state, we must have the spins unpolarized. By comparing the situation to an exactly solvable one, it can be shown that there is only bound state for Eq. (3.24) [114].

We consider only the ground-state problem and leave the question of excited states for further work. First, we will solve the model analytically within the

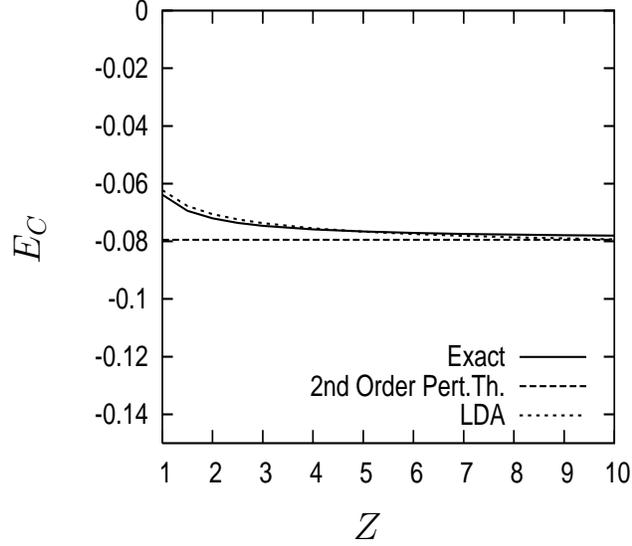


Figure 3.2: Correlation energy for Diracium,  $\lambda = 1$ , as obtained from  $E_C \approx E_{exact} - E_{exx}$ . The dashed line is second order perturbation theory, the bars line is LDA, and the solid line is exact.

exact-exchange approximation. Then, we solve with the local-density approximation to the correlation energy. Finally, we will present the exact energy eigenvalues.

### 3.6 Exact Exchange Treatment of Diracium

In exact exchange DFT, we write the total energy as a functional of the density,

$$E[n] = T_s[n] + U_H[n] + E_X[n] + \int dx v_{\text{ext}}(x) n(x) \quad (3.25)$$

We minimize with respect to  $n$ , and constrain

$$\int_{-\infty}^{\infty} dx n(x) dx = 1 = P[n]. \quad (3.26)$$

The Euler-Lagrange equation is

$$\frac{\delta E}{\delta n} - \mu \frac{\delta P[x]}{\delta n} = 0, \quad (3.27)$$

and we find

$$\left( -\frac{1}{2} \frac{d^2}{dx^2} - Z\delta(x) + \frac{\lambda}{2} v_{KS}(x) \right) \phi_{KS}(x) = \epsilon_{EXX} \phi_{KS}(x) \quad (3.28)$$

defining  $v_{KS} = \frac{\delta U_H}{\delta n(y)} + \frac{\delta E_X}{\delta n(y)} = n(y)$ . There is only one occupied KS orbital, and it is doubly occupied with one of each spin-type. The ground-state energy eigenvalue is

$$\epsilon_{EXX} = -\frac{1}{2} \left( Z - \frac{1}{2}\lambda \right)^2, \quad (3.29)$$

and the eigen-function is

$$\phi = \frac{1}{\sqrt{\lambda}} \left( Z - \frac{1}{2}\lambda \right) \operatorname{csch} \left[ \left( Z - \frac{1}{2}\lambda \right) |x| + \operatorname{arccoth} \left( \frac{Z}{Z - \frac{1}{2}\lambda} \right) \right]. \quad (3.30)$$

The total EXX energy is given by Eq. (2.34),

$$E_{EXX} = \sum \epsilon_{EXX} + U_H[n] + E_X[n] - \frac{1}{2}\lambda \int dx n^2(x). \quad (3.31)$$

The exact-exchange energy is thus

$$E_{EXX} = -Z^2 + \frac{Z\lambda}{2} - \frac{\lambda^2}{12} = -Z^2 \left( 1 - \frac{1}{2} \left( \frac{\lambda}{Z} \right) + \frac{1}{12} \left( \frac{\lambda}{Z} \right)^2 \right). \quad (3.32)$$

It is interesting to note that Eq. (3.28) is in fact the non-linear Schrödinger equation with a delta-function external potential. That means that the literature on Hartree-Fock solutions and the non-linear Schrödinger equation is really an approximate DFT method!

This solution of Eq. (3.28) was previously mentioned in astrophysics as a model for dense nuclear-matter in high magnetic fields [207]. It would be interesting to explore how density functional analysis of Diracium and Deltium could further that research.

### 3.7 The Local Density Correlation Treatment of Diracium

Now, we apply the local density approximation derived in Section 3.4. A rough approximation to the LDA correlation energy for Diracium can be gotten by plugging the exact-exchange density, derived from the orbitals Eq (3.30), into the simple LDA correlation functional, Eq. (3.33),

$$E_C^{LDA}(Z, \lambda) \approx -\frac{\lambda^2}{\pi^2}$$

$$+\frac{2\lambda^4}{\pi^4} \frac{\beta}{Z - \lambda/2} \left[ \arctan(\beta) - \arctan\left(\beta \frac{Z - \lambda/2}{Z}\right) \right] \quad (3.33)$$

with  $\beta = \sqrt{\lambda^3/(\pi^2(Z - \lambda/2)^2 - 1)}$ . Adding the LDA correlation to the EXX total energy generally improves the accuracy as well if not better than the self-consistent LDA.

The KS equation using in the local density approximation to the correlation is

$$-\frac{1}{2} \frac{d^2}{dx^2} \phi_{KS}(x) - Z\delta(x)\phi_{KS}(x) + \lambda|\phi_{KS}(x)|^2\phi_{KS}(x) + v_c(x)\phi_{KS}(x) = -\epsilon_{KS}\phi_{KS}(x). \quad (3.34)$$

We solved Eq. (3.34) numerically. First, we guess the eigenvalue and then integrate the Schroedinger equation (3.34) using the Numerov scheme [10]. The Numerov scheme solves differential equations of the form,

$$\ddot{x}(t) = f(t)x(t) \quad (3.35)$$

highly accurately by transforming to

$$w(t) = \left(1 - \frac{h^2}{12}f(t)\right)x(t) \quad (3.36)$$

and solving

$$w(h) + w(-h) - 2w(0) = h^2f(0)x(0) + \mathcal{O}(h^6). \quad (3.37)$$

When shooting, we start from the known exponential asymptotic form of the orbital and integrate toward the origin. We check to see how well the trial solution satisfies the derivative discontinuity required by the delta-function external potential and use this information to guess a new eigenvalue. Then, we shoot again. We repeat until the discontinuity is satisfied. With the valid wave-function, we create a density and start over. This is done until the density does not change appreciably between iterations and self-consistency is achieved.

In the low density limit, Eq. (3.34) remains bound. We can see this by expanding the KS potential in the low-density limit:

$$-\frac{1}{2} \frac{d^2}{dx^2} \phi_{KS}(x) - Z\delta(x)\phi_{KS}(x) + \frac{3}{8}\pi^2 \phi_{KS}(x) = -\epsilon_{KS}\phi_{KS}(x). \quad (3.38)$$

There is no explicit  $\lambda$  dependence in this equation. This is correct because the  $\lambda$  dependence is contained in the limit taken above, and the LDA is kinetic-like in this limit. The solution to Eq. (3.38) is:

$$\phi_{KS}(x) = N \sqrt{\operatorname{csch}\left(2\sqrt{2\epsilon}(x+x_0)\right)} \quad (3.39)$$

with

$$N = \left(2\frac{\epsilon}{\pi^2}\right)^{\frac{1}{4}} \quad (3.40)$$

and

$$x_0 = \frac{1}{2\sqrt{2\epsilon}} \operatorname{arccoth}\left(\frac{Z}{\sqrt{2\epsilon}}\right). \quad (3.41)$$

The negative of the KS eigenvalue is

$$\epsilon_{KS} = \frac{1}{2}Z^2 \operatorname{sech}^2 \pi = 0.00744195/2Z^2 \quad (3.42)$$

This approximation is an upper bound to the full LDA Hartree-Exchange correlation potential. Therefore, if the electron stays bound for all  $Z$  using this approximation, it would also stay bound for the full LDA potential. For small enough  $Z$ , this approximation will become reliable.

### 3.8 The Exact Solution of Diracium

The exact solution to Diracium is hard to come by. The simplest guess, a wave function which satisfies all the boundary conditions and satisfies the Schrödinger equation locally everywhere, just does not work. To see this try

$$\Psi(x_1, x_2) = N e^{-Z|x_1| - Z|x_2| + \frac{1}{2}\lambda|x_1 - x_2|}. \quad (3.43)$$

The normalization is

$$N = (2Z - \lambda) \sqrt{\frac{Z}{4Z - \lambda}} \quad (3.44)$$

The reason it does not work is that it does not give the same eigenvalue globally.

At best this is a variational wave-function and predicts an approximate energy,

$$E = -(2Z - \lambda)^2 \left( \frac{Z}{4Z - \lambda} \right) \left[ \frac{1}{2} + \frac{4Z^2 + \lambda^2}{4Z(2Z - \lambda)} \right] \quad (3.45)$$

Rosenthal first found the exact solution [114] transforming the problem to momentum space and reducing it to the solution of a one-dimensional integral equation. The real-space wave-function is the Fourier transform of the momentum space one,

$$\psi(x_1, x_2) = \frac{1}{2\pi^2} \int dk_1 dk_2 \left( \frac{F(k_1) + F(k_2) - \frac{\lambda}{Z} H(k_1 + k_2)}{k_1^2 + k_2^2 + p^2} \right) e^{-ik_1 x_1 - ik_2 x_2} \quad (3.46)$$

with  $E = -\frac{1}{2}Z^2 p^2$ ,

$$F(k) = \int dx \psi(x, 0) e^{ikx}, \quad (3.47)$$

and

$$H(k) = \int dx \psi(x, x) e^{ikx}. \quad (3.48)$$

$H(k)$  is related to  $F(k)$  through

$$H(k) = \left( \frac{\sqrt{2p^2 + k^2}}{\sqrt{2p^2 + k^2} - \lambda/(Z\pi)} \right) \frac{2}{\pi} \int dk' \frac{F(k')}{(k' - k)^2 + k'^2 + p^2}. \quad (3.49)$$

We find  $F(k)$  through the solution of the integral equation,

$$F(k)\phi(k) = \int_{-\infty}^{\infty} dx K(k, k') F(k') \quad (3.50)$$

with

$$\phi(k) = 1 - (k^2 + p^2)^{-\frac{1}{2}} \quad (3.51)$$

and

$$K(k, k') = \frac{1}{\pi} \frac{1}{k^2 + k'^2 + p^2} - \frac{2\lambda}{Z\pi} \int dk'' \left( \frac{1}{k^2 + (k - k'')^2 + p^2} \right) \left( \frac{1}{k'^2 + (k' - k'')^2 + p^2} \right) \left( \frac{(2p^2 + k''^2)^{\frac{1}{2}}}{(2p^2 + k''^2)^{\frac{1}{2}} + \lambda/Z} \right) \quad (3.52)$$

Let  $x = \frac{k}{k+1}$  and  $dx = x^2/k^2 dk$ , and use a Gauss-Legendre mesh with 20 points which is adequate for convergence. After discretizing space and replacing integration by a summation, we just need to solve a matrix equation,

$$\mu \mathbf{F} = \mathbf{K} \mathbf{F} \quad (3.53)$$

with  $\mu = 1$ . We guess  $p$ , solve the matrix problem, re-guess  $p$ , and repeat until  $\mu = 1$ .

Although the method converges quickly to the exact energy eigenvalue, it is not well-suited to give real space wave-functions and densities,

$$n(x) = \int dy \Psi^*(x, y) \Psi(x, y). \quad (3.54)$$

It is difficult to obtain the real-space density from this scheme since the limited sampling of points in  $k$ -space makes the Fourier transforms inaccurate. It would be nice to extract the exact density because we could consider how the density changes just as the system becomes ionized. It may be possible to obtain the density by solving the two dimensional Green's function problem with the exact  $p$  in an analogous way to scattering theory. This is currently under investigation.

Finally, we can use the virial theory to get the components of the energy  $T$  and  $V_{ee} + V_{ext}$ .  $V_{ee}$  and  $V_{ext}$  can be evaluated by solving  $k$  space integrals.

### 3.9 Comparison of the Diracium Results

In Table 3.1, we see that the LDA is greatly more accurate than the EXX functional and often more accurate than second order perturbation theory. Second

Z	Exact	LDA	EXX	2 Pert.
0.3	not bound	barely bound	not bound	-0.102793
0.377115	-0.71112592	-0.022954394	not bound	-0.11646054
0.5	-0.12928246	-0.117931436	not bound	-0.16279341
1	-0.64721014	-0.642029296	-0.583333	-0.66279341
2	-3.1553897	-3.15293417	-3.083333	-3.1627934
3	-7.6579478	-7.65692814	-7.583333	-7.6627934
4	-14.159193	-14.1590661	-14.08333	-14.162793
5	-22.659930	-22.6604182	-22.58333	-22.662793
6	-33.160416	-33.1613589	-33.08333	-33.162793
7	-45.660761	-45.6620553	-45.58333	-45.662793
8	-60.161018	-60.1625938	-60.08333	-60.162793
9	-76.661217	-76.6630239	-76.58333	-76.662793
10	-95.161376	-95.1626741	-95.08333	-95.162793
100	-9950.1625	-9950.16676	-9950.083	-9950.1628

Table 3.1: Total energies for Diracium within various approximations with  $\lambda = 1$ . Exact is from a numerical solution of the problem as outlined by Ref. [114], the second order perturbation values are also given in the same reference. EXX is exact exchange. LDA is according to the parametrization Eq. 3.20.

$Z_{crit}$	Exact	LDA	EXX
Total Energy	0.377115	0.67	0.77
Eigenvalue	0.377115	0.0	0.5

Table 3.2: . Critical  $Z$ 's for dissociation. LDA is according to the parametrization Eq. 3.20.

order perturbation theory comes at a much larger computational cost since the second order contribution requires calculation of the entire spectrum of excited states. Since LDA is non-perturbative, it is more accurate near  $Z_{crit}$  when the system becomes unstable and ionizes.

### 3.10 Delta-Function Interacting Hooke's Atom

Another test of this one-dimensional LDA is the delta-interacting Hooke's atom,

$$\hat{H} = -\frac{1}{2} \frac{d^2}{dx_1^2} - \frac{1}{2} \frac{d^2}{dx_2^2} + \frac{1}{2} \omega^2 x_1^2 + \frac{1}{2} \omega^2 x_2^2 + \lambda \delta(x_1 - x_2),$$

$$(3.55)$$

where  $\omega$  determines the strength of the harmonic well potential. This model has been used to model one-dimensional quantum dots [98] and has been considered in the context of time-dependent DFT [115]. The exact wave-function is given in terms of Whittaker functions and confluent hyper-geometric functions [98]. The total energy is

$$E = \frac{1}{2}\omega + \epsilon \quad (3.56)$$

with  $\epsilon$  obtained from

$$\sqrt{2\omega} \Gamma\left(\frac{1}{4} - \frac{\epsilon}{2\omega}\right) / \Gamma\left(\frac{3}{4} - \frac{\epsilon}{2\omega}\right) = -\lambda. \quad (3.57)$$

Since the Hooke's atom stays bound for arbitrarily weak  $\omega$ , we can test the LDA in the low density limit.

The exact result for the total energy in this limit is

$$E = 2\omega. \quad (3.58)$$

In Table 3.3, we see that LDA greatly improves over the exact exchange formalism for all values of  $\omega$ . The LDA reproduces the low-density, small  $\omega$ , limit accurately. While the LDA overestimates the correlation in the high-density limit, it underestimates it in the low-density limit.

### 3.11 The Accuracy of Delta-Function Density Functional Theory

The one-dimensional local density approximation is accurate because:

- The exact treatment of exchange
- Self-interaction free
- The interaction term is local

$\omega$	Exact	EXX	LDA
0.001	0.00195		0.00201
0.01	0.01851	0.03107	0.01883
0.1	0.16141	0.20959	0.16157
1	1.30675	1.37897	1.30353
10	11.15733	11.24020	11.14949
100	103.881057	103.967581	103.870274

Table 3.3: Total energies for the delta-function Hookes Atom within various approximations,  $\lambda = 1$ . Exact is from a numerical solution of Eqs. 3.56 and 3.57. EXX is exact exchange. LDA is according to the parametrization Eq. 3.20.

In three dimensions these conditions might not always be met. It is interesting to point out that local DFT works well for strong local correlation.

In this chapter, we have examined a one-dimensional density functional theory of delta-function interacting fermions. We noted that exact exchange is in fact an explicit density functional and developed a local density functional for approximation for correlation. We have applied these functionals successfully to two simple models. In the future, we hope to use this model interaction to study problems in DFT in general. For example, we plan to use the LDA to examine ground state symmetry problems in stretched  $H_2$  and an interacting-electron solid (a generalized Kroennig-Penney model) to investigate the band gap problem. We plan to use the excited state Bethe-Ansatz results to derive a local current density functional for this interaction. We hope to investigate the critical behavior of this model system as the potential is weakened and the system ionizes. This is difficult to do for any three dimensional system as exact results in the critical limit must be carefully extracted. This delta-function interaction has already been used to analyze the scattering theory and in pedagogy, and we hope that this simple LDA will find fruitful applications there as well.

## Chapter 4

### Uniform Density and Spin Density Scaling

In most applications, we are concerned with the Coulomb-interacting problem in three dimensions. In this chapter, we return to the study of Coulomb interacting density functional theory. We review scaling and virial constraints on the exchange-correlation energy functional, and then, generalize these to the case of spin-density functional theory.

