AN AB INITIO INVESTIGATION OF VAN DER WAALS-RICH SYSTEMS
AND A MACHINE LEARNING APPROACH TO FINDING ANALYTICAL
FUNCTIONS DESCRIBING TABULATED DATA

BY

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<th>Description</th>
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<tr>
<td>CCSD(T)</td>
<td>Coupled cluster with singles, doubles, and perturbative triples</td>
</tr>
<tr>
<td>CI</td>
<td>Configuration interaction</td>
</tr>
<tr>
<td>DFT</td>
<td>Density functional theory</td>
</tr>
<tr>
<td>GGA</td>
<td>Generalized gradient approximation</td>
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<tr>
<td>HF</td>
<td>Hartree-Fock</td>
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<tr>
<td>HOMO</td>
<td>Highest occupied molecular orbital</td>
</tr>
<tr>
<td>LDA</td>
<td>Local density approximation</td>
</tr>
<tr>
<td>MP2</td>
<td>Möller-Plesset perturbation theory at second order</td>
</tr>
<tr>
<td>PBE</td>
<td>Perdew-Burke-Ernzerhof exchange correlation functional</td>
</tr>
<tr>
<td>QE</td>
<td>Quantum-Espresso</td>
</tr>
<tr>
<td>SOMO</td>
<td>Singly occupied molecular orbital</td>
</tr>
<tr>
<td>TISE</td>
<td>Time independent Schrödinger equation</td>
</tr>
<tr>
<td>vdW</td>
<td>Van der Waals</td>
</tr>
<tr>
<td>vdW-DF</td>
<td>Van der Waals density functional</td>
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Abstract

van der Waals interactions are weak, non-specific forces arising at the atomic scale. Although they are weak—much weaker than a covalent or ionic interaction—they occur in large numbers, and in total, can make a significant contribution to the properties of a system. Several systems are herein explored whose properties are influenced strongly by van der Waals interactions. These systems are investigated largely through the non-local van der Waals density functional (vdW-DF) working within density functional theory (DFT), with accurate quantum chemistry calculations and experimental results to serve as a reference against which we compare our results. Properties calculated for \((\text{H}_2\text{O})_n\) with \(n = 1–5\) showed systematic improvement when van der Waals interactions were included. The low-temperature phase of Mg(BH\(_4\))\(_2\) is incorrectly predicted by standard local or semi-local approximations. However, the inclusion of van der Waals interactions brings theory in line with experiment. Dimers of phenalenyl and the nitrogen- and boron-substituted closed-shell analogues show an interesting collection of phenomena, including a 2-electron/multi-center bond and an anomalous barrier in a rotational total energy profile caused by electron kinetic energy. In the final part of this work, the theoretical groundwork is laid for a computational tool that uses network concepts to perform analytical calculations. These network functions are capable of learning the mathematical connection in a set of data. A course to use network functions to improve DFT through a search for a kinetic energy functional and an improved exchange-correlation functional is discussed.
Chapter 1

Introduction

This dissertation is split into three parts covering two very different general themes. The subject of Parts I and II is chemical physics, with a particular emphasis on van der Waals interactions. Part I (Chapters 2 through 4) outlines the theoretical background needed to understand the methods used and Part II (Chapters 5 through 7) discusses these methods’ application to several interesting systems. The second major theme of this dissertation is a machine learning technique, dubbed network functions that uses the idea of computational networks to learn the functional relationship in a set of training data comprised of a set of independent variables and their associated dependent variable. Part III (Chapters 8 and 9) explores these ideas and how they may be used to improve modern density functional theory.

1.1 Chemical Physics

The field of chemical physics is concerned with the physics of chemical systems. These can be anything from metallic crystals to isolated molecules or atoms. Knowledge of how atoms interact within these systems is key to understanding material properties, chemical reactions, biological processes, the environment, and just about every endeavor that is important to humans. For this reason, much work has gone
into developing methods that can accurately model atomic systems to yield energies and other important physical properties. Theory and computation are inextricably linked in this process; new theories allow for the development of new computational methods and computer modeling fosters new theoretical understanding. Additionally, computer modeling is an ideal means of testing new theories, as a large number of systems and properties can be calculated relatively quickly.