#### 4.1 Uniform Density Scaling

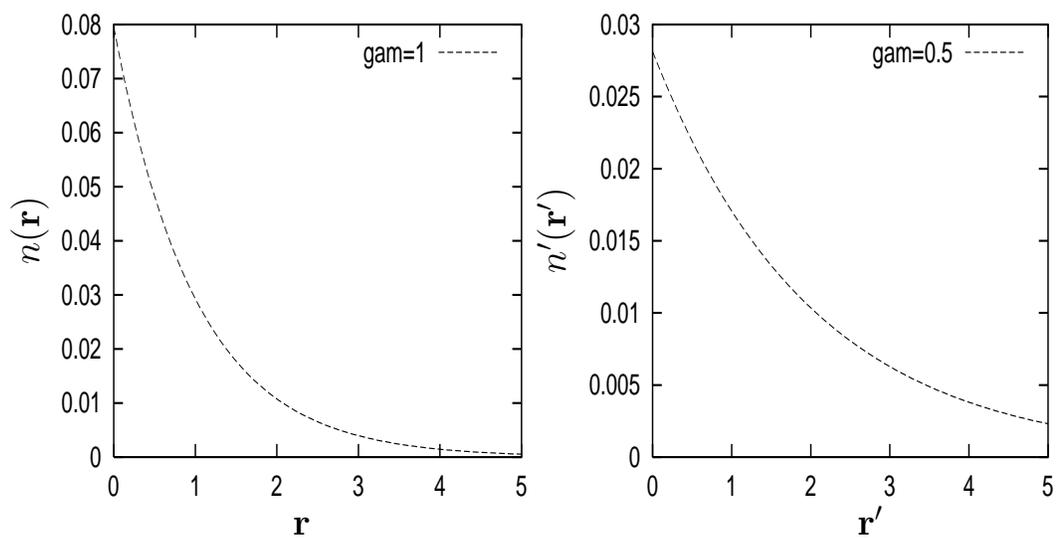


Figure 4.1: Uniform Density Scaling of an exponential density,  $n(r) = e^{-r}/4\pi$ , by a factor  $\gamma = 1/2$ .

As mentioned in Chapter 2, exact constraints limit the possible forms of approximations to  $E_{\text{xc}}$  and provide guidance for the construction of approximations [36]. For total electron density functionals, Levy and Perdew [93] discovered a set of important scaling and integral requirements that the exact functionals must satisfy. They introduced the concept of uniform coordinate density scaling. This scaling takes a density  $n(\mathbf{r})$  into

$$n_\gamma(\mathbf{r}) = \gamma^3 n(\gamma\mathbf{r}), \quad 0 \leq \gamma < \infty, \quad (4.1)$$

and is a natural way to explore the behavior of density functionals. Integrating Eq. 4.1 over all space always yields the same number of electrons. Uniform density scaling is equivalent to changing all the length scales in the problem. Because of the Coulombic interaction term, the ground state system is not invariant under this transformation. Figure 4.1 shows graphically the effect of scaling an exponentially decaying density. Many properties of the exact exchange-correlation functional have been found by studying its behavior under this scaling [90, 116, 117].

For example, the exchange energy changes as

$$E_{\text{x}}[n_\gamma] = \gamma E_{\text{x}}[n]. \quad (4.2)$$

All commonly-used approximations, such as the local density approximation (LDA), the generalized gradient approximation (GGA), and hybrids of GGA with exact exchange [42] satisfy this relation as it is imposed upon their construction. However, for correlation, only inequalities can be derived.

$$E_{\text{c}}[n_\gamma] > \gamma E_{\text{c}}[n] \quad (\gamma > 1), \quad (4.3)$$

which some approximations satisfy [35, 36] while others do not [34].

## 4.2 The Virial Theorem

Levy and Perdew further showed that translational invariance implies virial theorems relating potentials to energies. An example is

$$E_x[n] = - \int d^3r n(\mathbf{r}) \mathbf{r} \cdot \nabla v_x[n](\mathbf{r}) \quad (4.4)$$

with a more complicated corresponding relation for correlation. The virials have been used to construct energy densities directly from potentials [118]. Exact statements about exact functionals are nontrivial and extremely useful in the construction and analysis of approximate functionals. Functionals that violate these exact conditions are unlikely to give reliable and physical results when applied to wide ranges of materials.

## 4.3 The Generalization to Uniform Separate Spin Density Scaling

Modern density functional calculations do not employ *density* functionals but rather use *spin*-density functionals. The basic idea is to replace  $E_{xc}[n]$  with  $E_{xc}[n_\uparrow, n_\downarrow]$  so that the universal functional depends explicitly on both the up and down-spin electron densities. Formal justification for this scheme was first given by Barth and Hedin [119] and later by Rajagopal and Calloway [120] although some fundamental questions remain [121]. There are several compelling reasons for using spin-density functionals instead of total electron density functionals. First, spin-density functionals can more accurately describe systems with odd numbers of electrons [122]. spin-density functionals allow the treatment of electrons in collinear magnetic fields and yield magnetic response properties [123]. Accurate calculation of these properties would be far more difficult in total-density functional theory. The reason is that a local spin-density functional is a non-local total density functional. One cannot exaggerate how useful spin density functional

theory has been in accurately and efficiently calculating physical properties.

To help develop improved spin-density functionals, it would be of great interest to develop a formalism that probes the spin-dependence of functionals and yields exact conditions about their spin-dependence. Here, we investigate whether scaling techniques developed for total density functionals can be generalized to spin-density functional theory. Towards this end, we generalize uniform coordinate scaling of the density, Eq. (4.1), to separate scaling of spin-densities:

$$\begin{aligned} n_{\uparrow\alpha}(\mathbf{r}) &= \alpha^3 n_{\uparrow}(\alpha\mathbf{r}), & 0 \leq \alpha < \infty \\ n_{\downarrow\beta}(\mathbf{r}) &= \beta^3 n_{\downarrow}(\beta\mathbf{r}), & 0 \leq \beta < \infty. \end{aligned} \quad (4.5)$$

According to this scheme, a spin-unpolarized system becomes spin-polarized for  $\alpha \neq \beta$ . There are many other ways we could have chosen to alter the spin densities. For example, we could require that the total density remain constant while the polarization changes. However, such a transformation would require introduction of ensembles because fractions of electrons would be changing spin. The present scheme is simply the logical extension of coordinate scaling to separate spin-densities.

A principal result of this work is that, under such a transformation, a spin-dependent virial theorem holds true. This theorem can be used to carefully check the convergence of spin-density functional calculations. It also provides a method for calculating the exact dependence of the correlation energy on spin-density for model systems for which accurate Kohn-Sham potentials have been found. Finally, it can be integrated over the scale factor  $\alpha$  to give a new formal expression for the functional,  $E_{\text{xc}}$ .

Considerable progress has been made in density functional theory by writing  $E_{\text{xc}}$  as an integral over a coupling constant  $\lambda$  in what is called the adiabatic connection relationship [29, 30]. For example, the success of hybrid functionals such as B3LYP [42, 85] can be understood in terms of this adiabatic connection

[124, 87]. The adiabatic connection is simply related to uniform coordinate scaling [125, 126]. By analogy, we relate spin-scaling to a spin-coupling constant integration, and we define a suitable generalization for this definition with a coupling constant for each spin-density.

We illustrate our formal results with several cases. For the uniform electron gas, we can perform this scaling exactly. We show how this transformation relates energies to changes in spin-polarization. In this case, considerable care must be taken to deal with the extended nature of the system. We also show the results of spin-scaling densities of small atoms using presently popular approximations. We close with a discussion of the fundamental difficulty underlying this spin-scaling approach.

We demonstrate all scaling relationships by scaling the up-spin densities. Results for scaling the down-spins are obtained in a similar fashion. Just swap the spin labels!

#### 4.4 General Properties of Spin-Scaling

The first interesting property of the spin-scaling transformation, Eq. (4.5), is that it conserves the total number of electrons globally even though the scaled spin density might tend towards zero at any point. Even when  $\alpha \rightarrow 0$ , the up electrons do not vanish, but are merely spread over a very large volume. As  $\alpha$  diminishes, the two spin-densities occupy the same coordinate space, but on two very distinct length scales. The scaled density presumably then has vanishingly small contribution to the correlation energy. For finite systems, we can consider this limit as the effective removal of one spin-density to infinitely far away. Assuming that interaction between opposite spins vanishes in this limit, we have a way of effectively removing one spin-density from the system. We will discuss what this means for extended systems later when we treat the uniform gas.

Another interesting property of the spin-scaling transformation is that a scaling of one spin density can always be written as a total density scaling plus an inverse spin-scaling of the other spin; that is

$$E_{\text{XC}}[n_{\uparrow\alpha}, n_{\downarrow}] = E_{\text{XC}}[\{ n_{\uparrow}, n_{\downarrow}/\alpha \}_{\alpha}] \quad (4.6)$$

where the parenthesis notation on the right indicates scaling the total density. Thus, without loss of generality, we need only scale one spin-density.

To understand what happens when a single spin-density is scaled, we first study exchange. Because the spin up and down Kohn-Sham orbitals are independent, the exchange energy functional can be split into two parts, one for each spin [127]. The scaling relationships for total density functional theory generalize for each term independently. For an up-spin scaling, we find

$$\begin{aligned} E_{\text{X}}[n_{\uparrow\alpha}, n_{\downarrow}] &= \frac{1}{2}E_{\text{X}}[2n_{\uparrow\alpha}] + \frac{1}{2}E_{\text{X}}[2n_{\downarrow}] \\ &= \frac{\alpha}{2}E_{\text{X}}[2n_{\uparrow}] + \frac{1}{2}E_{\text{X}}[2n_{\downarrow}]. \end{aligned} \quad (4.7)$$

When  $\alpha \rightarrow 0$ , we are left with only the down contribution to exchange. Separate spin-scaling allows us to extract the contribution from each spin-density separately, e.g.,  $dE_{\text{X}}[n_{\uparrow\alpha}, n_{\downarrow}]/d\alpha$  at  $\alpha = 1$  is the contribution to the exchange energy from the up density. A plot of  $E_{\text{X}}[n_{\uparrow\alpha}, n_{\downarrow}]$  versus  $\alpha$  between 0 and 1 yields a straight line and is twice as negative at 1 as at 0.

Separate spin-scaling of the correlation energy is more complicated. Unlike  $E_{\text{X}}[n_{\uparrow}, n_{\downarrow}]$ ,  $E_{\text{C}}[n_{\uparrow}, n_{\downarrow}]$  cannot trivially be split into up and down parts. The Levy method of scaling the exact ground-state wave-function does not yield an inequality such as Eq. (4.3) because the spin-scaled wave-function is not a ground-state of another Coulomb-interacting Hamiltonian. Nor does it yield an equality as in the spin-scaled exchange case, Eq. (4.7), because the many-body wave-function is not simply the product of two single spin wave-functions. In both cases, the two spins are coupled by a term  $1/|\mathbf{r} - \alpha\mathbf{r}'|$ .

To obtain an exact spin-scaling relationship for  $E_{\text{XC}}$ , we take a different route. Consider a change in the energy due to a small change in the up-spin density:

$$\delta E_{\text{XC}} = E_{\text{XC}}[n_{\uparrow} + \delta n_{\uparrow}, n_{\downarrow}] - E_{\text{XC}}[n_{\uparrow}, n_{\downarrow}]. \quad (4.8)$$

Use  $v_{\text{XC}\uparrow}(\mathbf{r}) = \delta E_{\text{XC}}/\delta n_{\uparrow}(\mathbf{r})$  to rewrite  $\delta E_{\text{XC}}$  as

$$\delta E_{\text{XC}} = \int d^3r \delta n_{\uparrow}(\mathbf{r}) v_{\text{XC}\uparrow}[n_{\uparrow}, n_{\downarrow}](\mathbf{r}). \quad (4.9)$$

to first order in  $\delta n_{\uparrow}$ . Now, consider this change as coming from the following scaling of the density,  $n_{\uparrow\alpha}(\mathbf{r}) = \alpha^3 n_{\uparrow}(\alpha\mathbf{r})$ , where  $\alpha$  is arbitrarily close to one. The change in the density is related to the derivative of this scaled density:

$$\left. \frac{dn_{\uparrow\alpha}(\mathbf{r})}{d\alpha} \right|_{\alpha=1} = 3n_{\uparrow}(\mathbf{r}) + \mathbf{r} \cdot \nabla n_{\uparrow}(\mathbf{r}). \quad (4.10)$$

Use Eqs. (4.9) and (4.10), and integrate by parts to find

$$\left. \frac{dE_{\text{XC}}[n_{\uparrow\alpha}, n_{\downarrow}]}{d\alpha} \right|_{\alpha=1} = - \int d^3r n_{\uparrow}(\mathbf{r}) \mathbf{r} \cdot \nabla v_{\text{XC}\uparrow}[n_{\uparrow}, n_{\downarrow}](\mathbf{r}). \quad (4.11)$$

Eq. (4.11) is an exact result showing how  $dE_{\text{XC}}/d\alpha|_{\alpha=1}$  can be extracted from the spin-densities and potentials. For an initially unpolarized system,  $n_{\uparrow} = n_{\downarrow} = n/2$ , and  $v_{\text{XC}\uparrow} = v_{\text{XC}\downarrow} = v_{\text{XC}}$ . Thus the right-hand-side of Eq. (4.11) becomes half the usual virial of the exchange-correlation potential. This virial is equal to  $dE_{\text{XC}}[n_{\alpha}]/d\alpha|_{\alpha=1} = E_{\text{XC}} + T_{\text{C}}$  where  $T_{\text{C}}$  is the kinetic contribution to the correlation energy. Thus, for spin-unpolarized systems,

$$\left. \frac{dE_{\text{C}}[n_{\uparrow\alpha}, n_{\downarrow}]}{d\alpha} \right|_{\alpha=1} = \frac{1}{2} (E_{\text{C}} + T_{\text{C}}). \quad (4.12)$$

For initially polarized systems, there is no simple relation between the two types of scaling.

To generalize Eq. (4.11) to finite scalings, simply replace  $n_{\uparrow}$  on both sides by  $n_{\uparrow\alpha}$ , yielding:

$$\left. \frac{dE_{\text{XC}}[n_{\uparrow\alpha}, n_{\downarrow}]}{d\alpha} \right|_{\alpha=1} = - \frac{1}{\alpha} \int d^3r n_{\uparrow\alpha}(r) \mathbf{r} \cdot \nabla v_{\text{XC}\uparrow}[n_{\uparrow\alpha}, n_{\downarrow}](\mathbf{r}). \quad (4.13)$$

We can then write the original spin-density functional as a scaling integral over this derivative:

$$E_{\text{xc}}[n_{\uparrow}, n_{\downarrow}] = \lim_{\alpha \rightarrow 0} E_{\text{c}}[n_{\uparrow\alpha}, n_{\downarrow}] + \int_0^1 d\alpha \frac{dE_{\text{xc}}[n_{\uparrow\alpha}, n_{\downarrow}]}{d\alpha}. \quad (4.14)$$

This is a new expression for the exchange-correlation energy as an integral over separately spin-scaled densities where the spin-scaled density is scaled to the low-density limit. With some physically reasonable assumptions, we expect

$$\lim_{\alpha \rightarrow 0} E_{\text{c}}[n_{\uparrow\alpha}, n_{\downarrow}] = E_{\text{c}}[0, n_{\downarrow}]. \quad (4.15)$$

For example, if the anti-parallel correlation hole vanishes as rapidly with scale factor as the parallel-spin correlation hole of the scaled density, this result would be true. Numerical results indicate that this is the case for the approximate functionals used in this paper. Nevertheless, we have not proven Eq. (4.15) here.

A symmetric formula can be written down by scaling the up and down-spins separately and averaging:

$$\begin{aligned} E_{\text{xc}}[n_{\uparrow}, n_{\downarrow}] &= \frac{1}{2} \lim_{\alpha \rightarrow 0} (E_{\text{xc}}[n_{\uparrow\alpha}, n_{\downarrow}] + E_{\text{xc}}[n_{\uparrow}, n_{\downarrow\alpha}]) \\ &+ \frac{1}{2} \int_0^1 d\alpha \int d^3r n_{\uparrow\alpha}(\mathbf{r}) \mathbf{r} \cdot \nabla v_{\text{xc}\uparrow}[n_{\uparrow\alpha}, n_{\downarrow}](\mathbf{r}) \\ &+ \frac{1}{2} \int_0^1 d\beta \int d^3r n_{\downarrow\beta}(\mathbf{r}) \mathbf{r} \cdot \nabla v_{\text{xc}\downarrow}[n_{\uparrow}, n_{\downarrow\beta}](\mathbf{r}). \end{aligned} \quad (4.16)$$

This result is the spin-density functional generalization of spin-decomposition, coordinate scaling, and the virial theorem. Each of these ideas yields separate results for pure exchange or uniform coordinate scaling, but all are combined here. Notice that the potentials depend on both spins, one scaled and the other unscaled. This reflects the difficulty in separating up and down-spin correlations.

The proof of Eq. (4.16) is true for exchange-correlation, but in taking the weakly-correlated limit. The result also holds true for exchange. In the exchange case, Eq. (4.16) reduces to Eq. (4.7) with equal contributions from the limit terms and the virial contributions. To obtain this result, recall how  $E_{\text{x}}$  scales

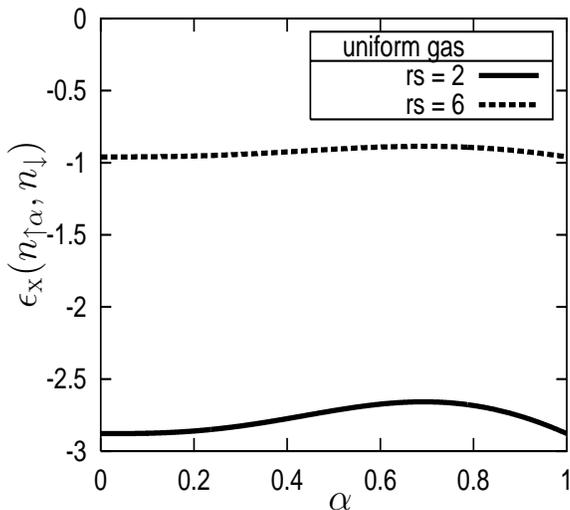


Figure 4.2: spin-scaling of a uniform gas: exchange energy per particle,  $\epsilon_x(n_{\uparrow\alpha}, n_{\downarrow})$ , at  $r_s = 2$  (dotted line) and 6 (solid line).

(4.2). Since the energy contribution from each spin is separate and since the scaling law is linear, the limits in the first two terms of Eq. (4.16) are doable without any extra physical assumptions. The virial terms are a bit more difficult to handle as the exchange potentials change under scaling. In the end, the first two terms contribute half the exchange energy while the virial terms contribute the other half.

## 4.5 Spin-Scaling on the Uniform gas

To illustrate the effect of spin-scaling, we examine the uniform electron gas, a system for which we have essentially exact results. Great care must be taken to define quantities during separate spin-scaling of extended systems. Begin with a spin-unpolarized uniform electron gas of density  $n$  and Wigner-Seitz radius

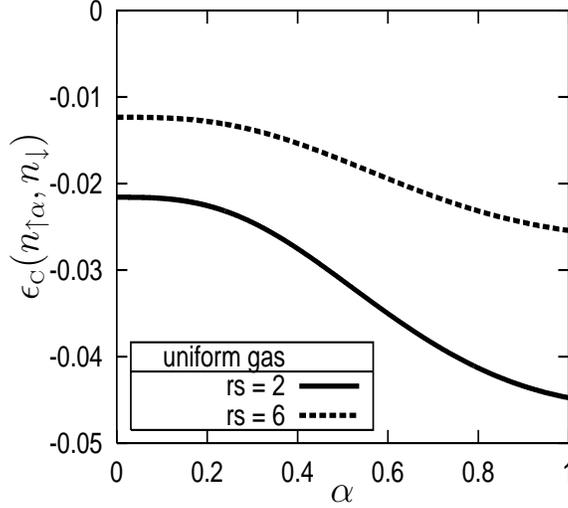


Figure 4.3: spin-scaling of a uniform gas: correlation energy per particle,  $\epsilon_C(n_{\uparrow\alpha}, n_{\downarrow})$ , at  $r_s = 2$  (dotted line) and 6 (solid line).

$r_s = (3/4\pi n)^{1/3}$ . When one spin density is scaled, the system becomes spin-polarized, and relative spin-polarization is measured by

$$\zeta = \frac{n_{\uparrow} - n_{\downarrow}}{n_{\uparrow} + n_{\downarrow}}. \quad (4.17)$$

We assume that for a spin-polarized uniform system, the exchange-correlation energy per electron,  $\epsilon_{xc}^{\text{unif}}(r_s, \zeta)$ , is known exactly. We use the correlation energy parameterization of Perdew and Wang [35] to make our figures.

To perform separate spin-scaling of this system, we focus on a region deep in the interior of any finite but large sample. A simple example is a jellium sphere of radius  $R \gg r_s$ . The correlation energy density deep in the interior will tend to that of the truly translationally invariant uniform gas as  $R \rightarrow \infty$ . At  $\alpha = 1$ , we have an unpolarized system with  $n_{\uparrow} = n_{\downarrow} = n/2$ . The up-spin-scaling,  $n_{\uparrow} = \alpha^3 n/2$ , changes both the total density and the spin-polarization. Deep in the interior

$$r_s(\alpha) = r_s \left( \frac{2}{1 + \alpha^3} \right)^{1/3} \quad (4.18)$$

where  $r_s$  is the Seitz radius of the original unpolarized gas, and

$$\zeta(\alpha) = \frac{\alpha^3 - 1}{\alpha^3 + 1}. \quad (4.19)$$

The energy density here is then

$$e_{\text{xc}}(\alpha) = e_{\text{xc}}^{\text{unif}}(n_{\uparrow\alpha}, n_{\downarrow}) = e_{\text{xc}}^{\text{unif}}(r_s(\alpha), \zeta(\alpha)), \quad (4.20)$$

and the energy per particle is

$$\epsilon_{\text{xc}}(\alpha) = e_{\text{xc}}(\alpha)/n(\alpha) \quad (4.21)$$

where  $n(\alpha)$  is the interior density.

To illustrate the effects of this spin-scaling, consider the simple exchange case. Deep in the interior, we have a uniform gas of density  $n_{\uparrow\alpha}$  and  $n_{\downarrow}$ , and the energy densities of these two are given by Eq. (4.7), since the integrals provide simple volume factors. The Slater factor of  $n^{4/3}$  in the exchange density of the uniform gas produces a factor of  $(1 + \alpha^4)$ . When transforming to the energy per electron, there is another factor of  $(1 + \alpha^3)$  due to the density out front. Thus, the exchange energy per electron is

$$\epsilon_{\text{x}}(\alpha) = \left( \frac{1 + \alpha^4}{1 + \alpha^3} \right) \epsilon_{\text{x}}^{\text{unpol.}}(n) \quad (4.22)$$

This variation is shown in Fig. (4.2). This result may appear to disagree with Eq. (4.7), but it is valid deep in the interior only. To recover the total exchange energy, one must include those electrons in a shell between  $R$  and  $R/\alpha$  with the full polarized uniform density  $\alpha^3 n/2$ . The exchange energy integral includes this contribution, and then agrees with Eq. (4.7).

Near  $\alpha = 1$ , Eq. (4.22) yields  $(1 + \alpha) \epsilon_{\text{x}}^{\text{unpol.}}/2$  in agreement with a naive application of Eq. (4.7). This is because, in the construction of the energy from the energy per electron, the factor of the density accounts for changes in the number electrons to first order. So, the derivative at  $\alpha = 1$  remains a good measure of the contribution to the total exchange energy from one spin-density. On the other

hand, as  $\alpha \rightarrow 0$ , the exchange energy per electron in the interior returns to that of the original unpolarized case. This reflects the fact that exchange applies to each spin separately so that the exchange per electron of the down-spin-density is independent of the presence of the up-spin-density.

Figure 4.3 shows the uniform electron gas correlation energy per particle scaled from unpolarized ( $\alpha = 1$ ) to fully-polarized limits ( $\alpha = 0$ ). Again, the curves become flat as  $\alpha \rightarrow 0$  because for small  $\alpha$ , there is very little contribution from the up-spins. Now, however, there is a dramatic reduction from  $\alpha = 1$  to  $\alpha = 0$  because of the difference in correlation between unpolarized and fully-polarized gases. Note that the correlation changes tend to cancel the exchange variations.

## 4.6 Calculations on Atoms

We use the ADF code to generate ground state atomic densities.

The code finds the wave function on a real space log mesh using the Numerov method to integrate the Schroedinger equation and the shooting method to hone in on the Kohn-Sham eigenvalues. The calculation is, like the one in the last chapter, lopped over until self-consistency is achieved. All angular orbital parts are averaged over. The code can handle exact exchange. However, we do not use this feature.

The following results are obtained by solving the KS equation within various approximations to get a ground state density. The density was then scaled and splined to a larger mesh when necessary, and plugged into various functionals.

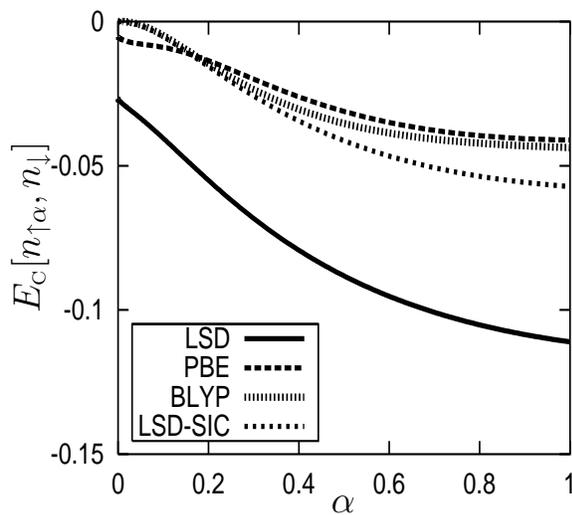


Figure 4.4: spin-scaling of the He atom density using various approximate functionals for  $E_C$ : local spin density approximation (solid line), generalized gradient approximation (PBE, dashed line), BLYP (bars), self-interaction corrected LSD (short dashes).

## 4.7 Spin-Scaling on Finite Systems

Next, we examine the behavior of finite systems under separate-spin-scaling. We choose the He and Li atoms to demonstrate the effects on the simplest non-trivial unpolarized and spin-polarized cases. For each system, we solve the Kohn-Sham equations using a specific density functional approximation. The resulting self-consistent densities are then spin scaled and the approximate energies evaluated on the scaled densities using that same functional. Since these are approximate functionals, neither the densities nor the energies are exact. We are unaware of any system, aside from the uniform gas, for which exact spin-scaled plots are easily obtainable. For now, we must compare plots generated from approximate functionals. Even the simple atomic calculations presented here were rather demanding since, especially for very small spin-scaling parameters, integrals containing densities on two extremely distinct length scales are needed.

The He atom (Fig. 4.4) is spin unpolarized at  $\alpha = 1$ . Scaling either spin

Approx.	$E_x$	$E_c$	$E_c[n_\uparrow, 0]$	$dE_c/d\alpha$
LSD	-0.862	-0.111	-0.027	-0.022
PBE	-1.005	-0.041	-0.005	-0.002
SIC	-1.031	-0.058	0.000	-0.011
BLYP	-1.018	-0.044	0.000	-0.005
exact	-1.026	-0.042	0.000	-0.003

Table 4.1: He atom energies, both exactly and within several approximations. All energies in Hartrees; all functionals evaluated on self-consistent densities.

density gives the same results. The LSD curve gives far too much correlation and does not vanish as  $\alpha \rightarrow 0$ . We expect that in the fully scaled limit, as we have argued in section 4.4, the correlation energy should vanish. This is because the two electrons are now on very different length scales and so should not interact with each other. The residual value at  $\alpha \rightarrow 0$  reflects the self-interaction error in LSD for the remaining (unscaled) one-electron density. The PBE curve is on the right scale but also has a residual self-interaction error as  $\alpha \rightarrow 0$ . The BLYP functional [33, 34] is popular in quantum chemistry and gets both limits correct. However, the functional’s lack of self-interaction error is because the correlation energy vanishes for *any* fully polarized system. This vanishing is incorrect for any atom other than H or He. Finally, the LSD-SIC curve [27] is probably the most accurate in shape (if not quantitatively) since this functional handles the self-interaction error appropriately. We further observe that the curves appear quite different from those of the uniform gas. The atomic curves are much flatter near  $\alpha \rightarrow 1$  and have appreciable slope near  $\alpha \rightarrow 0$ . This is because these energies are integrated over the entire system, including the contribution from the entire spin-scaled density, whereas the energy densities in the uniform gas case were only those in the interior.

Quantitative results are listed in Table 4.1. The exact He values, including the derivative at  $\alpha = 1$ , using Eq. (4.12), were taken from Ref. [128, 129]. Note that PBE yields the most accurate value for this derivative. The BLYP

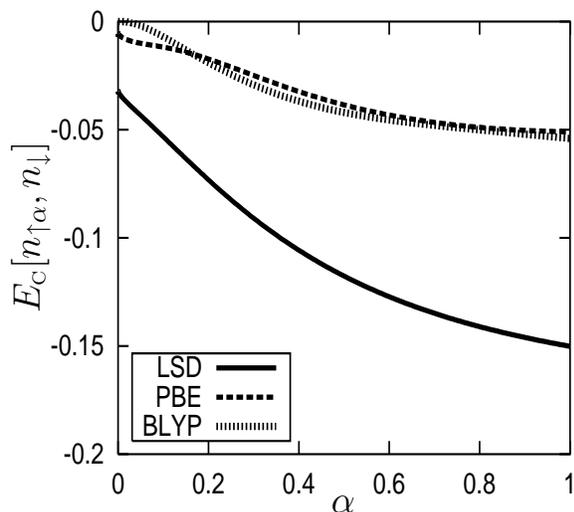


Figure 4.5: up-spin-scaling of the Li atom density using various approximate functionals for  $E_C$ : local spin density approximation (solid line), generalized gradient approximation (PBE, dashed line), BLYP (bars).

correlation energy is too flat as a function of scale parameter. BLYP produces too small a value for  $T_C$  leading to a lack of cancellation with  $E_C$  and a subsequent overestimate of the derivative at  $\alpha = 1$ . LSD-SIC has a similar problem. The LSD value, while far too large, is about 8% of the LSD correlation energy, close to the same fraction for PBE, and not far from exact. However, the important point here is that results from separate spin-scaling are a new tool for examining the accuracy of the treatment of spin-dependence in approximate spin-density functionals.

The Li atom (Figs.4.5 and 4.6) is the smallest non-trivial odd-electron atom. We choose the up-spin density to have occupation  $1s2s$ . As the up-spin is scaled away, as in Fig. 4.5, we find a curve very similar to that of He, Fig. 4.4. The primary difference is the greater correlation energy for  $\alpha = 1$ .

On the other hand, scaling away the down-density gives a very different picture, Fig. 4.6. The most dramatic changes in the correlation energy now occur at small  $\alpha$ . Near  $\alpha \rightarrow 1$ , the system energy is quite insensitive to spin-scaling, especially in GGA. This is exactly opposite to what we have seen for the uniform gas.

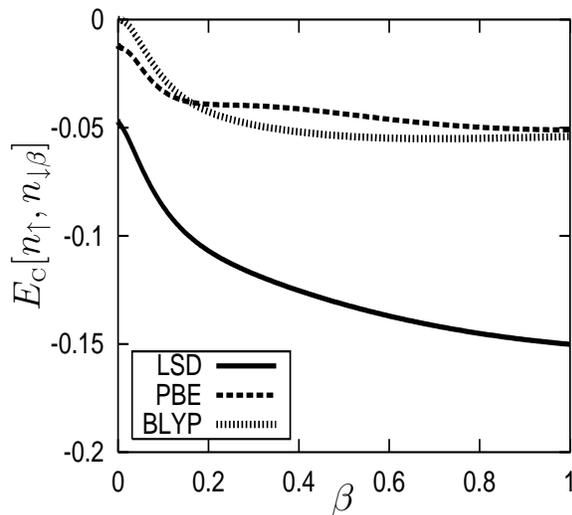


Figure 4.6: down-spin-scaling of the Li atom density using various approximate functionals for  $E_C$ : local spin density approximation (solid line), generalized gradient approximation (PBE, dashed line), BLYP (bars).

Approx.	$E_x$	$E_C$	$E_C[n_\uparrow, 0]$	$dE_C/d\alpha$	$E_C[0, n_\downarrow]$	$dE_C/d\beta$
LSD	-1.514	-0.150	-0.047	-0.037	-0.032	-0.019
PBE	-1.751	-0.051	-0.012	-0.004	-0.005	-0.001
BLYP	-1.771	-0.054	-0.054	-0.020	0.000	-0.005
exact	-1.781	-0.046	-	-	0.000	-

Table 4.2: Li atom energies, both exactly and within several approximations. All energies in Hartrees, all functionals evaluated on self-consistent densities.

It is an open question whether this would be observed with the exact functional. For up-spin-scaling, we expect the correlation energy to vanish as  $\alpha \rightarrow 0$ . But for down-spin scaling one expects a finite correlation energy in the limit  $\beta \rightarrow 0$ . The two spin-up electrons remain and are still correlated. In this case, the BLYP functional errs noticeably since it predicts no correlation energy for the remaining two electrons.

Quantitative results for Li are given in Table 4.2. The exact result for  $E_x$  is the  $E_x$  of a self-consistent OEP calculation. Using the highly accurate energy prediction from [130], we deduce the exact  $E_C = E_T - E_{T,OEP}$ . The other exact

results are not extractable from the literature here, but could be calculated from known exact potentials and densities [73]. Even in this simple case, an SIC calculation is difficult. For the up-spin-density, one would need to find the  $1s$  and  $2s$  orbitals for each value of  $\alpha$  that yield the spin-scaled densities.

## 4.8 Constructing a Spin Adiabatic Connection

Here, we define an analog of the adiabatic connection within the spin-scaling formalism. Traditionally, we think of  $\lambda$  as a parameter in the Hamiltonian, but this way of thinking becomes prohibitively complicated in spin-density functional theory. We would have to define three coupling constants:  $\lambda_\uparrow$ ,  $\lambda_\downarrow$ , and  $\lambda_{\uparrow\downarrow}$ . Even if we did that, it would be non-trivial to relate changes in these coupling constants to changes in the electron density. Instead, we *define* a relationship between spin-scaling and a spin-dependent *coupling parameter*. For total-density scaling, the relationship between scaling and evaluating a functional at a different coupling constant is [93, 125]

$$E_{\text{xc}}^\lambda[n] = \lambda^2 E_{\text{xc}}[n_{1/\lambda}]. \quad (4.23)$$

The adiabatic connection formula is

$$E_{\text{xc}} = \int_0^1 d\lambda \frac{dE_{\text{xc}}^\lambda}{d\lambda} = \int_0^1 d\lambda U_{\text{xc}}(\lambda). \quad (4.24)$$

By virtue of the Hellmann-Feynman theorem,  $U_{\text{xc}}(\lambda)$  can be identified as the potential contribution to exchange-correlation at coupling constant  $\lambda$ . The integrand  $U_{\text{xc}}(\lambda)$  can be plotted both exactly and within density functional approximations, and its behavior lends insight into deficiencies of functionals [131]. For separate spin-scaling, we apply the same ideas but now to

$$\Delta E_{\text{xc}}[n_\uparrow, n_\downarrow] = E_{\text{xc}}[n_\uparrow, n_\downarrow] - E_{\text{xc}}[0, n_\downarrow], \quad (4.25)$$

the exchange-correlation energy difference between the physical system and the system with one spin-density removed while keeping the remaining spin-density

	LSD	PBE	SIC	BLYP	exact
$\Delta U_{\text{xc}}(0)$	-0.43	-0.50	-0.53	-0.51	-0.51
$\Delta U_{\text{xc}}(1)$	-0.58	-0.57	-0.62	-0.59	-0.60
$\Delta E_{\text{xc}}$	-0.54	-0.54	-0.57	-0.55	-0.56

Table 4.3: Spin adiabatic connection  $\Delta U_{\text{xc}}(\lambda_{\uparrow})$  for He atom, both exactly and in several approximations.

fixed. For polarized systems, this quantity depends on which spin-density is removed. We define

$$\Delta E_{\text{xc}}^{\lambda_{\uparrow}} = \lambda_{\uparrow}^2 \Delta E_{\text{xc}}[n_{1/\lambda_{\uparrow}}, n_{\downarrow}] \quad (4.26)$$

and

$$\Delta U_{\text{xc}}(\lambda_{\uparrow}) = d\Delta E_{\text{xc}}^{\lambda_{\uparrow}}/d\lambda_{\uparrow}, \quad (4.27)$$

so that

$$\Delta E_{\text{xc}} = \int_0^1 d\lambda_{\uparrow} \Delta U_{\text{xc}}(\lambda_{\uparrow}). \quad (4.28)$$

This produces a spin-dependent decomposition of the exchange-correlation energy, related to separate spin-scaling rather than total density scaling, with the integral now including the high-density limit. As  $\lambda_{\uparrow} \rightarrow 0$ , exchange dominates, and  $U_{\text{xc}}(\lambda_{\uparrow}) \rightarrow U_{\text{x}}(\lambda_{\uparrow})$  which is just  $E_{\text{x}}[2n_{\uparrow}]/2$  according to the simple results for exchange in Sec. 4.4. Furthermore, in the absence of correlation,  $U_{\text{xc}}(\lambda_{\uparrow})$  is independent of  $\lambda_{\uparrow}$ . This is not true if one uses Eq. (4.23).