Computational methods have been developed over the past 50 years or more that, today, allow for accurate calculation of many properties of interesting chemical systems. The most successful of these methods are based directly on quantum mechanics, which is the governing set of physics at the atomic and molecular scale. Since its development in the 1920’s, quantum mechanics has provided the framework for our understanding of all chemical systems. Not surprisingly, however, its use is fraught with complexity and its demanding computational cost means that the quantum-mechanical treatment of only small systems can be afforded. Nevertheless, tireless methodological and algorithmic advances have progressed the field of computational chemical physics to the point where real questions about macroscopic physics may begin to be answered. Today, methods exist that allow thousands of atoms to be treated with full quantum-mechanical rigor. We are at a junction where simple proteins and strands of DNA may now be accurately modeled. Future developments will likely lead us to a time where quantum-mechanical simulations of full proteins are a routine task. For the moment, the work of method development within the field must continue to allow progression to that point.

There are many systems of interest to chemical physics, but the systems presented in the work herein all have a common component; they are composed of separate molecular fragments whose properties are significantly affected by weak van der Waals interactions. These interactions are ubiquitous in nature and are believed to be strong enough to, for example, allow a gecko to stand on the ceiling.\textsuperscript{1} Furthermore,
the interactions are non-specific, in the sense that they do not require specific geometric arrangements, chemical species, or other special conditions in order to function, though these do play a role in their strength. Despite their prevalence and obvious power, it has been believed for the past decade or more that van der Waals interactions play little role in that vast area of chemical physics concerned with condensed matter. It was believed that atoms in a crystalline environment interact too strongly via other mechanisms for van der Waals interactions to play a significant role. While it is true that van der Waals effects are small compared with e.g. covalent bonds, it is now becoming apparent that their effect is sizable enough to change even qualitative aspects of the behavior of condensed chemical systems,\textsuperscript{2,3} as will be demonstrated in this work. Even in small molecules, where the importance of van der Waals effects has always been known, their consideration is proving necessary to obtain an accurate description of, at times, even qualitative behavior.\textsuperscript{4}

In the work herein, the role of van der Waals interactions will be discussed relative to several systems. Most of these systems were hitherto thought to be adequately treated without explicit inclusion of van der Waals interactions, at least in the sense that addition of van der Waals interactions would not improve agreement with experiment (or high-level theory in the case of small systems). We show that van der Waals interactions play an important role in the qualitative behavior of several systems. Much of this work is afforded by our implementation of the van der Waals density functional (vdW-DF), originally developed by Dion et al.,\textsuperscript{5} within the Quantum-Espresso package.\textsuperscript{6} This functional allows for accurate treatment of van der Waals interactions within density functional theory (DFT), a workhorse computational approach within chemical physics.

This discussion of chemical physics in this work is organized as follows: Chapter 2 will lay out the quantum-mechanical groundwork for computational chemical physics as it is used throughout this work. Chapter 3 will discuss the role of van der Waals
interactions in nature and in chemical physics, including their inclusion in DFT via the vdW-DF, while Chapter 4 lays out some practical considerations that must be kept in mind when running calculations. Part II will move on to applications of the theories to several systems including ice and small water clusters in Chapter 5, crystals of Mg(BH$_4$)$_2$ in Chapter 6, and systems of the bi-radical phenalenyl dimer and some dimers made of closed-shell analogues in Chapter 7.

### 1.2 Network Functions

The second major theme of this dissertation regards a completely different topic that, nevertheless, can be connected back to DFT. Computationally, a function is nothing more than an ordered set of operations, done to a set of inputs, which produces some final output. This can be thought of as a set of nodes, each doing a particular operation or set of operations on its inputs to produce an output. The way these nodes are connected, then, determines what function is being performed on an overall input set $I_0$ to produce an output $\tau$. These abstract nodes can be made in a computer by granting each computational unit the ability to perform a simple computation leading to the carrying out of a set of fundamental operations (e.g. multiplication, addition, exponentiation, and taking the logarithm) on the data. The way these nodes are connected, and the types of operations they can do determine what functions may be represented by them.