This spin adiabatic connection formula should prove useful for the improvement of present-day functionals in the same way that the adiabatic connection formula has been useful for improving total density functionals. For example, it might be possible to perform Görling-Levy perturbation theory [132] in this parameter ( $\lambda_{\uparrow}$ ) or to extract a correlation contribution to kinetic energy [133]. We show the spin adiabatic connection for the He atom in Fig. 4.7. In generating each adiabatic connection plot, we now take the scaled spin-density to the high

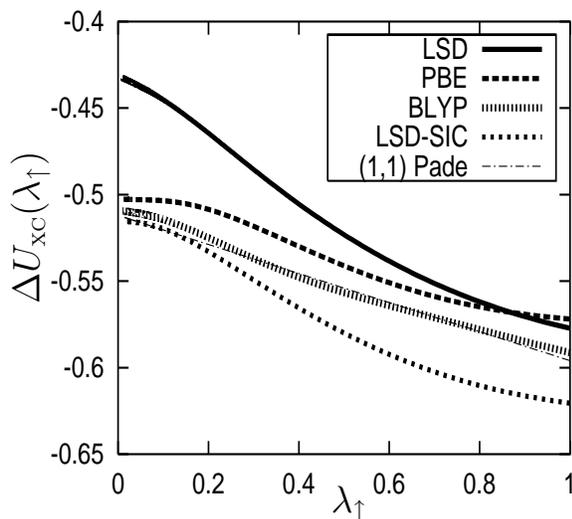


Figure 4.7: Single spin adiabatic connection for He atom: local spin density approximation (solid line), generalized gradient approximation (PBE, dashed line), BLYP (bars), self-interaction corrected LSD (short dashes), *Exact* (fancy dashes).

density limit. The area under each curve is precisely  $\Delta E_{xc}$  for a particular approximation. To get  $E_{xc}[n_{\uparrow}, n_{\downarrow}]$ , we must add the contribution from the unscaled spin,  $E_{xc}[0, n_{\downarrow}]$ . The spin adiabatic connection curve looks quite similar to the regular adiabatic connection curve: for the He atom,  $\Delta U_{xc}(\lambda_{\uparrow})$  becomes more negative with  $\lambda$  everywhere and is close to linear. This suggests that the spin correlation effects are weak for this system, just as the correlation effects are.

To better understand how popular approximations perform, we would like to compare with the exact curve. In principle, this requires a sophisticated wavefunction calculation designed to reproduce the spin-scaled densities at every point in the adiabatic connection curve. Here, we use a simple interpolation that should be highly accurate. Analytic formulae give exact limits for  $\Delta U_{xc}(\lambda_{\uparrow})$ . At the small  $\lambda_{\uparrow}$  limit, exchange dominates, and we are left with the exchange contribution from the scaled spin to the total energy:

$$\Delta U_{xc}(\lambda_{\uparrow} = 0) = \frac{1}{2} E_x[n] \quad (4.29)$$

At the other end,

$$\begin{aligned} \Delta U_{\text{xc}}(\lambda_{\uparrow} = 1) &= 2E_{\text{xc}}[n_{\uparrow}, n_{\downarrow}] - 2E_{\text{xc}}[0, n_{\downarrow}] \\ &\quad - dE_{\text{xc}}[n_{\uparrow\alpha}, n_{\downarrow}]/d\alpha|_{\alpha=1} \end{aligned} \quad (4.30)$$

For a spin-unpolarized two-electron system like the He atom, this becomes

$$\begin{aligned} \Delta U_{\text{xc}}(\lambda_{\uparrow} = 1) &= E_{\text{x}}/2 + 2E_{\text{C}} - (E_{\text{C}} + T_{\text{C}})/2 \\ &\quad (2 \text{ electrons, unpol.}) \end{aligned} \quad (4.31)$$

For He at  $\lambda_{\uparrow} = 1$ ,  $\Delta U_{\text{xc}}(\lambda_{\uparrow}) = -0.60$ . To approximate the exact curve, we use a (1,1) pade. The values  $\Delta U_{\text{xc}}(0)$ ,  $\Delta U_{\text{xc}}(1)$ , and  $\Delta E_{\text{xc}}$  fix the three unknown parameters. This pade turns out to be nearly a straight line.

Table 4.3 shows the exact limits and the limits given by several popular functionals. BLYP reproduces both limits most accurately and is mostly linear. This should come as no surprise as BLYP yields good energies and accounts for He's self-interaction error (if a bit serendipitously). However, we do not expect such good results from BLYP when using it on Li. For Li, as we have seen in section 4.7, BLYP predicts no correlation energy when only one electron is scaled away. BLYP will fail noticeably and uncontrollably in this case. The LSD functional dramatically underestimates the single-spin exchange energy and, therefore, gets the small  $\lambda_{\uparrow}$  limit quite wrong. This reflects the usual error for LDA exchange. However, notice how well LSD performs at  $\lambda_{\uparrow} = 1$ . The value here is only a 3% overestimate of the exact value, much better than the 9% overestimate for the exchange-correlation energy. Furthermore, the LSD derivative as  $\lambda_{\uparrow} \rightarrow 1$  is almost exact. PBE and LDA-SIC are qualitatively similar, the greater error in LSD-SIC being due to the errors in LSD. Both show a flattening of the curve as  $\lambda_{\uparrow} \rightarrow 0$ , much more than BLYP. Our *exact* curve is too crudely constructed to indicate which behavior is more accurate.

Ideally, we would compare approximations to the exact adiabatic plot for this and other systems such as the Li atom. The plots are not easy to generate. But

even so, analysis of the exact limits is sufficient to garner a deeper understanding of how functionals treat and mistreat spin-densities.

## 4.9 Remarks about Spin-Scaling

Both scaling and the adiabatic decomposition formula have proven extremely useful in studying and constructing total density functionals. We have suggested the possibility of scaling spin-densities separately, derived a new virial theorem, given new exact results for the He atom, and pointed out the difficulties of deducing exact theorems from this decomposition. While exact calculations are difficult to perform and exact results appear difficult to prove within this approach, any results would be very useful and likely to improve spin-density functional theory's treatment of magnetic properties.

We close with a significant challenge to developing separate spin-scaling. In the total density scaling of Eq. (4.1), the density is both squeezed (or spread) and is also translated. The squeezing is independent of the choice of origin, but the translation is not. This origin-dependence should not affect the exchange-correlation energy because space is translationally invariant. However, when an individual spin-density is scaled, the remaining spin-density remains fixed in space. This means the resulting density depends on the choice of origin for the separate spin-scaling. So while  $E_C[n_{\uparrow\alpha}, n_{\downarrow}]$  is a spin-density functional of  $n_{\uparrow\alpha}$  and  $n_{\downarrow}$ , it is *not* a pure spin-density functional of the original spin-densities because of this origin dependence. Most likely, a method of transforming away this origin dependence, as found for virial energy densities in [134], will be needed to make this spin-scaling technique more physical and useful. For atoms, we made the obvious choice of origin at the center of the nucleus. Origin dependence will become acute in applications to molecules and even worse for solids. On the other hand, the non-uniform coordinate scaling of Görling and Levy [135] suffers from

the same difficulties for non-spherical densities but has still produced useful limits for approximate density functionals [136].

However, it is important to stress that the spin-virial relationship is unaffected by this challenge. For  $\alpha$  arbitrarily close to 1, the spin-scaled energies are independent of the choice of origin, and these difficulties are irrelevant. The spin virial relationship is an exact constraint and gives us a useful measure of how the correlation energy is affected by small changes in the spin-densities. It also leads to a natural decomposition of energy changes due to separate spin-densities. It should be useful in determining whether calculations are self-consistent for each spin-density separately. This might be useful, for example, in systems where it is important to calculate small differences between spin-densities.

## Chapter 5

# The Adiabatic Connection and its Strongly Interacting Limit: Testing the Strictly Correlated Electron Hypothesis

In this chapter, we will use another tool, the adiabatic connection, to analyze the unknown exchange-correlation energy functional. The adiabatic connection curve will be accurately calculated beyond the physical interaction strength using a simulated scaling method. This is done for the Hooke's atom, two interacting electrons in a harmonic well potential. Extrapolation of the accurate curve to the infinite coupling limit agrees well with the strictly correlated electron (SCE) hypothesis. The interaction strength interpolation is shown to be a good, but not perfect, fit to the adiabatic curve.

### 5.1 Using the Adiabatic Connection to Study Functionals

A formal and general expression for the exchange-correlation energy is according to the adiabatic connection [29],

$$E_{\text{xc}}[n] = \int_0^1 d\lambda U_{\text{xc}}[n](\lambda). \quad (5.1)$$

where  $U_{\text{xc}}[n](\lambda)$  is the exchange-correlation potential energy of a density,  $n$ , at coupling constant,  $\lambda$  (see Eq. (5.3)). Analysis of the integrand,  $U_{\text{xc}}[n](\lambda)$ , leads to many rigorous relationships that the exact exchange-correlation energy satisfies and approximate functionals should satisfy. For example, Görling and Levy obtained a perturbation series expression for the exchange-correlation energy

[132] by expanding about the weak interaction limit. Another fruitful result is the understanding of why hybrid functionals like PBE0 [137] and B3LYP [85] perform so well [131, 87, 124].

Because the exchange-correlation energy is the area under the adiabatic connection curve between  $\lambda = 0$  to 1, most interest in  $U_{\text{xc}}(\lambda)$  has been confined to this domain. However, there is no fundamental reason to restrict study to this domain. In fact, certain exact properties of the adiabatic connection curve outside this domain have been used to better approximate the curve between  $\lambda = 0$  and  $\lambda = 1$  [138]. One example is the consideration of the strong interaction limit,  $\lambda \rightarrow \infty$ . A model for this strongly interacting limit is the strictly correlated electron (SCE) hypothesis [138] which states that, because of the strong Coulomb repulsion, the individual electrons distribute themselves as far apart as possible but are constrained to yield a given density. Finding one electron uniquely pins the others into position. Among other predictions, this SCE model says that  $U_{\text{xc}}$  can also be expanded about the strong interaction strength limit ( $\lambda \rightarrow \infty$ ). Information from this infinite limit, combined with the Görling-Levy expansion about  $\lambda = 0$ , leads to the suggestion of the interaction strength interpolation (ISI) for the entire curve. Exchange-correlation energies from the ISI are considerably more accurate than those using only the first two terms in the perturbation series [139].

Another reason to consider large coupling strengths is that approximate exchange-correlation energy functionals for this limit might be more accurate [140]. It has long been known that standard approximate density functionals, such as the local density approximation (LDA) or the PBE generalized gradient approximation (GGA), are better for exchange-correlation together than they are for exchange alone. This is due to a cancellation of errors between approximations to the exchange and correlation energy [124, 141]. If this cancellation between exchange and correlation grows with larger coupling constants, approximate density

functionals in this regime will be more accurate.

This chapter is a detailed study of some of these suggestions. We employ a simulated scaling procedure [142], originally developed for the range  $\lambda = 0$  to 1, and extend the simulated adiabatic connection curve to larger coupling constants. At some point along the adiabatic connection curve, the simulated scaling method is expected to break down. Nevertheless, the curve can be extrapolated from there to the infinite coupling limit. This analysis yields interesting new information about the strong interaction limit.

We work with Hooke’s atom because it remains bound no matter how strongly the electrons interact. Hooke’s atom is the unpolarized two-electron system described by the Hamiltonian [143] ,

$$\hat{H} = -\frac{1}{2} (\nabla_1^2 + \nabla_2^2) + \frac{k}{2} (\mathbf{r}_1^2 + \mathbf{r}_2^2) + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}, \quad (5.2)$$

where  $k$  is the harmonic force constant,  $\mathbf{r}_1$  and  $\mathbf{r}_2$  are the position operators for each electron, and  $\nabla_1^2$  and  $\nabla_2^2$  are the Laplacian operators for each. This is not just an exactly solvable model with Coulomb interactions but also an important *physical system*. For example, many authors have used this system to model quantum dots [144, 145].

Although we could have performed calculations for the Hooke’s atom at various harmonic well strengths, we will focus on  $k = 1/4$ . For this spring constant, the Hooke’s atom happens to admit an analytic solution [146]. Furthermore, for this  $k$  value, the correlation energy is comparable to that of the Helium atom.

The simulated curves indicate that the SCE predictions for  $U_{\text{xc}}(\infty)$  are correct. Next, assuming the validity of the SCE hypothesis, we generate a highly accurate simulation of the entire curve. This allows us to calculate higher derivatives of  $U_{\text{xc}}(\lambda)$  around key points:  $\lambda = 0$ , 1, and  $\infty$ . This information should be useful for the testing and improvement of existing functionals. We also compare the interaction strength interpolation (ISI) with the accurate simulated result.

## 5.2 Görling-Levy Perturbation Theory

The integrand of Eq. (5.1) is

$$U_{\text{xc}}[n](\lambda) = \langle \Psi_n^{\text{min},\lambda} | \hat{V}_{\text{ee}} | \Psi_n^{\text{min},\lambda} \rangle - U[n], \quad (5.3)$$

where  $U[n]$  is the Hartree energy,  $\hat{V}_{\text{ee}}$  is the electron-electron Coulomb interaction, and  $\Psi_n^{\text{min},\lambda}$  is the wave-function that minimizes  $\langle \Psi_n^{\text{min},\lambda} | \hat{T} + \lambda \hat{V}_{\text{ee}} | \Psi_n^{\text{min},\lambda} \rangle$  and yields the density  $n(\mathbf{r})$ . The functional,  $U_{\text{xc}}[n](\lambda)$ , as a function of  $\lambda$  makes up the adiabatic connection curve. At  $\lambda = 0$ , Eq. 5.3 is just  $E_{\text{x}}$ , the exchange energy evaluated at a given density. Later, for convenience, we will subtract this contribution and write  $U_{\text{c}}(\lambda) = U_{\text{xc}}(\lambda) - E_{\text{x}}$ .

At small  $\lambda$ , one may write the Görling-Levy series for  $U_{\text{xc}}$  [147, 148]:

$$U_{\text{xc}}[n](\lambda) = E_{\text{x}}[n] + 2E_{\text{c}}^{\text{GL2}}[n]\lambda + \mathcal{O}(\lambda^2), \quad \lambda \rightarrow 0 \quad (5.4)$$

where  $E_{\text{x}}$  is the exchange energy, and  $E_{\text{c}}^{\text{GL2}}[n]$  is the second order contribution to the correlation energy. The exchange-energy functional for an polarized system is

$$E_{\text{x}}[n] = -\frac{1}{2} \sum_{kk'}^{\text{occ}} \int \int \frac{\phi_k^*(r) \phi_k(r') \phi_{k'}(r') \phi_{k'}^*(r)}{|r - r'|}, \quad (5.5)$$

and Görling-Levy correlation term is

$$E_{\text{c}}^{\text{GL2}}[n] = -\sum_{\nu=1}^{\infty} \frac{|\langle \Phi_{KS} | \hat{V}_{\text{ee}} - \hat{V}_{\text{H}} - \hat{V}_{\text{x}} | \Phi_{KS}^{\nu} \rangle|^2}{E_{KS}^{\nu} - E_{KS}}. \quad (5.6)$$

where  $\Phi_{KS}^{\nu}$  is the  $\nu$ th excited state of the KS Hamiltonian [147, 132]. To get the exchange-correlation energy from Eq. (5.4), we need to integrate from  $\lambda = 0$  to 1. Unfortunately, there is no guarantee that the series will converge and that the higher order terms are negligible [139].

## 5.3 The Strong Coupling Limit

Further exact properties of  $U_{\text{xc}}$  might be useful to help understand the adiabatic curve and to use this information to construct a new functional. An interesting

limit is when  $\lambda \rightarrow \infty$ . This leads us to the second theoretical point, the strong coupling limit. This limit corresponds to strongly interacting electrons which still yield the physical density. In this limit, the integrand is finite [90]. We can expand  $U_{\text{xc}}(\lambda)$  about the infinite limit:

$$U_{\text{xc}}[n](\lambda) = U_{\text{xc}}[n](\infty) + U'_{\text{xc}}[n](\infty)/\sqrt{\lambda} + \mathcal{O}(1/\lambda), \quad \lambda \rightarrow \infty \quad (5.7)$$

where  $U_{\text{xc}}[n](\infty)$  and  $U'_{\text{xc}}[n](\infty)$  are the zeroth and first terms in the expansion.

## 5.4 The Strictly Correlated Electron Hypothesis

It has been suggested that the electrons behave in a strictly correlated manner at this limit [138]. The electrons still produce a given density distribution, but finding one electron determines the position of all the others. Information about this limit can be incorporated into an interpolation formula which reproduces both limits exactly and can be integrated analytically.

For spherically symmetric two-electron systems in three dimensions, the SCE model admits an exact solution for  $U_{\text{xc}}(\infty)$  and provides one of two contributions to  $U'_{\text{xc}}(\infty)$  [149]. One question asked in this chapter is how large the missing contribution to  $U'_{\text{xc}}(\infty)$  is. We will calculate the SCE limit and part of the first correction term for the Hooke's atom  $k = 1/4$  according to the expressions given by Seidl in Ref. [149].

According to the Seidl hypothesis, the electrons behave in a strictly correlated manner at this limit. By strict correlation, we mean that determination of the position of one electron constrains the position of all the other electrons so that knowledge of one electron position determines all the electrons positions. However, it must be stressed that the electrons still yield the physical density distribution.

For spherically symmetric two-electron systems in three dimensions, the SCE

model admits an exact solution for  $U_{\text{xc}}(\infty)$ .

$$U_{\text{xc}}^{\text{SCE}}[n](\infty) = V_{\text{ee}}^{\text{SCE}}[n](\infty) - U_{\text{H}}[n] \quad (5.8)$$

The Hartree piece,  $U[n]$ , can be calculated exactly with the equation (2.27). This leaves the  $V_{\text{ee}}$  to be evaluated. If the electron positions are strict functions of one another, we may write the  $V_{\text{ee}}$  term as

$$V_{\text{ee}}^{\text{SCE}}[n](\infty) = 2\pi \int dr \frac{r^2 n(r)}{r + f(r)}. \quad (5.9)$$

We have replaced  $|\mathbf{r} - \mathbf{r}'|$  with  $r + f(r)$  since we know that the electrons must be on opposite sides of the nucleus. Then,

$$U_{\text{xc}}(\infty) = 2\pi \int dr \frac{r^2 n(r)}{r + f(r)} - U_{\text{H}}[n] \quad (5.10)$$

We only need to find  $f(r)$ , the position of a second electron given the position of the first at  $r$ . This amounts to solving the differential equation,

$$f'(r) = \frac{r^2 n(r)}{f(r)^2 n(f(r))}. \quad (5.11)$$

with the starting condition  $4\pi \int_0^{r_0} dr r^2 n(r) = 1$  at  $f(r_0) = r_0$ . Given set of density values and the  $r$  points they are defined on, we solve this equation numerically using a sixth order Runge-Kutta scheme.

If one assumes that the electrons oscillate about this SCE electron limit in quantum harmonic oscillator potential, we can obtain an expression for  $U'_{\text{xc}}(\infty)$ .

## 5.5 The Interaction Strength Interpolation, A Rung Five Functional

The combined information from the first two terms of the Görling-Levy series and the strong interaction limit can be used to create a rung five functional. Rung five because the exact-exchange depends on the occupied orbitals and the second

order correlation term depends on the unoccupied orbitals. This is the Interaction Strength Interpolation (ISI) models Eq. (5.3) [139] :

$$U_{\text{xc}}(\lambda)[n] = U_{\text{xc}}(\infty) - X/(\sqrt{1 + Y\lambda} + Z) \quad (5.12)$$

with  $x = -2E_{\text{c}}^{\text{GL2}}[n]$ ,  $y = U'_{\text{xc}}(\infty)$ ,  $z = E_{\text{x}}[n] - U_{\text{xc}}(\infty)$ ,  $X = xy^2/z^2$ ,  $Y = x^2y^2/z^4$ , and  $Z = xy^2/z^3 - 1$ . The functional (5.12) can be integrated using Eq. (5.1) to obtain  $E_{\text{xc}}$ . Eq. (5.12) satisfies the known limits of the adiabatic connection but is not size consistent.

## 5.6 Relationship Between Scaling and Coupling Constant

The relationship between coupling constant and scale factor, is important for the procedure we used to simulate the adiabatic connection curve. A density,  $n(\mathbf{r})$ , is scaled according to Eq. (4.1). The exchange-correlation energy at a coupling constant,  $\lambda$ , and density,  $n(\mathbf{r})$ , is simply related to the exchange-correlation energy at a scaled density [126, 93]:

$$E_{\text{xc}}^{\lambda}[n] = \lambda^2 E_{\text{xc}}[n_{1/\lambda}]. \quad (5.13)$$

The integrand in Eq. (5.1) is  $U_{\text{xc}}(\lambda) = dE_{\text{xc}}^{\lambda}/d\lambda$ . Under both coupling constant and scaling transformations, we can sometimes show how parts of the exact energy transform. For example,

$$E_{\text{x}}^{\lambda}[n] = \lambda E_{\text{x}}[n] \text{ or } E_{\text{x}}[n_{\gamma}] = \gamma E_{\text{x}}[n]. \quad (5.14)$$

We use this observation later to identify scale factors between two scaled densities.

## 5.7 Solving Hooke's Atom at Different Harmonic Well Strengths

Hooke's atom is described by the Hamiltonian, Eq. (5.2). It is separable in  $u = r_2 - r_1$  and  $R = \frac{1}{2}(r_1 + r_2)$ . One part is a harmonic oscillator with mass 2

and eigenvalue,  $E_R = \frac{3}{2}\sqrt{k}$ . The other term is

$$\left(-\nabla_u^2 + \frac{1}{2}ku^2 + \frac{1}{u}\right)\phi(u) = E_u\phi(u).$$

At  $k = \frac{1}{4}$ , the solution is

$$\phi(u) = C\left(1 + \frac{u}{2}\right)e^{-\frac{u^2}{8}}, \quad (5.15)$$

and the exact ground-state density is

$$n(r) = \frac{\pi\sqrt{2\pi}}{4\pi^{\frac{5}{2}}(5\sqrt{\pi} + 8)r} e^{-\frac{1}{2}r^2} \left[ 7r + r^3 + \frac{8}{\sqrt{2\pi}}re^{-\frac{1}{2}r^2} + 4(1 + r^2)\text{erf}\left(-\frac{1}{2}r^2\right) \right] \quad (5.16)$$

with the energy  $E_{tot} = 2$  or  $E_u = \frac{5}{4}$  plus  $E_R = \frac{3}{4}$ .

For arbitrary  $k$ , the solution can not be expressed in terms of elementary functions, but can nevertheless be calculated. For example, a series solution for the ground-state is one way to find the exact result:

$$c_{n+2} = \frac{(2n + 1 - \epsilon)c_n + \sqrt{\frac{2}{\omega}}}{c_{n+1}(n + 2)(n + 1)}. \quad (5.17)$$

We can solve the recursion relationship numerically. Once  $\epsilon$  and the  $c_n$ 's are obtained, the density and other properties can be found. The exact results for Hooke's atom are readily compared to functional approximations by taking the numerically exact densities as input into approximate functionals.

## 5.8 Testing the Simulated Scaling Method

In order to generate highly accurate adiabatic connection plots, we use the procedure developed by Frydel, Terilla, and Burke [142]. To find the adiabatic connection curve, we need  $E_{xc}^\lambda[n]$  for a set of  $\lambda$ 's. For Hooke's atom, we know the exact densities and the exact  $E_{xc}$  at different  $k$  values. Instead of changing  $\lambda$ , which is difficult, we use Eq. (5.13). A small change in the strength of external potential yields another density, qualitatively similar to the original density but

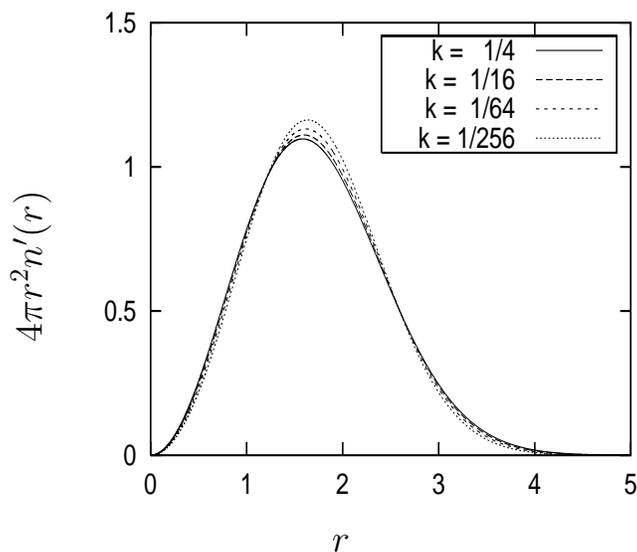


Figure 5.1: Simulated scaling of the density. We start with Hooke’s atom at  $k = 1/4$ . Then, we solve at various other coupling constants and use simulated scaling to return us as closely as possible to the  $k = 1/4$  density.

on a different scale. If we can solve the system exactly at this different external potential strength, we have an approximation to the exchange-correlation energy for a scaled density. When the densities do not qualitatively change shape much, this scheme is highly accurate. To find  $U_{xc}(\lambda)$ , we differentiate Eq. (5.13) with this highly accurate approximation to the exact  $E_{xc}[n_{1/\lambda}]$ . Including a first order correction term increases the accuracy of this method:

$$\begin{aligned}
 E_C[n_\gamma] &\approx E_C[n'] + \int d^3r v_C[n'](\mathbf{r}) (n_\gamma(\mathbf{r}) - n'(\mathbf{r})) \\
 &+ \mathcal{O}(\delta n)^2,
 \end{aligned}
 \tag{5.18}$$

Table 5.1: Simulated scaling  $k$  and  $\lambda$  equivalences using the  $E_x$  scaling rule, Eq. (5.19), to determine  $\lambda$ .

k	$\lambda$	k	$\lambda$
1/4	1.000	1/4	1.000
1/16	1.460	1	0.689
1/64	2.151	4	0.478
1/256	3.197	16	0.334

where  $v_c(\mathbf{r}) = \delta E_c[n]/\delta n(\mathbf{r})$  is the correlation contribution to the Kohn-Sham potential. This method gives highly accurate energies for Hooke's atom ( $k = 1/4$ ) and for Helium when  $\lambda$  varies from 0 to 1. The error at  $\lambda = 0$  is 0.3 mHartrees, and the estimated error for  $\lambda$  close to one less than 1 mHartree [142].

For each simulated scaling, we must assign an appropriate scale factor, but which properly scaled density does the approximately scaled density mimic? The original paper discusses several possibilities. They all require knowing how a chosen component of the energy changes with uniform density scaling. We use the  $E_x$  method:

$$\lambda = 1/\gamma = E_x[n]/E_x[n']. \quad (5.19)$$

Since we use  $E_x$  to assign  $\lambda$ , the  $U_x(\infty)$  contribution to  $U_{xc}(\infty)$  necessarily scales properly for all values of  $\lambda$ , and so we show only  $U_c(\lambda)$ .

In this paper, we examine the adiabatic connection curve at large interaction strengths. This method only works for  $\lambda > 1$  for systems that remain bound as the external potential is weakened. Even with this restriction, the method must ultimately fail as  $\lambda \rightarrow \infty$ . Specifically for Hooke's atom, Cioslowski showed that at a certain critical strength for the external potential,  $k_c = 0.0016$  ( $\lambda_c = 4.138$ ), the density changes shape qualitatively [150]. Beyond this value, the simulated scaling might no longer be a good approximation to exact-scaling. On the other hand, the method fails for He almost immediately as the two electron ion unbinds at nuclear charge,  $Z = 0.9$ .

To test this procedure and to develop a rule for its reliability, we apply the procedure in a case where we already know the correct answer, namely with an approximate functional. A generalized gradient approximation (GGA) mimics the complexity of the true functional better than, say, the local density approximation. Because of its first principle derivation and reliability, we use PBE here [36]. Since we have the analytic form for the PBE functional, we can scale the input density to generate the entire adiabatic curve, Fig. 5.2. The curve is shown

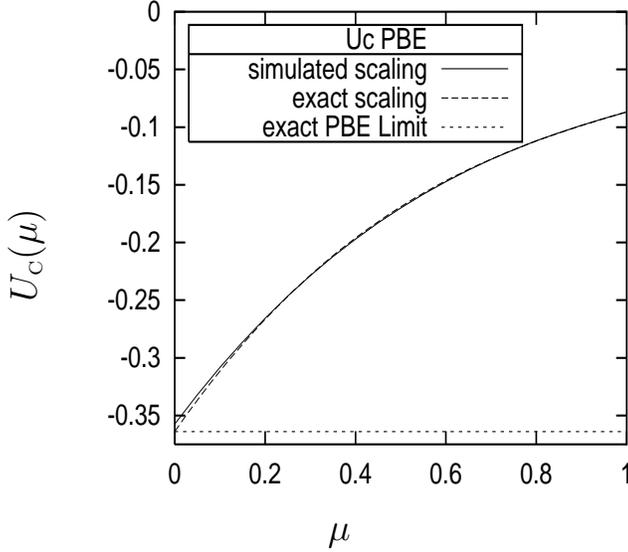


Figure 5.2: PBE adiabatic connection curve for Hooke's atom ( $k = 1/4$ ):  $U_c(\mu = 1/\sqrt{\lambda})$ . The solid line is generated using simulated scaling of the density and the dashed curve by exactly scaling the known functional. The exact PBE  $U_c(\mu = 0)$  limit is shown (short dashes).

as a function of  $\mu = 1/\sqrt{\lambda}$  so that the region  $\lambda \in 1, \infty$  can appear on a finite sized plot.

PBE results for certain key  $\lambda$  values are listed in Table 5.4. An explicit expression [140] for the PBE functional as  $\mu \rightarrow 0$  is

$$U_{xc}^{PBE}(\infty)[n] = \int d^3r n(r) \epsilon_x(n) \left( F_x^{PBE}(s) + \frac{0.964}{1 + y + y^2} \right) \quad (5.20)$$

where  $y = 0.2263 s^2$ ,  $s$  is the reduced gradient,  $\epsilon_x(n)$  is the exchange energy per particle of the uniform gas, and  $F_x^{PBE}(s)$  is an exchange enhancement factor [36].

We need a criterion for how far along the adiabatic connection we can trust the simulated density scaling to mimic the exactly-scaled density. Our criterion is to terminate the simulations at  $\mu = \mu_c = 1/\sqrt{\lambda_c} = 0.4916$  where the density qualitatively changes shape [150]. Even at this point, the first order correction in Eq. (5.18) still improves upon the zeroth order simulation. This is a highly

conservative estimate; it is likely that the curves are accurate to smaller  $\mu$ 's.

To get a prediction for  $U_c(\mu = 0)$ , we must extrapolate the simulation to  $\mu = 0$ . This is done by fitting the simulated data to an  $n^{\text{th}}$  order polynomial and extrapolating this polynomial to  $\mu = 0$ . The third order polynomial connecting four sample points best reproduces the known  $U_c^{\text{PBE}}(\infty)$ . In Fig. 5.2, we show the exactly-scaled PBE functional and the polynomial interpolation. We see that the simulated curve is almost on top of the exact curve. However, they do differ slightly in the  $U_c(\mu = 0)$  values. For the simulated curve,  $U_c(\mu = 0) = -0.357$ , and the scaled result is  $-0.363$  from Eq. (5.20), a 6 mHartree error.

## 5.9 Extrapolating to the Infinite Interaction Strength Limit

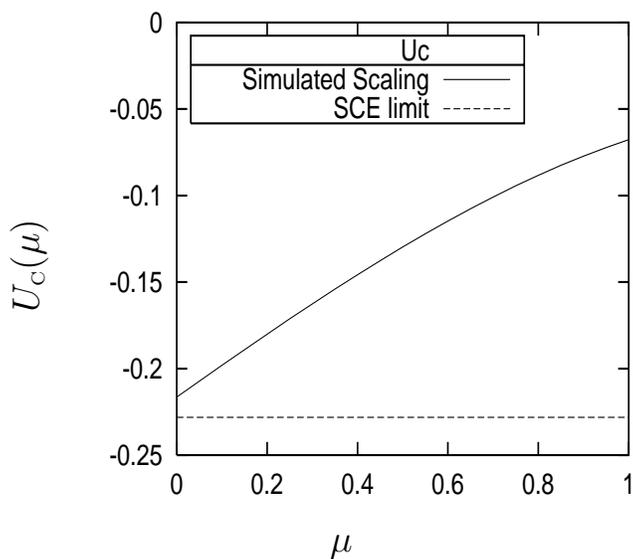


Figure 5.3: The adiabatic connection curve for Hooke's atom ( $k = 1/4$ ):  $U_c(\mu)$ . The solid line is the simulated curve. The SCE limit is shown as a dashed line.

The simulated adiabatic connection curve for Hooke's atom  $k = 1/4$  in Fig. (5.3) approaches the SCE  $U_c(\mu = 0)$  limit. As in section 5.8 for the PBE functional, we reproduce the entire curve by fitting the simulated points to a third

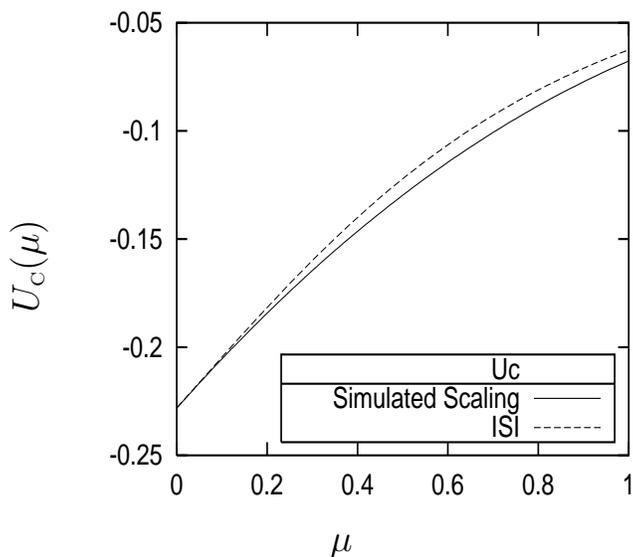


Figure 5.4: Simulated adiabatic connection curve for Hooke’s atom ( $k=1/4$ ):  $U_c(\mu)$ . The solid line is the simulated curve with the SCE  $U_c(\mu = 0)$ . The dashed curve is the ISI using exact inputs.

order polynomial. Since the simulated scaling method is only reliable between  $\mu = 1/2$  and 1, we must extrapolate the curve over the domain  $\mu = 0$  to  $1/2$  by a polynomial. The extrapolated prediction for  $U_c(\mu = 0)$ ,  $-0.206$ , is 22 mHartrees from the strictly correlated electron prediction,  $-0.228$ . We do not expect as good agreement as in section 5.8 because the true  $E_C$  functional is more complicated than a GGA, and we regard the result as consistent with the SCE hypothesis.

## 5.10 Simulating the Entire Adiabatic Connection Curve

In section 5.9, we used an extrapolation scheme to complete the adiabatic curve. Here, we combine the simulated part with the SCE electron limit to produce a highly accurate adiabatic connection curve for all coupling strengths. From this curve, we calculate the first terms in Taylor expansions about both  $\lambda = 0$  and 1, and  $\mu = 0$  and 1. Using these new results, we assess the accuracy of the Interaction Strength Interpolation (ISI) with accurate inputs.

The  $\mu < 1$  simulated adiabatic connection curve is shown in Fig. 5.4. The

Table 5.2: Higher derivatives of  $U_c(\mu)$  with respect to  $\mu$  for Hooke’s atom ( $k = 1/4$ ).

$\mu$	$U_c(\mu)$	$U'_c(\mu)$	$U''_c(\mu)$
0	-0.228	0.235	-0.156
1	-0.068	0.088	0.221

Table 5.3: Higher derivatives of  $U_c(\lambda)$  with respect to  $\lambda$  for Hooke’s atom ( $k = 1/4$ ).

$\lambda$	$U_c(\lambda)$	$U'_c(\lambda)$	$U''_c(\lambda)$	$U_c^{(3)}(\lambda)$	$U_c^{(4)}(\lambda)$
0	0.0000	-0.101	0.095	-0.107	0.124
1	-0.0677	-0.044	0.032	-0.032	0.039

curve was generated by fitting the simulated data points from  $\mu = 0.5$  to 1 and including the SCE  $U_c(\mu = 0)$  in the point set. We used a third order polynomial, the order that best reproduced the adiabatic curve for the PBE functional in section 5.8. This curve should be an excellent approximation to the exact curve. From the plot, we see that the derivative  $dU_c(\mu)/d\mu$  is positive everywhere along the adiabatic curve. This implies that  $dU_c(\lambda)/d\lambda$  is negative, and the adiabatic curve is convex. All calculated  $U_c(\lambda)$  curves for  $0 \leq \lambda \leq 1$  have  $dU_c(\lambda)/d\lambda < 0$ , but the inequality has never been generally proven. Our result extends this observation to  $\lambda \geq 1$  for this system.