A *network function* is nothing more than a function, which is made up of a set of computing nodes, arranged as an acyclic, directed graph. Each computing node can carry out a simple calculation, with the precise details being encapsulated by a trainable set of parameters. These nodes can be linked into complex networks, creating an arbitrary composition of operations, thus many analytical functions can be represented in this way.
Expansion of a function in a set of orthonormal basis functions is routine within computational chemical physics. Typically, this is done by picking a prescribed form for the basis functions and performing a least-squares sense fit to the function being fitted. In principle, a network function can do no worse than standard fitting approaches such as expanding in power or Fourier series, and in practice should do much better. One way to think of the approach is as expanding functions in an arbitrary basis. Not just an adjustable basis, but fully arbitrary and chosen by the computer to provide the best fit. The trick, of course, is figuring out how to turn a collection of computing nodes into a network that can accurately represent a desired function. This boils down to training the network.

Training intelligent networks of any kind is a difficult and laborious process; the situation is the same with network functions. If a sufficient network is trained, however, it becomes the function of interest, taking in the correct number of inputs and yielding identical output over its entire range, including well outside the range of training data. In practice, one would usually get an approximation to the desired function, but it should be a good approximation and it is forever improvable up until the point where it becomes exact, which is often guaranteed to happen with a finite number of nodes. Efficient algorithms for training are paramount to the usefulness of approaches like these.

Network functions tie back to DFT because there are unknown functionals within DFT, the elucidation of which would greatly advance the field. In particular, the kinetic energy cannot, at present, be written accurately as a functional of the density. The ability to write it as such would enable orbital-free DFT calculations, which would not only speed up the calculation of material properties but would also simplify the conceptual framework within which they are calculated. As a second example, the exchange-correlation functional exists to correct DFT for certain quantum-mechanical aspects that are missed in a classical electrodynamics treatment and to add in the
effects of electron correlation, which is intimately linked with material properties. There are many approximations of this functional but all suffer from drawbacks. An improved functional learned from accurately calculated data could advance the field and allow for computation of systems that are otherwise not treated well within DFT.

The theme of network functions is discussed in Part III of this work. The basic background and theory is covered in Chapter 8. Some simple examples are given in Chapter 8 along with future directions including planned uses within density functional theory.
Part I

Background
Chapter 2

Methods of Quantum Mechanics

2.1 The Schrödinger equation

One of the principal ingredients of computational chemical physics is the time independent Schrödinger equation (TISE), written as

\[ \hat{H} |\psi\rangle = E |\psi\rangle , \]  

(2.1)

where \( \hat{H} \) is the Hamiltonian operator, \( E \) is the energy of eigenstate \( |\psi\rangle \), and the unknown function \( |\psi\rangle \) is the wave function, the calculation of which uniquely determines all the observable properties of the system. When specialized to interacting atoms in empty space, the Hamiltonian can be written (in atomic units)

\[ \hat{H} = -\frac{1}{2} \sum_I \frac{1}{M_I} \nabla^2_I - \frac{1}{2} \sum_i \nabla^2_i - \sum_i \sum_I \frac{Z_I}{|\vec{r}_i - \vec{R}_I|} \]

\[ + \sum_{i<j} \frac{1}{|\vec{r}_i - \vec{r}_j|} + V_{ext} + \sum_{I<J} \frac{Z_I Z_J}{|\vec{R}_I - \vec{R}_J|} , \]  

(2.2)

where capital letters refer to nuclear degrees-of-freedom (including nuclear charge \( Z \)) and lower case letters refer to electronic degrees-of-freedom. This convention will be used throughout this work. The terms on the right-hand side of Equation 2.2
give, respectively, the kinetic energy of the nuclei, the kinetic energy of the electrons, the electron-nuclei interaction energy, the electron-electron repulsion, any external potential applied to the system, and the nucleus-nucleus repulsion term. The constant $M_I$ is the mass of the $I^{th}$ nucleus given in electron masses—approximately 1836 times the number of nucleons. The sums in Equation 2.2 run over all pairs of electrons (for the double sum on $i$ and $j$) and all pairs of atomic nuclei (for the double sum on $I$ and $J$).