Derivatives of  $U_c(\mu)$  are obtained from the coefficients in the polynomial extrapolation. Two higher derivatives of  $U_c(\mu)$  with respect to  $\mu$  are shown in table 5.2. Seidl’s model for  $U'_c(\mu = 0) = 0.281$  [149] does not agree with the accurate

Table 5.4: Accurate results for Hooke’s atom with  $k = 1/4$  evaluated on the exact densities.

	$E_x$	$2E_c^{GL2}$	$E_c$	$U_c(\mu = 1)$	$U_c(\mu = 0)$	$U'_c(\mu = 0)$
PBE	-0.493	-0.168	-0.051	-0.087	-0.363	0.561
Exact	-0.515	-0.101	-0.039	-0.068	-0.228	0.235

Table 5.5: Interaction Strength Interpolation Results for Hooke’s atom with  $k = 1/4$ . *Accurate* and *model* refer to the value of  $U'_c(\mu = 0)$ . The accurate value is from our simulation and the model is from Seidl’s model [149].

Method	$U'_c(\mu = 0)$	$U_c(\lambda = 1)$	Error	$E_c$	Error
ISI (accurate)	0.235	-0.063	8 %	-0.036	6 %
ISI (model)	0.281	-0.060	11 %	-0.035	9 %

$U'_c(\mu = 0)$ . This indicates that the missing contributions to the SCE  $U'_c(\mu = 0)$  mentioned by Seidl are, at least for this system, not negligible.

Several higher derivatives of  $U_c(\lambda)$  with respect to  $\lambda$  are listed in table 5.3. Here, we need not restrict ourselves to a third order polynomial interpolation because we have a dense sampling of data points over the range  $\lambda = 0$  to 4. The higher derivatives reported in terms of  $\lambda$  are expected to be highly accurate.

The interaction strength interpolation (ISI), as originally formulated [139], is an interpolation scheme for the entire adiabatic connection curve. It used exact values at  $\lambda = 0$  and carefully chosen GGA values at  $\mu = 0$ . We now ask how well the ISI with accurate inputs compares to the simulated curve. The answer tells us how good the choice of curve in the ISI is. For the inputs to the ISI, we use the exact  $E_x$  and  $E_C^{GL2}$  which are derivable from the simulated curves in Ref. [142] and are given in Table 5.4. For  $U_{xc}(\infty)$ , we use the SCE prediction which, judging from the results in section 5.9, we believe to be exact. For  $U'_c(\mu = 0)$ , we input two different values: the accurate simulated value and Seidl’s prediction. The results are shown in table 5.5. The ISI interpolation does not perform exceptionally well with accurate inputs as already noticed in [151]. For example, the magnitude of  $U_{xc}(1)$  is underestimated by 5 mHartrees. Perhaps, this is a result of the way the  $U'_c(\mu = 0)$  limit is included in the interpolation equation. For this system, incorporating the accurate value for  $U'_c(\mu = 0)$  in the ISI does *not* greatly improve its accuracy.

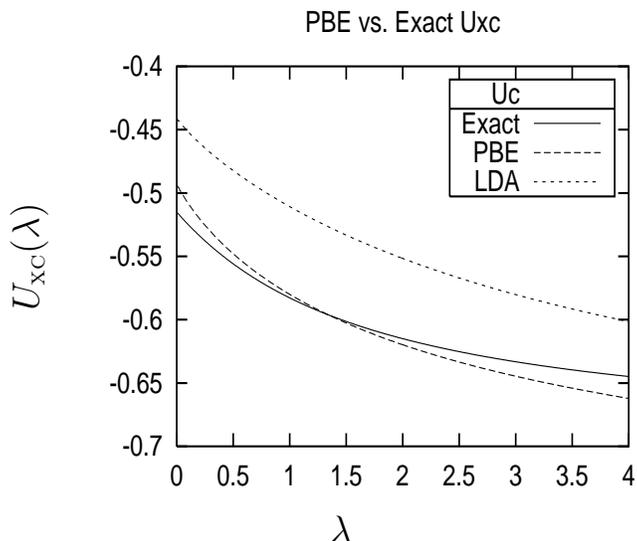


Figure 5.5: Adiabatic connection curve for Hooke’s Atom using various functionals: The exact curve is the solid line, the PBE is the long dashed line, and the local density approximation (LDA) is the short dashed line.

In Fig. 5.5, we see how the PBE and LDA adiabatic connection curves compare to the accurate curve. The PBE curve clearly crosses the accurate curve. Because its exact limit,  $\lim_{\mu \rightarrow 0} U_{xc}^{LDA}(\mu) = 1.964 E_x^{LDA}$ , is below the SCE prediction, the LDA curve must also cross the accurate one at some larger interaction strength. Since both curves cross the exact curve at some  $\lambda > 1$ , the cancellation of errors between exchange and correlation in  $E_{xc}^\lambda$  will eventually grow smaller beyond some critical interaction strength and become an addition of errors. It has been argued that because the exchange correlation on-top hole grows more local as the interaction strength increases [124, 152], local functionals for  $E_{xc}^\lambda$  would work better as  $\lambda$  increases. This is certainly true for our system in the range,  $0 \leq \lambda \leq 1$ ; however, the adiabatic plots indicate that as  $\lambda$  grows, the energy depends on the density in an increasingly nonlocal way. The accuracy of the on-top hole is less relevant to the total energies in the strongly interacting region of the adiabatic connection curve. This is related to a self-correlation error as noted in [140]. Both LDA and GGA functionals rely on the LDA treatment of the uniform gas, and the LDA cannot properly reproduce the Wigner crystallization limit due

to this strong self-correlation error [153]. Meta-GGAs are self-correlation free and behave better in this limit [82].

### 5.11 Assessment of the Strictly Correlated Electron Hypothesis and the Interaction Strength Interpolation

In this work, we have extended the method of Ref. [142] to simulate the adiabatic connection curve to interaction strengths greater than the physical value for a simple model system. In doing so, we kept in mind that the method must fail at some  $\mu_c$  as  $\mu \rightarrow 0$  ( $\mu = 1/\sqrt{\lambda}$ ) and performed an extrapolation to the strong interaction limit. This simulated curve agreed with the SCE hypothesis. To generate a highly accurate curve for  $\mu = 0$  to 1, we included the SCE  $U_c(\mu = 0)$  in the set of points and interpolated. Using this accurate adiabatic curve, we found higher derivatives at key coupling constants:  $\lambda = 0, 1$ , and  $\infty$ . Finally, we compared some popular approximate functionals to the accurate curve.

## Chapter 6

# The Adiabatic Connection and its Weakly Interacting Limit: A Close Examination of Exact-Exchange Band Gaps

Now, we turn our attention to the other end of the adiabatic connection, the small  $\lambda$  limit. In this limit, the first order contribution to the exact exchange-correlation functional is the exact-exchange functional. This is a non-local orbital functional and satisfies different constraints than the local density approximation. We will use exact-exchange to investigate the problem of how well density functionals predict band gaps in solids. This is related to what physical meaning, if any, the Kohn-Sham orbitals have.

### 6.1 The Band Gap Problem in DFT

In solid-state physics, the local density approximation (LDA) correctly describes ground-state properties like the density and equilibrium lattice structures. A notable exception to this success is the failure to describe energy gaps. The fundamental energy gap,  $E_g$ , is defined as the difference between the ionization potential,  $I_p$ , and electron affinity,  $A$ . The ionization potential and the affinity are defined as total energy differences between the  $N - 1$  and  $N$  electron systems and the  $N$  and  $N + 1$  electron systems respectively. Thus, the fundamental gap can be found from ground-state energies of systems with different numbers of electrons:

$$E_g = I - A = E[N + 1] + E[N - 1] - 2E[N], \quad (6.1)$$

where  $E[N+1]$ ,  $E[N]$ , and  $E[N-1]$  are the ground-state energies of the systems with  $N+1$ ,  $N$ , and  $N-1$  electrons respectively. Since the fundamental gap is a ground-state property, it should be well-described by ground-state DFT.

It has been shown that the fundamental gap can be re-expressed in the following form[155, 156]:

$$E_g = E_g^{KS} + \Delta_{xc}, \quad (6.2)$$

where  $\Delta_{xc}$  is called the discontinuity, and

$$E_g^{KS} = \epsilon_{N+1}(N) - \epsilon_N(N), \quad (6.3)$$

is called the Kohn-Sham orbital gap or just KS gap. The notation  $\epsilon_L(M)$  is the eigenvalue for the  $L^{\text{th}}$  KS orbital in the  $M$  electron system. In ensemble density functional theory, the constraint on integer number of electrons is relaxed, and the discontinuity is defined as [154]

$$\Delta_{xc} = \lim_{\omega \rightarrow 0} \left\{ \frac{\delta E_{xc}[n]}{\delta n} \Big|_{N+\omega} - \frac{\delta E_{xc}[n]}{\delta n} \Big|_{N-\omega} \right\}_N. \quad (6.4)$$

In exact KS theory, the ionization potential,  $I_p$ , is equal to the eigenvalue of the highest occupied KS orbital eigenvalue. This means that the ionization potential can be found from the  $N$  electron system. For approximate functionals, the relationship between the ionization potential and the highest occupied orbital eigenvalue is not known.

## 6.2 Introduction to Exact Exchange and Orbital Functionals

Exact exchange (EXX) in DFT is the Fock exchange integral evaluated on the KS orbitals,  $\phi_k(r)$ 's [157],

$$E_x[n] = -\frac{1}{2} \sum_{kk'}^{occ} \int \int \frac{\phi_k^*(r) \phi_k(r') \phi_{k'}(r) \phi_{k'}^*(r')}{|r - r'|} \quad (6.5)$$

for a fully spin-polarized system. These orbitals minimize  $T_S[n]$  for a given density  $n(r)$  and are, therefore, implicit functionals of the electron density. Since  $T_S$  and  $E_X$  depend on the orbitals, they are both implicit functionals of the density.

The exact-exchange scheme and the Hartree-Fock differ because the Hartree-Fock and KS orbitals are not the same. In the Hartree-Fock scheme these orbitals obey an equation with the semi-local potential while in the KS scheme they are determined by the KS equations with a local-multiplicative potential.

One of the most difficult things about performing EXX calculations is determining the local-multiplicative potential,  $v_x[n](r) = \delta E_X[n]/\delta n(r)$ . The potential can be obtained by the chain-rule differentiation:

$$v_x(r) = \frac{\delta E_X[n]}{\delta n(r)} = \sum_k^{occ} \int \int \left[ \frac{\delta E_X[n]}{\delta \phi_k(r')} \frac{\delta \phi_k(r')}{\delta v_{KS}(r'')} + c.c. \right] \frac{\delta v_{KS}(r'')}{\delta n(r)}. \quad (6.6)$$

Optimized effective potential (OEP) and optimized potential method (OPM) refer to the numerical scheme to take the functional derivative and are often used to label exact-exchange calculations. The solution of Eq. (6.6) usually involves solving a complicated integral equation. Because of this, exact exchange calculations are much slower and more difficult than LDA calculations. Self-consistent exact-exchange calculations are much more complicated than LDA ones and can be comparably as slow as GW calculations.

The exact-exchange functional solves several known problems with local and semi-local functionals. Namely, EXX potentials have the correct asymptotic behavior,  $v(\mathbf{r}) \sim -1/r$ , and are self-interaction free. Loosely, self-interaction-free means that the functional will give the correct results for one-electron atoms!

It is inconsistent to add local correlation to an orbital functional for exchange. The reason is that local correlation violates several exact constraints on  $E_{xc}$  that  $E_x$  was carefully constructed to satisfy! Nevertheless, real systems do have correlation, and so, in our calculations, we sometimes include correlation in a crude way by adding the local density contribution to the orbital exchange.

Another advantage of exact-exchange DFT is that the exchange-discontinuity can be calculated exactly:

$$\Delta_x = \langle c | \hat{V}_{nl} - \hat{V}_x | c \rangle - \langle v | \hat{V}_{nl} - \hat{V}_x | v \rangle \quad (6.7)$$

where  $|c\rangle$  and  $|v\rangle$  are the lowest conduction and the highest valence orbitals [163, 193]. In the systems that we will consider and at the  $\Gamma$  point in the Brillouin zone,  $\hat{V}_{nl}$  is the non-local Fock operator and  $\hat{v}_x$  is the Kohn-Sham OEP exchange operator.

### 6.3 Previous Work with Exact Exchange

For over two decades, the exact-exchange functional has been successfully applied to atoms and molecules [158, 157]. Only recently has it been applied to semiconductors, insulators and metals [159, 160, 161, 163, 191, 164, 165].

A surprising result of the EXX calculations for sp-semiconductors is that the KS energy gaps are very close to the experimental fundamental gaps with an error of about 1-3%. This contrasts typical LDA results in which the gaps are always too small. In the EXX case, a larger gap than in LDA is to be expected because the EXX potential is self-interaction free and, thus, binds more strongly than LDA potential. For example, the EXX-KS eigenvalues in atoms are greater in magnitude than their LDA counterparts. Since the occupied valence orbitals generally have a greater self-interaction contribution than the more de-localized unoccupied orbitals, the EXX-KS gap should widen compared to that of the LDA.

It is curious that exact-exchange calculations should predict sp-semiconductor band gaps well. For one, Hartree-Fock calculations do poorly at predicting band gaps. More importantly, it is unknown if the KS band structure should give the exact band gaps [155, 156]. The prevailing belief is that the *exact* KS gaps are smaller than the true gaps for solids [?]. As there are no exact KS potentials for solids available, this belief is yet unverified. It is not known how large the

discontinuity  $\Delta_{xc}$ , Eq. (6.4), of the *exact* exchange-correlation density-functional is. A KS potential has been derived from GW calculations and has been used to test this idea [166]. It was found that the presumably accurate KS potential for Si gave fundamental gaps much smaller than the experimental ones.

The EXX functional is the only density functional so far predicting band gaps close to experiment. This success has some important practical consequences. One of them is the possibility of using the KS eigenvalue spectrum as a first, approximate description of excitations and as a fast tool to interpret experiments. Another, perhaps more important, is a better starting point for more accurate calculations of excitations via the time-dependent density-functional theory.

In this chapter, we assess the performance of exact-exchange for materials very different from sp-semiconductors, namely, the column VIII crystals. Solid Ne, Ar, Kr and Xe are special systems since they are composed of almost independent atoms. The individual tightly bound close-shell atoms bind very weakly with one another. In fact, the shape of the charge density for isolated atoms and for solids is rather similar and we might expect the energetics to be similar as well. Because the electron charge is localized around the atom and is far from uniform, these systems are a difficult case for LDA. Indeed, as will be seen in Table 6.4, the LDA description of the equilibrium structural properties for these solids is much less satisfactory than usual. These solids are large-gap insulators with experimental fundamental gaps ranging between 21.4 eV for neon and 9.8 eV for xenon. They also have large exciton binding energies on the order of several eV.

Since the solids are a loosely-bound ensemble of atoms, a comparison between various electronic properties in the solid phase and in isolated atoms is meaningful and interesting. We will investigate both cases, solid and gas, with LDA and EXX. As will be seen later, in the atomic case EXX resembles highly accurate Kohn-Sham results when available. LDA correlation mixed with exact-exchange deteriorates the quality of results except in the cases when total-energy differences

are involved. Then, an account of correlation seems to be necessary.

Our results show that EXX, with and without LDA correlation, widens the LDA-KS gaps of column VIII solids by about 1.3 - 3.4 eV. The KS gaps are not as close to the experimental gaps as reported for sp-semiconductors. When considered along with previous observations that the EXX-KS gaps for diamond[163] and MgO[159] are smaller than the experimental gaps, our results suggest that EXX does not generally reproduce the fundamental gap.

For atoms, the exact KS gaps between the highest occupied orbital and unoccupied orbitals, it has been suggested, might be better approximations to the *excitonic* or *optical* gaps than to the quasi-particle or fundamental gaps[167]. The latter is defined by generalization of Eq. (6.1) to higher excited states, and the former is the gap between the ground and excited-states of the  $N$ -electron system. Some calculations using *almost exact* Kohn-Sham atomic potentials seem to support this idea[168], but it is not always clear that KS orbital eigenvalue differences should approximate the optical gaps. This is investigated in detail in Ref. [172].

Our EXX results for column VIII atoms (Section 6.7) show that in this case the KS eigenvalue differences are closer to the optical gap than the fundamental gap.

For the semiconductors, the exciton binding energy is very small (on the order of meV), and the optical and fundamental gaps are not sufficiently resolved to be able to identify which gap the KS one is closest to. Until more accurate correlation-energy functionals are known, little more can be said about the KS gaps in semiconductors.

For column VIII solids, the optical and quasi-particle gaps differ by several eV, and the electronic structure for the solids is similar to that of the isolated atoms. The calculations could shed light on the situation. What we have found is that the EXX KS-gaps for column VIII solids are, unlike the case of semiconductors,

significantly smaller than the quasi-particle gaps. They are also smaller than the experimental optical gaps by about 20 % of the experimental value. A fundamental question remains then: would *exact* correlation approximately align the KS and optical gaps for column VIII solids, or does correlation in the solid phase have a qualitatively different character and role than it does for finite, atomic systems?

## 6.4 Bloch's Theorem and Plane-Wave Methods

In our calculations, we use a plane-wave basis. There are several advantages to working in a plane-wave basis-set. The basis vectors are orthogonal and complete, the kinetic energy operator is diagonal. Most importantly for our purposes, the basis set can be systematically improved. Ref. [169] gives a good review of the details of the plane-wave and pseudo-potential method.

Bloch's theorem tells us that for a periodic potential, we can write each single-particle non-interacting orbital as a product of a plane-wave and a periodic function,

$$\Psi_{n,k}(r) = e^{ik \cdot r} u_{n,k}(r), \quad (6.8)$$

where  $k$  is a label.  $u_k(r)$  is periodic in  $R$ , a vector from one unit cell to another:

$$u_{n,k}(r + R) = u_{n,k}(r). \quad (6.9)$$

The periodic function can be expressed in terms of reciprocal lattice vectors,  $G$ 's,

$$u_{n,k}(r) = \sum_G c_{n,k}(G) e^{iG \cdot r}. \quad (6.10)$$

The set of  $G$ 's is defined as the vectors which satisfy  $G \cdot R = 2\pi$ . The  $k$ 's are defined only up to the addition of a reciprocal lattice vector,  $G$ . A continuous distribution of  $k$ 's with no doubling is called the Brillouin zone. The shape of the Brillouin zone reflects the geometry of the crystal.

In the calculations, sums over the Brillouin zone must be done to obtain the density and other quantities. For example, a typical sum would be

$$\int_{BZ} dk f(k) \approx \frac{(2\pi)^3}{\text{Vol}} \sum w_i f(k_i) \quad (6.11)$$

where Vol is the volume of the sample. It is too expensive to calculate a dense sampling of  $k$  points. Fortunately, it can be shown that an accurate approximation to this sort of integral is possible with a sparse sampling of carefully selected  $k$  points. In particular, we sample points of low symmetry in the irreducible wedge of the Brillouin zone and use symmetry to obtain a larger set of terms. In our calculations, the special  $k$  points minimize the error in the discretization according to a scheme by H. J. Monkhorst and J. D. Pack [170].

We can expand the Bloch function in terms of reciprocal lattice vectors,

$$\phi_{k,n}^{KS}(r) = \frac{1}{\sqrt{V}} \sum_G C_{k,n}(G) e^{i(k+G)r}.$$

The Fourier transform of the potential is

$$v(G) = \frac{1}{8\pi^3} \int d^3\mathbf{r} v(r) e^{-iG\cdot\mathbf{r}}. \quad (6.12)$$

In order to get the KS potential, the density is calculated in real space according to

$$n(\mathbf{r}) \approx \sum_{k,occ} |\phi_k|^2(\mathbf{r}). \quad (6.13)$$

The potential is calculated in one real-space cell, and then, Fourier-transformed to reciprocal space.

In reciprocal space, the Kohn-Sham equation is

$$\left[ \sum_{G'} \frac{1}{2} |k + G'|^2 \delta_{G,G'} + v_{KS}(G - G') \right] c_n(k + G') = \epsilon_n c_n(k + G) \quad (6.14)$$

This is one matrix problem in  $G$  for each  $k$  value sampled. The equation can be diagonalized using standard Lapack routines. We impose a cut-off so that the

matrix is finite in size and can be diagonalized in a finite time,

$$\frac{1}{2}|G + k|^2 \leq E_{cut}. \quad (6.15)$$

In our calculations, we use semi-local pseudo-potentials so that  $v_{KS}(G - G')$  is replaced with the semi-local version,  $v_{KS}(G, G')$ .

## 6.5 Pseudo-Potentials

Valence electrons<sup>1</sup> occupy the highest energy occupied orbitals and are chemically active. The rest of the electrons are core electrons. We can greatly reduce the size of a calculation by replacing the core electrons with an effective potential. In *frozen-core approximation*, we imagine that the core electrons are unaffected by changes in the valence. The effective potentials replace the Coulomb potentials centered on the nuclei.

Even with this simplification, calculations on real solids are demanding. One of the reasons is that the valence orbitals must be orthogonal to the core orbitals. For example, orbital oscillations near the nucleus would mean that the cut-off for a plane-wave basis would be large. The need for a large basis-set can be alleviated by carefully choosing the effective potential. A pseudo-potential gives orbitals that are equal to the exact ones beyond some radius. Below that radius, the pseudo-orbitals are chosen to be free of unwanted nodes and oscillations.

In most modern calculations, *ab initio* pseudo-potentials are popular. These are typically constructed from purely first principles. First, an atomic code finds the KS orbitals for a given  $Z$  atom. The orbitals are matched to pseudo orbitals beyond a critical radius, and the pseudo-potential is found by inverting the pseudo-Schrödinger equation with these orbitals.

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<sup>1</sup>By electrons, we mean non-interacting electrons or Kohn-Sham electrons.

Ensuring that the pseudo-orbitals are smooth requires that the pseudo-potentials depend on the angular momentum eigenvalues,  $l$ :

$$\hat{V}_{pseudo}(r) = \sum_{l,m} V_l(r) |l, m\rangle \langle l, m|. \quad (6.16)$$

Thus, smooth pseudo-potentials are semi-local. In principle, a fully local pseudo-potential is possible but the potential would not be smooth [171].

Kohn-Sham DFT is strictly only valid for local multiplicative external potentials, but pseudo-potentials are often semi-local. The validity of the formalism comes into question. The DFT pseudo-potential method is often justified by its success. In generalized KS theory, there is no problem with the semi-local potential [173, 68].

While there is no compelling theoretical reason to abandon semi-local pseudo-potentials, there is a practical one. Semi-local pseudo-potentials are inconvenient for plane-wave calculations. Kleinman-Bylander scheme transforms a semi-local pseudo-potential to an effectively local one [174].

The pseudo potential should represent the effective core potential one non-interacting electron in the valence experiences. The construction, thus far, gives us an effective pseudo-potential from the core and the other valence electrons. We need to remove the valence-valence interactions to get the ionic pseudo-potential. Typically, this is done as follows:

$$v_l^{pseudo}(r) = v_l(r) - v_H[n_v](r) - v_{XC}[n_v + n_c](r). \quad (6.17)$$

We remove all the Hartree interaction of the valence and all of the exchange-correlation. It is often convenient to use a model charge-density for the core. In the regions where the core and the valence overlap, it is important that this charge density matches the exact one. Elsewhere the charge density can be chosen with some freedom. A convenient choice is to assume vanishing charge density at the nucleus. For the exact-exchange scheme this is not as simple to do since

$v_x(r)$  is not known explicitly as a functional of the density. The result is that an alternative screening procedure is needed [175].

In our calculations, we use an EXX compatible Troullier-Martins type pseudo-potential calculated from the Moukara et al. code [175].

## 6.6 The Implementation of Exact-Exchange

The exact-exchange potential can be computed analytically in a basis set by requiring that a linear change in the potential cause a linear change in the charge density. This is formally shown in Ref. [163, 164]. In a plane-wave basis, the Fourier transformed exchange potential is

$$v_x(G) = \sum_{G' \neq 0} [F(G') - F^*(G')] \tilde{\chi}_0^{-1}(G, G'), \quad (6.18)$$

where  $\tilde{\chi}_0$  is the inverse of the momentum space response function,  $\tilde{\chi}_0(G, G')$ . The  $G = G'$  component is removed to ensure that only charge conserving variations are allowed.

$$\tilde{\chi}_0(G, G') = \frac{4}{Vol.} \sum_{cvk} \frac{\langle vk | e^{-iG \cdot \mathbf{r}} | ck \rangle \langle ck | e^{iG' \cdot \mathbf{r}} | vk \rangle}{\epsilon_{vk} - \epsilon_{ck}}, \quad G \neq G', \quad (6.19)$$

and

$$F(G) = \frac{2}{V} \sum_{vck} \frac{\langle vk | \hat{V}_x^{NL} | ck \rangle \langle ck | e^{-iG \cdot \mathbf{r}} | vk \rangle}{\epsilon_{vk} - \epsilon_{ck}}, \quad (6.20)$$

where

$$v_x^{NL}(k, G, G') = -\frac{4\pi e^2}{V} \sum_{vqG_i} \frac{C_{vq}(G + G_i) C_{vq}^*(G' + G_i)}{|q - k + G_i|^2}. \quad (6.21)$$

The label  $v$  refers to valence orbitals, and  $c$  refers to conduction orbitals. We sum over all conduction orbitals in our basis.

In our actual calculations for each approximate  $E_{xc}$  (LDA, EXX and EXXc), we generated a pseudo-potential using the same functional [176, 177, 164]. For

Ne	LDA	EXX	EXXc	QMC	CI	Expt.
1s	-824.34	-838.30	-840.38	-838.18	-838.30	
2s	-35.97	-46.73	-48.40	-44.93	-45.01	
2p	-13.54	-23.14	-24.76	-21.61	-21.69	-21.56
3s	-0.07	-5.23	-5.77	-4.97		-4.9
3p		-3.11	-3.40	-3.00		-2.94
4s		-1.95	-2.03	-1.90		-1.89
3d		-1.57	-1.63	-1.55		-1.53

Table 6.1: Neon atom energy levels (in eV). The KS orbital energies are from LDA, exact exchange (EXX) and exact exchange with LDA correlation (EXXc). Column QMC gives the eigenvalues obtained with the highly accurate Kohn-Sham potential of Ref. [19]. Column CI presents results of highly accurate Kohn-Sham calculation of Ref. [21].

solid krypton and xenon, we performed a relativistic calculation and account for the spin-orbit interaction perturbatively.

The cut-off energy for the plane-wave basis was typically 50 – 120 Hartree and determined by convergence. Convergence means that the plane wave cut-off is large enough so that increasing the cut-off no longer changes the band gaps by more than  $\approx 0.1$  eV. The k-summations consist of 2 mean value points in the irreducible part of the Brillouin zone. We perform all calculations at the experimental lattice constants: Ne( $8.435 a_0$ ), Ar( $9.94 a_0$ ), Kr( $10.66 a_0$ ), and Xe( $11.59 a_0$ ). The column VIII solids have an FCC structure.

## 6.7 Exact Exchange on Finite Systems: Ne, Ar, Kr and Xe

It is interesting and instructive to start our investigation by analyzing the properties of the isolated atoms where the density-functional calculations are more advanced and can test various approximations. Atomic DFT is more advanced in this context in two senses. First, highly accurate KS potentials are available

Ar	LDA	EXX	EXXc	CI	Expt.
1s	-3095.39	-3112.99	-3115.42	-3113.82	
2s	-293.61	-303.27	-305.13	-302.59	
2p	-229.67	-237.46	-239.36	-236.85	
3s	-24.02	-29.90	-31.37	-28.79	
3p	-10.40	-16.07	-17.48	-14.88	-15.76
4s	-0.26	-4.37	-4.94		-4.08
4p		-2.77	-3.09		-2.66
3d		-1.86	-2.29		-1.83

Table 6.2: Argon atom energy levels (in eV). The KS orbital energies are from LDA, exact exchange (EXX) and exact exchange with LDA correlation Column CI presents results of highly accurate Kohn-Sham calculation of Ref. [21].

for a few light atoms like Ne[178, 179] and Ar[179]. Second, for a finite system, it is computationally feasible to calculate the fundamental gap, Eq.(6.1), from the total-energy differences. In this section, we will present several results for the column VIII atoms and draw some conclusions about the validity of certain approximations.

In Tables 6.1 and 6.2, the KS eigenvalues for Ne and Ar are presented. The results are for LDA, pure exact-exchange (EXX), exact-exchange plus LDA correlation (EXXc) and highly accurate, almost exact KS potentials. The column denoted QMC in Table 6.1 shows the orbital eigenvalues calculated by Umrigar and Gonze[178] from a Quantum Monte Carlo ground-state density for the Ne atom. The column denoted CI in Tables 6.1 and 6.2 shows Morrison and Zhao’s results [73] from highly accurate configuration interaction densities. The column called *Expt.* contains the negative of the experimental first ionization-potentials. The column also contains the experimental binding energies of a few excited states. The binding energies of unoccupied states are the experimental optical gaps between the ground state and a relevant excited state minus the ionization potential. The reported optical gaps are a weighted average of singlet

		Ne	Ar	Kr	Xe
Expt:	$E_g$	21.56	15.76	14.00	12.13
Expt:	$E_{og}$	16.63	11.57	9.94	8.35
LDA:	I-A	22.66	16.17	14.44	12.73
	$\Delta\epsilon_{KS}$	13.47	10.14	8.76	7.50
	$E_{og}$	17.74	11.96	10.32	8.87
EXX:	I-A	19.83	14.77	13.22	11.66
	$\Delta\epsilon_{KS}$	17.91	11.70	9.81	8.12
	$E_{og}$	15.16	10.96	9.58	8.32
EXXc:	I-A	21.31	16.03	14.61	12.79
	$\Delta\epsilon_{KS}$	18.99	12.54	10.58	8.82
	$E_{og}$	16.08	11.72	10.28	8.97

Table 6.3: Fundamental energy gaps  $E_g$ =I-A and optical gaps from experiment and calculations in neutral atoms Ne, Ar, Kr and Xe.  $E_{og}$  is the multiplet-averaged experimental transition energy from the ground state to  $p^5s^1$  state.  $E_{og}$  is the calculated total-energy difference between the ground state and the excited atom in the ( $p^5s^1$ ) configuration.  $\Delta\epsilon_{KS}$  is the Kohn-Sham gap.

and triplet optical gaps. In tables 6.1 and 6.2, we report only the experimental binding energy for the highest occupied state. This is because the eigenvalue of the highest occupied state has a physical meaning; it is the negative of the ionization potential. For the unoccupied states, it has been suggested that the KS eigenvalues approximate the experimental binding energies of the excited atom well [167, 168]. This idea has been explicitly verified for helium[167], beryllium [167] and neon atoms[168] and some plausible arguments have been put forward to explain why [167].

The LDA eigenvalues are smaller in magnitude than their EXX and EXXc counterparts. This is mostly due to the large self-interaction error inherent in LDA. Another consequence of the self-interaction error is that LDA typically has only one unoccupied orbital. The EXX eigenvalues for Ne and Ar are deeper than the exact ones. This means that the EXX scheme binds Ne and Ar too strongly. Exact correlation would correct for this over-binding. Adding LDA correlation

to EXX deepens the eigenvalues even more. For example, the EXX uppermost occupied eigenvalues are roughly 1.5, 0.3 eV deeper than the exact KS eigenvalues for Ne and Ar respectively. In the EXXc scheme the difference grows to 3.2 and 1.7 eV respectively. For occupied states, the expected behavior of *exact* correlation in DFT is similar to the role of correlation in the many-body Green's functions approach. There, correlation shifts the eigenvalues, or poles of the one-particle Green's functions, in the opposite direction as Hartree-Fock. Thus, the binding energies of occupied orbitals are far too strong within Hartree-Fock. The EXX KS occupied orbitals are more bound than the exact KS orbitals, but the effect is much smaller than in Hartree-Fock.

The analogy between Hartree-Fock and exact-exchange breaks down for unoccupied states. In this case, EXX results in deeper unoccupied orbitals than experiment finds and adding LDA correlation makes them even deeper. On the other hand, Hartree-Fock theory hardly binds at all. This striking difference between EXX and Hartree-Fock is because Hartree-Fock has an exponentially decaying potential for the unoccupied orbitals. In contrast, the EXX potential has a Coulombic tail for all orbitals. The Hartree-Fock potential is self-interaction free only for occupied orbitals, whereas the KS potential (exact and EXX) is self-interaction free for all orbitals.

For the heavier atoms Kr and Xe, we performed a full relativistic OEP calculation since relativistic effects should be important. In these cases, we have neither the exact KS potentials nor eigenvalues with which to compare the results. However, a comparison with the experimental first ionization-potential shows that, when spin-orbit interaction is neglected, the exact exchange calculation slightly overbinds the uppermost occupied level. Here again, LDA correlation added to exact-exchange lowers the eigenvalues. For lighter atoms, adding LDA correlation to exact-exchange results degrades one-electron properties.

For finite systems, it is possible to relate certain excitations with total-energy

differences. This is the case with the first ionization potential,  $I = E[N - 1] - E[N]$ , electron affinity,  $A = E[N] - E[N + 1]$ , and the energy gap  $E_g$ , Eq.(6.1). The electron affinity,  $A$ , defined by a total energy difference, is zero within LDA for most atoms. This is because LDA does not bind the corresponding  $N + 1$  electron system. In the case of column VIII atoms, however, the experimental affinity does vanish, and the LDA result is adventitiously correct. Since the affinity vanishes, the gap must equal the ionization energy. Using Eq. (6.1) and LDA for the atomic gap is problematic because LDA does not bind the  $N + 1$  system needed to find the affinity. On the other hand, because the LDA discontinuity disappears, and the orbitals eigenvalue are well defined Eq. (6.2) gives a prediction for the gap. The discontinuity disappears because the LDA potential depends continuously on the density. The same problem plagues EXX which does not bind the  $N + 1$  system as far as our calculations suggest. EXXc gives a small, but finite, value for the affinity. Table 6.3 shows the atomic energy gaps,  $E_g$ , the experimental ones and then those calculated from total-energy differences within LDA, EXX and EXXc schemes.

The energy gaps are compared to the KS eigenvalue differences  $\Delta\epsilon_{KS}$ . In addition, the (triplet-singlet averaged) first optical-gap and the *total-energy optical gap*,  $E_{og} = E[N]^* - E[N]$  are presented. Here,  $E[N]$  is the total ground-state energy and  $E[N]^*$  is the total energy of an excited state in which there is a hole in the uppermost p-shell and an electron in the next s-shell. We calculate both using the same ground-state energy functionals.

First, we note that the KS gap rather poorly approximates the experimental fundamental gap. The average deviation over the four elements between the KS and true gaps is 5.9, 4.0, 3.1 eV for LDA, EXX and EXXc schemes. As shown by the data, LDA KS gaps deviate the most. When expressed in percents, LDA, EXX, and EXXc KS gaps account for 63 %, 75 % and 80 % of the experimental fundamental gaps respectively. This is not surprising since there is no reason

that the KS gap should be close to the fundamental gap. For Ne (Table 6.1), the highly accurate KS energy gap amounts to 77 % of the experimental one. For Ar (Table 6.2), we estimate the exact KS gap to be of about 68 % of the experimental one. The situation changes when we compare KS energy gaps to experimental optical gaps. It turns out that LDA, EXX and EXXc schemes reproduce the atomic optical gaps with 13 %, 3 % and 9 % respectively. The highly accurate KS gap of Ne amounts to 99.9 % of the optical gap. In particular, the good agreement of the EXX scheme with experiment is to be noted. An interesting question is whether similar trends take place in the solid phase. We might expect the answer to be yes if the solid is composed of an array of weakly interacting atoms.

The experimental fundamental gap of column VIII atoms agrees fairly well with the calculated total-energy differences (Eq. 6.1). For all four elements, the different functionals reproduce the experimental atomic gaps, on average, to 4 %, 6 % and 3 % accuracy respectively. A total-energy calculation for the *optical gaps* agrees by about 5 %, 5 % and 4 % with experiment for LDA, EXX and EXXc schemes respectively. In the total-energy difference calculations, accounting for correlation seems to be important since the best total-energy difference results come from the EXXc scheme, the worst with the exact-exchange only.

## 6.8 Exact Exchange of Large Gap Extended Systems: Solid Ne, Ar, Kr and Xe

In this section, we will consider the results for solid Ne, Ar, Kr and Xe.