The usual first approach to simplify Equation 2.2 is to regard the nuclei as classical point particles. The justification for this approach lies in the large value of $M_I$ for many nuclei, which generally makes the first term in the equation relatively small compared to the other terms. Thus, it is sometimes (though not always) a good approximation to regard the first term in Equation 2.2 as small and neglect it. This approximation is known as the Born-Oppenheimer approximation and its use reduces Equation 2.1 to

$$\left[ -\frac{1}{2} \sum_i \nabla_i^2 + \sum_{i<j} \frac{1}{|\vec{r}_i - \vec{r}_j|} + V_{\text{ext}} + \sum_{I<J} \frac{Z_I Z_J}{|\vec{R}_I - \vec{R}_J|} \right] |\psi\rangle = E |\psi\rangle , \quad (2.3)$$

where the potential created by the nuclei at their positions $\{\vec{R}_I\}$ is now considered as part of the external potential in which the electrons are moving. Accordingly, the nuclei-electron interaction term has been absorbed into the external potential, $V_{\text{ext}}$.

The Born-Oppenheimer approximation effectively decouples the nuclear degrees-of-freedom (treated classically) from the electronic degrees-of-freedom (treated quantum mechanically). The final term in brackets in Equation 2.3 is the nucleus-nucleus repulsion energy. Since the Born-Oppenheimer approximation treats nuclei as classical point particles, this term is just an additive constant to the energy and can be disregarded in solving for the wave function.

The Born-Oppenheimer approximation represents a significant simplification of
the TISE, and its use is generally warranted. In fact, it is an excellent approximation for heavy nuclei, but becomes quite poor for light elements, most notably hydrogen. There are many systems where the quantum nature of hydrogen atoms plays a crucial role in the physical behavior.\textsuperscript{7–11}

For the purposes of this work the TISE will be written

\[
\begin{array}{c}
\left[-\frac{1}{2} \sum_i \nabla_i^2 + \sum_{i<j} \frac{1}{|\vec{r}_i - \vec{r}_j|} + V_{\text{ext}}\right]|\psi\rangle = E |\psi\rangle ,
\end{array}
\]

where the first term is the electron kinetic energy, the second is the electron-electron repulsion, \( V_{\text{ext}} \) includes the nuclear potential and any external potential, and the nucleus-nucleus interaction term is a simple constant to be added to the total energy \( E \).

### 2.1.1 Exact Solutions

There are exceedingly few systems for which analytical solutions of Equation 2.4 can be found. These include the hydrogen atom (to be discussed next), the infinite or finite square well, the quantum harmonic oscillator, and various alterations to these. The primary reason Equation 2.4 is difficult to solve is the electron-electron interaction term, which renders the TISE a non-separable partial differential equation. For this reason, many models that seek to find analytical solutions to the TISE assume non-interacting electrons, rendering the equation separable. These approximations are sometimes good, as in the nearly-free electron gas model of metallic conductors.\textsuperscript{12} In general, however, such approaches serve mainly as a starting point to more rigorous numerical approaches.

Practically speaking, a numerically exact solution to the full many-body wave function is intractable for all but the smallest systems anyway. For example, suppose we have a single water molecule with its 10 electrons. The wave function depends on
all 10 sets of coordinates so it is a 30 dimensional function. To store even a binary
function (i.e. either 0 or 1) on a laughably coarse grid of 10 points in each dimension
would take $10^{30}$ bits or about $10^{18}$ TB of storage.

2.1.2 The Hydrogen Atom and Hydrogenic Atoms

Since the hydrogen atom contains only one electron, there is no electron-electron
coupling term and the Schrödinger equation can be separated and solved exactly. The
typical approach taken to solve Equation 2.4 for the hydrogen atom is to separate it
in terms of a radial piece, $\tilde{R}(r)$, and an angular piece, $\tilde{Y}(\theta, \phi)$. The determination of
these functions is messy, but the solutions can be written down exactly as$^{13}$

$$\Psi_{nlm} = \tilde{R}_{nl}(r)Y^m_l(\theta, \phi), \quad (2.5)$$

with

$$\tilde{R}_{nl}(r) = -\left\{ \left( \frac{2Z}{na_0} \right)^3 \frac{(n-l-1)!}{2n [(n+l)!]^3} \right\}^{\frac{1}{2}} e^{-\frac{2}{\rho}} \rho^{l+\frac{1}{2}} \frac{d^{l+1}}{d\rho^{l+1}} \left[ e^{\rho} \frac{d^{n+l}}{d\rho^{n+l}} (\rho^{n+l} e^{-\rho}) \right], \quad (2.6)$$

with $\rho$ defined as

$$\rho = \left( \frac{2Zr}{na_0} \right), \quad (2.7)$$

$Y^m_l(\theta, \phi)$ are the spherical harmonics, and $a_0$ is the Bohr radius, about 0.529 Å. These
wave functions are applicable to hydrogen and, in fact, any atom with atomic number
$Z$ with all but one electron removed. Such atoms are termed hydrogenic atoms since,
with a single electron, they resemble hydrogen with a stronger nuclear charge.

With these wave functions the energy of the various levels can be calculated. In the
absence of spin-orbit coupling and external magnetic fields these levels are degenerate
for any given principal quantum number, \( n \), with energy (in electron volts)

\[
E_n = -13.6 \frac{Z^2}{n^2}.
\]  

(2.8)

The solutions to the hydrogen atom are important in chemical physics because they often form the starting guess for more elaborate methods that allow for multiple electrons within the system. Often when doing a calculation, the starting guess for a wave function is a superposition of hydrogenic wave functions centered on each atom. This linear combination of atomic orbitals is sufficient for some qualitative analysis and represents a good starting guess for most high-level calculations.

### 2.2 Wave Function Methods–Quantum Chemistry

As mentioned in the previous section, exact solutions to Equation 2.4 are rare, so numerical approximations must be used in the vast majority of cases. This is certainly true in chemical physics, where molecules and solids may have many interacting electrons. A class of methods, so called wave function methods, has been developed to solve the TISE approximately.

#### 2.2.1 The Hartree-Fock (HF) Method–Exact Exchange

One of the simplest approaches to find an approximate solution to the TISE is to assume that it is separable with respect to single-particle states. This is the approach taken by the Hartree-Fock (HF) method, which is one of the most widely used and, with some modifications to be discussed below, successful methods in computational chemical physics.\(^{14,15}\)

In the Hartree-Fock approach, one first assumes that the TISE can be separated
into a set of single-electron states, $\phi_i(\vec{r}_j)$, called orbitals. In principle, then, one could write the fully-interacting, many-body wave function for $N$ electrons as

$$\Psi(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N) = \phi_1(\vec{r}_1)\phi_2(\vec{r}_2) \cdots \phi_N(\vec{r}_N).$$  \hspace{1cm} (2.9)$$

In practice there is a problem with this approach, in that it neglects the fermionic nature of the electrons. This can be exactly accounted for in a straightforward way, by taking the right-hand-side of Equation 2.9 to be a single Slater determinant of the orbitals.\textsuperscript{16} That is, to write the fully-interacting, many-body wave function as

$$\Psi(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N) = \frac{1}{(N!)^{\frac{1}{2}}} \det \begin{vmatrix} \phi_1(\vec{r}_1) & \phi_2(\vec{r}_1) & \cdots & \phi_N(\vec{r}_1) \\ \phi_1(\vec{r}_2) & \phi_2(\vec{r}_2) & \cdots & \phi_N(\vec{r}_2) \\ \vdots & \vdots & \ddots \\ \phi_1(\vec{r}_N) & \phi_2(\vec{r}_N) & \cdots & \phi_N(\vec{r}_N) \end{vmatrix}. \hspace{1cm} (2.10)$$

The terms inside the determinant are all permutations of particles $\vec{r}_1 \cdots \vec{r}_N$ in orbitals $\phi_1(\vec{r}) \cdots \phi_N(\vec{r})$. Equation 2.10 forms a special linear combination of solutions of the form of that in Equation 2.9. Equating the wave function to a determinant in this way satisfies both (i) the Pauli-exclusion principle, which states that no two electrons can be in the same quantum state; equating two rows in the matrix gives a determinant of 0, and (ii) the anti-symmetry of a fermion wave function with respect to particle exchange; exchanging two rows in the matrix negates the determinant.