In Table 6.4, the experimental and calculated equilibrium lattice constants are presented. As already noted, column VIII solids resemble loosely-bound isolated atoms. For such systems, the total energy only weakly depends on the inter-atomic distances. Thus, the energy-volume curve is very flat and the system

hardly binds. In the absence of stronger inter-atomic interactions, the theoretical determination of equilibrium properties is subject to a large uncertainty. The usual convergence criteria for total-energy determination may be insufficient, and computational details, like pseudo-potential construction, can matter. To ensure reliability, we have double-checked the LDA results using independent, publicly available LDA codes [64, 180].

As shown in Table 6.4, the structural equilibrium properties of column VIII solids are very poorly described by all three functionals. For example, the error in the lattice constant for neon is more than 13 %. This discrepancy is unusually large; for most solids, LDA gives a lattice-constant within about 1-2%. For Ar, Kr and Xe, the LDA discrepancy is about 5% not as drastic as for Ne. However, the disagreement is still much larger than usual. In contrast to LDA which underestimates the lattice spacing, EXX overestimates it for Ar, Kr and Xe. Except when applied to neon, the combined scheme, exact-exchange plus LDA correlation (EXXc), is the closest to experiment. This result is similar to what was seen in section 6.7 for atomic calculations of total energy differences for which some accounting for correlation is important. None of these schemes reproduce the long-range van der Waals effects. These effects are responsible for the binding of column VIII solids, and so it is not surprising that the calculated structural properties differ so much from experiment.

Figures 6.2, 6.1, 6.3, and 6.4 show the band structures along the L- $\Gamma$ -X directions for Ne, Ar, Kr and Xe. Kr and Xe are treated relativistically. The solid lines represent the EXX band structure, and the dashed lines correspond to the LDA one. In Tables 6.5, 6.6, 6.7, and 6.8, the KS eigenvalues at high symmetry points  $\Gamma$ , X and L are presented. In Table 6.9, the KS energy gaps are compared with the experimental fundamental energy gaps and with the optical gaps for solid Ne, Ar, Kr and Xe. It is important to keep in mind that for this special class of atoms, the description of the LDA, EXX and EXXc electronic structure

might be expected to be less accurate in the solid phase than for atoms because in addition to only approximating at best short range correlation, the functionals do not account for the long range van der Waals effects.

It is interesting to consider how well LDA, EXX and EXXc describe the electronic structure of column VIII solids. In LDA, the KS gaps are, on average, 55 % of the experimental gaps. This is a typical result for solids, and slightly less accurate than for the atomic LDA limit. For column VIII solids EXX and EXXc reproduce about 68 % of the fundamental gap, whereas in the atomic limit the KS gap ranged on average to 74 % and 79 % of the experimental fundamental gaps for EXX and EXXc respectively. That the EXX and EXXc KS gaps in column VIII solids are not reproduced as accurately as for the semiconductors is noteworthy. However, the atomic results suggested that the EXX-KS gaps should not be expected to approximate the fundamental gaps as well as the optical gaps. Since the column VIII solids have a large exciton binding energy, the optical gap is appreciably smaller than the fundamental gap. What we observe in Table 6.9 is that the EXX and EXXc KS gaps are still pronouncedly smaller than optical gaps in the solids. The calculations reproduce the experimental optical gaps to about 80 % - 81 %. This is worse than in the atomic limit. It is not clear if this disagreement is because solids require more accurate treatment of correlation than atoms. Or perhaps, the KS gaps in solids need not be close to optical gaps at all. The column VIII solids are good materials to investigate this question; however, a definitive answer seems to require the use of more accurate correlation functionals. In section 6.7, exact-exchange with LDA correlation gave less accurate one-particle properties for isolated atoms. For solids, the accuracy of KS-EXXc gaps is slightly better than with pure EXX. This improvement could be an artifact of overbinding in the valence bands.

While the valence bands show a limited dispersion on Figs. 6.2 through 6.4, conduction bands exhibit a rather pronounced dispersion. This is consistent with

the observation that the Brillouin zone average of the valence band width, or the energy distance between occupied s and p bands, is very close to the energy gap between s and p valence orbitals in isolated atoms. This is not the case with the energy gaps between occupied and empty bands for corresponding orbitals in atoms. The solid gaps are appreciably smaller than in atoms.

Another remarkable result is that the LDA valence-band width is smaller than the EXX width for neon. For argon, both widths are comparable. For krypton and xenon, the EXX width is smaller. We recall that previous EXX calculations have shown for sp-semiconductors that EXX leads to narrower total valence-band widths than LDA. Only for diamond was the opposite observed.

We conclude by showing the effect of adding the exact-exchange contribution to the exact derivative discontinuity, Eq. (6.7), in Table 6.10. Notice that adding the exact-exchange discontinuities to the DFT exact-exchange gap returns us to the Hartree-Fock results.

## 6.9 Revisiting the Band Gap Problem in DFT

In this chapter, we have applied exact-exchange Ne, Ar, Kr and Xe. It was previously shown for isolated column VIII atoms that the accurate Kohn-Sham energy gap is an excellent approximation to the optical gap but not to the fundamental (quasi-particle) gap. The EXX KS gaps for these atoms are also in very good agreement (3 % on average) with experimental optical gaps. We asked whether the same holds for the solid phase. In contrast with previous results for sp-semiconductors, the EXX KS gaps in column VIII solids are appreciably smaller than the experimental fundamental gaps, and they are 20% smaller than the experimental optical gaps. It is not clear whether this result refutes the observations for atoms or whether a more accurate correlation functional is necessary. Row X solids are bound by van der Waals effects. Because the functionals applied in this



	Ne	Ar	Kr	Xe
$a_{Expt.}$	8.44	9.94	10.66	11.59
$a_{LDA}$	7.29	9.35	10.13	11.14
$a_{EXX}$	7.23	10.13	11.07	12.66
$a_{EXXc}$	7.06	9.80	10.77	12.06

Table 6.4: Equilibrium cubic lattice spacing (in a.u.) from experiment and calculations. Percents show the deviations of the lattice constant from experiment.

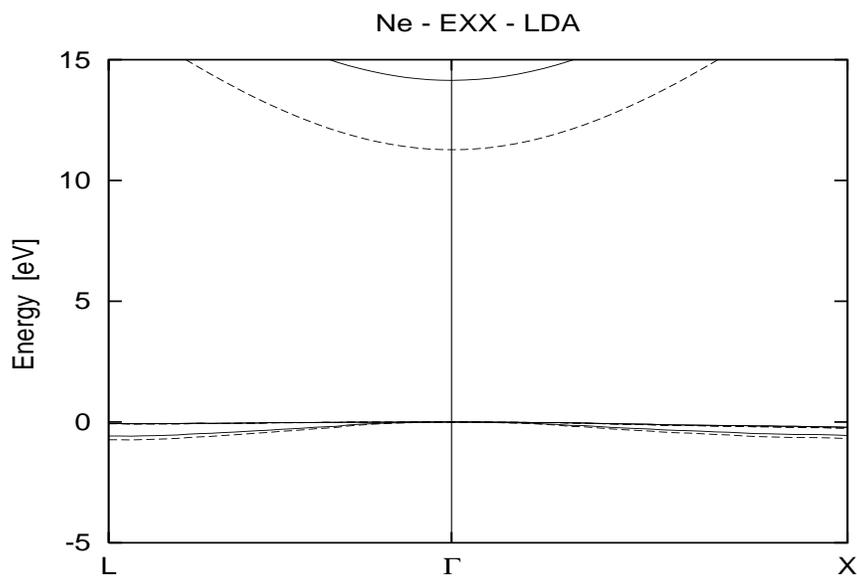


Figure 6.2: Band structure of Ne along the L- $\Gamma$ -X directions as calculated within EXX (solid lines) and LDA (dashed lines).

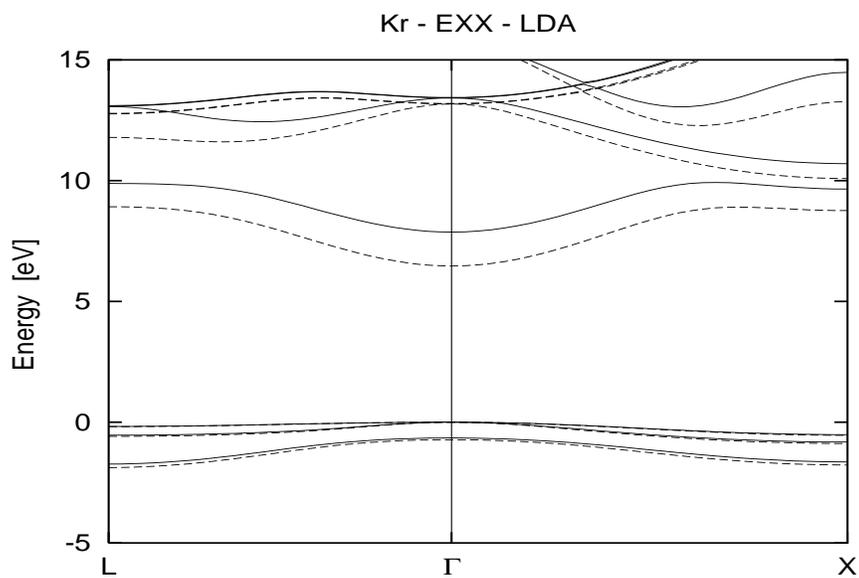


Figure 6.3: Band structure of Kr along the L- $\Gamma$ -X directions as calculated within EXX (solid lines) and LDA (dashed lines).

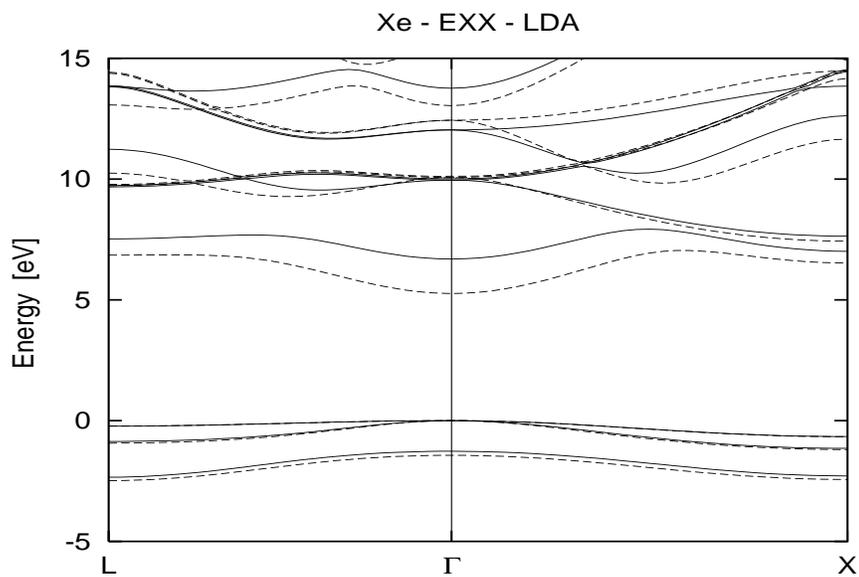


Figure 6.4: Band structure of Xe along the L- $\Gamma$ -X directions as calculated within EXX (solid lines) and LDA (dashed lines).

Ne	LDA	EXX	EXXc
$\Gamma$	-22.98	-24.04	-24.22
	0.00	0.00	0.00
	11.32	14.15	14.76
	29.26	31.71	32.28
X	-22.87	-23.96	-24.14
	-0.62	-0.56	-0.53
	-0.20	-0.22	-0.21
	18.21	21.24	21.91
	19.00	21.79	22.38
L	-22.90	-23.98	-24.16
	-0.69	-0.58	-0.55
	-0.07	-0.06	-0.06
	17.06	19.84	20.42
	17.21	20.05	20.68

Table 6.5: Ne-solid Kohn-Sham eigenvalues in eV from the LDA, EXX and EXX plus LDA correlation (EXXc) schemes at high-symmetry points.

Ar	LDA	EXX	EXXc
$\Gamma$	-14.57	-14.48	-14.51
	0.00	0.00	0.00
	8.16	9.61	10.14
	15.51	16.01	16.37
	17.89	18.08	18.37
X	-14.28	-14.20	-14.25
	-1.27	-1.14	-1.06
	-0.45	-0.42	-0.39
	10.85	12.02	12.57
	12.34	13.24	13.70
L	14.89	16.31	16.67
	-14.35	-14.27	-14.32
	-1.40	-1.25	-1.16
	-0.15	-0.14	-0.14
	11.03	12.17	12.65
	13.29	14.80	15.24
	15.12	15.69	16.09

Table 6.6: Ar-solid Kohn-Sham eigenvalues in eV from the LDA, EXX and EXX plus LDA correlation (EXXc) schemes at high-symmetry points.

Kr	LDA	EXX	EXXc
$\Gamma$	-14.81	-13.74	-14.62
	-0.73	-0.65	-0.67
	0.00	0.00	0.00
	6.47	7.87	8.02
	13.18	13.43	13.80
X	-14.55	-13.45	-14.39
	-1.77	-1.65	-1.59
	-0.88	-0.82	-0.79
	-0.54	-0.52	-0.49
	8.76	9.65	10.05
	10.09	10.70	11.11
	13.28	14.49	14.78
16.94	17.63	17.96	
L	-14.62	-13.53	-14.45
	-1.88	-1.74	-1.66
	-0.59	-0.54	-0.54
	-0.18	-0.18	-0.17
	8.92	9.88	10.16
	11.79	13.07	13.41
	12.77	13.09	13.47

Table 6.7: Kr-solid Kohn-Sham eigenvalues in eV from the LDA, EXX and EXX plus LDA correlation (EXXc) schemes at high-symmetry points. Spin-orbit splittings included.

Xe	LDA	EXX	EXXc
$\Gamma$	-13.01	-11.14	-12.71
	-1.44	-1.27	-1.34
	0.00	0.00	0.00
	5.26	6.69	6.51
	10.07	9.96	10.50
X	-12.70	-10.71	-12.41
	-2.43	-2.29	-2.24
	-1.20	-1.15	-1.09
	-0.67	-0.66	-0.61
	6.53	7.01	7.47
	7.43	7.64	8.17
	11.66	12.62	12.84
14.18	13.85	14.42	
L	-12.77	-10.81	-12.48
	-2.48	-2.34	-2.27
	-0.93	-0.86	-0.85
	-0.23	-0.23	-0.21
	6.85	7.53	7.78
	9.73	9.68	10.22
9.78	9.73	10.28	

Table 6.8: Xe-solid Kohn-Sham eigenvalues in eV from the LDA, EXX and EXX plus LDA correlation (EXXc) schemes at high-symmetry points. Spin-orbit splittings included.

eV	$E_g^{LDA}$	$E_g^{EXX}$	$E_g^{EXXc}$	$E_g^{Expt}$	$\Delta^{Expt}$
Ne	11.32	14.15	14.76	21.4	17.4
Ar	8.16	9.61	9.95	14.2	12.2
Kr	6.47	7.87	8.02	11.6	10.2
Xe	5.26	6.69	6.51	9.8	8.4

Table 6.9: Calculated and measured energy gaps in column VIII solids in eV.  $E_g^{LDA}$ ,  $E_g^{EXX}$  and  $E_g^{EXXc}$  are Kohn-Sham gaps from the LDA, pure EXX and EXX plus LDA correlation schemes respectively.  $E_g^{Expt}$  is the experimental fundamental gap.  $\Delta$  is the experimental optical gap.

	LDA	EXX	$+\Delta_x$	HF	Exp.
Ne	11.3	14.4	25.9	25.1 <sup>a</sup>	21.1 <sup>b</sup>
Ar	8.2	9.6	18.7	18.5 <sup>a</sup>	14.2 <sup>c</sup>
Kr	6.7	8.1	15.8	16.5 <sup>a</sup>	11.6 <sup>d</sup>
Xe	5.7	7.1	14.1	13.5 <sup>a</sup>	9.8 <sup>e</sup>

Table 6.10: Adding the exchange-only derivative discontinuity to the KS gaps at the  $\Gamma$  point. LDA means  $E_{xc}$  for both the core and valence. EXX means exact exchange and no correlation.  $\Delta_x$  is the derivative discontinuity. HF is the all electron Hartree-Fock orbital gap. <sup>a</sup>Ref.[181] <sup>b</sup>Ref.[182] <sup>c</sup>Ref.[183] <sup>d</sup>Ref.[182] <sup>e</sup>Ref.[182]

## Appendix A

### Codes Used in this Thesis

All codes will be available at `pbe@dft.rutgers.edu` in `/home/pbe/rudys_thesis/`.

#### A.1 Codes Specifically Written for this Thesis

- `Deltium.f`

Solves the Bethe-Ansatz equations for the ground-state energy density for Deltium, the one-dimensional uniform Fermi gas.
- `Diracium.f`

Calculates the ground-state energy or related quantities for Diracium, the one-dimensional delta-function-interacting analog of Helium, using a momentum space representation.
- `LDAShoot.f`

Uses the shooting method to solve the KS equations for exact-exchange and LDA in one dimension for a delta-functional external potential.
- `Hooke1d.f`

Uses the shooting method to solve the KS equations for exact-exchange and LDA in one dimension for a harmonic external potential.
- `HookeExact.nb`

Gives the exact ground-state energy for the one-dimensional analog of Hooke's atom. (Mathematica Notebook)

- PolyFit.f  
Fits a set of data points on the interval  $[0,1]$  to various order polynomials.
- GetW.f  
Solves SCE model for two electrons and returns the values for  $U_{xc}(\infty)$  and  $U'_{xc}(\infty)$ .
- WcPoli.f  
Performs similarly to PolyFit.f but uses points  $[0.5,1]$  and 0.
- MakePade.f  
Generates  $U_{xc}(\lambda)$  for various inputs and formulae, most notably, the Interaction Strength Interpolation.
- GetUc.f  
Converts the output of multi, ec.d, to  $U_{xc}(\lambda)$ .
- Superadft.f  
Finds the energy of spin-scaled densities of various atoms. (Doctored version of Adft.f)

## A.2 Major Codes Specifically Used in this Thesis

- Adft.f

Calculates the ground-state energy and related quantities for various atoms in three dimensions using various functional including exact-exchange.

- Multi.f

Finds the various components of the total energy for a given density. The density can be inputted or for Hooke's atom, exactly calculated.

- Exx.f

Solves for the band structure of various compounds using a plane-wave basis, pseudo-potentials, and exact-exchange.

- PWbulk.f

Solves for the band structure of various compounds using a plane-wave basis, pseudo-potential, and the local density approximation.

- fhi98md.f

Gives the exact exchange pseudo-potentials that are used in EXX.f.

<http://www.fhi-berlin.mpg.de/th/flimd/>

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