Practically speaking, the Hamiltonian of the HF method depends explicitly on the orbitals themselves through the Exchange and Coulomb operators, so the TISE is generally solved in an iterative, \textit{self-consistent} manner. A starting set of orbitals is guessed, often a linear combination of atomic orbitals, and used to generate the required operators. Plugging these into the TISE and solving for $|\psi\rangle$ yields a new set of orbitals. These can be used to regenerate the operators and continue the iterative
process until the orbitals obtained are self-consistent.

The problem with the Hartree-Fock method is that the TISE is, in general, not separable. The HF approach is a mean-field theory in which the orbitals are calculated assuming only an average orbital-orbital interaction. This misses some crucial physics. In particular, electrons interact via Coulomb forces, which depend critically on the precise positions of the electrons at any given moment, rather than a delocalized charge distribution. The strong Coulomb forces felt between electrons causes them to correlate their motion. This correlation, which is often defined as the difference in energy between an exact calculation and a complete basis set Hartree-Fock treatment, is responsible for most of the interesting effects in chemical physics. Correlation accounts for electrons deviating from “average” behavior and many system exhibit no binding when it is neglected.

Despite the weakness of missing electron correlation, the HF method serves as an excellent starting point for many approaches that seek to account for correlation (these are discussed below). A typical approach with wave function methods is to calculate the HF orbitals, then use them to apply explicit correlation schemes. If done carefully, such techniques produce some of the most accurate calculations currently possible.

2.2.2 Full Configuration Interaction (CI)

The most rigorous way to include the effects of correlation is to use the full configuration interaction method. In full CI, one calculates the Hartree-Fock orbitals as a starting point. Rather than forming $\Psi$ as a single Slater determinant of these orbitals, however, Slater determinants are formed for all possible excitations of electrons from their ground-state orbitals to unoccupied virtual orbitals. A linear combination of these Slater determinants is then used as the many-body wave function. If the basis set used is sufficient, and all possible excitations are considered, this approach yields
the numerically exact solution to the TISE.\textsuperscript{14}

Full CI is rarely used for two main reasons. The most important of these is its scaling behavior. Since all the electrons in the system must be permuted amongst all the orbitals (both occupied and virtual), the method scales factorially with system size. Thus, the full CI approach is utterly intractable for all but the simplest systems. The second problem with the CI approach is that, if the basis set used is not large enough, the method is not size consistent. In other words, if one calculates the energy of a system composed of two well-separated subsystems, the result will not, in general, be equal to the sum of the calculated energies of each subsystem calculated alone. This has to do with the number of excitations possible in the combined versus isolated subsystems. Variants of CI have been devised which are size-consistent, but the poor scaling of the method makes their use relatively uncommon.

2.2.3 Coupled Cluster (CC) Theory

The coupled cluster methods have been devised as an answer to the scaling problem of full CI. In the coupled cluster approach, only some of the possible excitations are accounted for. Generally, one includes either all single and double excitations or singles, doubles, and triples. In the latter case, the triple excitations are usually accounted for perturbatively rather than iteratively as it represents a dramatic saving of time. The method with perturbative triples is dubbed CCSD(T) and is the “gold standard” for quantum-chemical calculations.\textsuperscript{14} CCSD(T) energies are some of the most accurate possible on modern computers.

Coupled cluster theory scales much better than full CI. When triples are included perturbatively it scales as $\mathcal{O}(N^7)$. This makes it much more affordable than full CI but still limits it to relatively small systems of perhaps 30–50 atoms.\textsuperscript{17} Even then, if large basis sets are needed to account for the relevant physics the CCSD(T) method may be out of reach.
2.2.4 Møller-Plesset Perturbation Theory

A substantially cheaper approach is to use Møller-Plesset perturbation theory\(^{18}\) at second order (MP2) or higher orders (MP3, MP4, ...). In Møller-Plesset perturbation theory, one seeks to solve the TISE in the form

\[
\left[ \hat{H}_0 + \lambda \hat{H}' \right] \left| \Psi \right\rangle = E \left| \Psi \right\rangle ,
\]  

(2.11)

where \( \hat{H}_0 \) is a non-interacting Hamiltonian and \( \hat{H}' \), which is assumed to be small in effect relative to \( \hat{H}_0 \), represents the interaction term. The coupling parameter \( \lambda \) is tuned from 0 to 1 and “turns on” the perturbation. The solutions to \( \hat{H}_0 \) must be known, and are used as the starting wave functions. Energies and wave functions can be corrected to any order within a perturbative expansion.\(^{14}\) For example, the first-order correction to the energy of non-degenerate eigenstates is just the expectation value of the perturbing Hamiltonian with respect to the unperturbed eigenfunctions, \( E^{(1)} = \lambda \langle \Psi_0 | H' | \Psi_0 \rangle \).

In practice, the Møller-Plesset series is usually used only up to second order (MP2), as its scaling worsens with higher order and it has been shown that the perturbative series is not well behaved.\(^{19}\) Studies of the perturbative series have shown that solutions taken to higher order may improve, get worse, or oscillate, with little hint as to which is happening in a given situation.\(^{19,20}\) MP2 scales as \( \mathcal{O}(N^5) \) so it is substantially more affordable than coupled cluster methods. Systems of up to 100 atoms or so can be calculated with MP2,\(^{17}\) and results are generally reasonable, though they are not perfect. MP2 is known to over-bind many systems, especially those where \( \pi \)-stacking is involved.\(^{21}\)
2.3 Density Functional Theory (DFT)

Another approach to solve the dimensionality problem inherent in Equation 2.4 is to shift the focus from the many-body wave function, $\Psi(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N)$—a complex-valued function in $3N_{\text{electrons}}$ dimensions—to the charge density, $n(\vec{r})$—a real-valued function in just three spatial dimensions. The density can be readily computed and stored, regardless of the number of electrons. The wave function is the basic variable of a quantum system—all observable properties of the system can be derived from it. The density, while closely related to the wave function, is a distinct object. The theorems of Hohenberg and Kohn\textsuperscript{22} place the density on an equal footing as a basic variable of electronic quantum mechanics.

2.3.1 The Hohenberg-Kohn Theorems

In 1964, Hohenberg and Kohn\textsuperscript{22} published a paper in which they showed that if the energy of the system is written as a functional of the density, $E[n(\vec{r})]$, then the density that minimizes this functional, $n_0(\vec{r})$, is the ground-state density. Further, this ground-state density uniquely determines the potential that generated it. Thus, there is a one-to-one mapping between the density and the potential that gave rise to it. Since the potential uniquely determines the wave function, all electronic properties of the system can, in principle, be determined from $n_0(\vec{r})$.

The Hohenberg-Kohn theorems showed the importance of writing the energy as a density functional, $E[n(\vec{r})]$, but they didn’t say what that functional is. If the density functional were known exactly, it could be minimized to yield the true ground-state density. From there, all electronic properties of the system would be uniquely determined. Unfortunately, the true energy functional for most systems is unknown, so approximations to it must be made.
2.3.2 Kohn-Sham DFT

Real progress in DFT came when Kohn and Sham\textsuperscript{23} realized that, since the density is the key property, one can solve a non-interacting problem designed to give the same ground-state density as the fully interacting one. They then wrote the energy density functional as

$$E[n(\vec{r})] = E_{\text{kin}}[n(\vec{r})] + E_{\text{N-e}}[n(\vec{r})] + E_{\text{e-e}}[n(\vec{r})] + E_{\text{xc}}[n(\vec{r})],$$ \hspace{1cm} (2.12)

where \(E_{\text{kin}}\) is the kinetic energy, \(E_{\text{N-e}}\) is the total nucleus-electron interaction energy, \(E_{\text{e-e}}\) is the electron-electron repulsion energy, and \(E_{\text{xc}}\) is the exchange-correlation energy, which is needed to remove electron self-interaction and account for the many-body effects of electron correlation. If an explicit form of \(E[n(\vec{r})]\) were known, the problem of solving the Schrödinger equation could be completely recast into a functional optimization problem. Since the Hohenberg-Kohn theorems state that the density that minimizes the energy is the true ground-state density, a simple optimization of the energy functional with respect to the density, achieved with the help of the functional derivative \(\frac{\delta E[n(\vec{r})]}{\delta n(\vec{r})}\), would yield all properties of the system. Unfortunately, the true form of the functional \(E[n(\vec{r})]\) is not known, but useful approximations can be made using the form given in Equation 2.12. There are two problem terms in the equation. The first is \(E_{\text{kin}}\), in principle written as a functional of the density, but in practice written as a functional of the Kohn-Sham orbitals as

\[ E_{\text{kin}} = -\frac{1}{2} \sum_i \langle \phi_i | \nabla^2 | \phi_i \rangle. \]

An explicit form for the kinetic-energy as a density functional is not known, but approximations to it have been made and lead to so-called \textit{orbital-free DFT}. Typically, the kinetic energy is left as a functional of the Kohn-Sham orbitals, which can be readily calculated via a self-consistent minimization procedure similar to that commonly used in the Hartree-Fock method. The second problematic term in Equation 2.12 is the exchange-correlation functional, \(E_{\text{xc}}\), which is discussed
2.3.3 Exchange and Correlation

This exchange-correlation functional, $E_{xc}$, must account for all the physics that was lost when a non-interacting system was assumed. The self-interaction must be corrected for in the exchange piece, and all nonlinear effects of electron correlation must be handled properly by the correlation piece of the functional.

The form of $E_{xc}[n(\vec{r})]$ is not known, so in order for Kohn-Sham density functional theory to be a useful method, approximations to $E_{xc}$ must be made. The hope is that the bulk of the relevant physics can be captured in a relatively simple analytical form that can be readily calculated.

2.3.4 Standard Approximations to $E_{xc}[n(\vec{r})]$

The discussion of this section will be limited to the spin-restricted case in which one works with the total density $n(\vec{r})$. The equations herein can be easily extended to the spin-unrestricted case by allowing for two densities, a spin up density, $n_\uparrow(\vec{r})$, and a spin down density, $n_\downarrow(\vec{r})$, with $n(\vec{r}) = n_\uparrow(\vec{r}) + n_\downarrow(\vec{r})$.

One of the simplest approximations to make for $E_{xc}$ is to assume that it is a local functional. That is,

$$E_{xc}^{\text{local}} = \int F(n(\vec{r})) \, d^3 \vec{r},$$

(2.13)

where $F$ is some arbitrary function of the density. In this approximation $E_{xc}$ depends on only a single spatial point at a time.

This is the approach taken in the local density approximation (LDA). This approximation is generally a good one for slowly varying densities, and becomes exact in the limit of a homogeneous electron gas. The exchange part of the kernel function $F$ can be found analytically for the homogeneous electron gas. To find an explicit
form for the correlation part Ceperley and Alder performed quantum monte carlo
calculations on the homogeneous electron gas at various densities.\textsuperscript{24} From this work
came the standard form of the LDA,

\begin{equation}
E_{xc}^{\text{LDA}} = \int n(\vec{r}) \epsilon_{xc}^{\text{UEG}}(n(\vec{r})) \, d^3\vec{r},
\end{equation}

where $\epsilon_{xc}^{\text{UEG}}(n(\vec{r}))$ is the exchange-correlation density of the uniform electron gas at
a density of $n(\vec{r})$. This approximation is good when the density is slowly varying,
as is often the case in tightly packed crystalline environments. The approximation
performs more poorly when highly directional covalent bonds or sparse atomic con-
figurations are present.

The next level of approximation is to allow $E_{xc}$ to be \textit{semi-local}, that is, to allow
$F$ to depend on the charge density and its gradient at each point, as

\begin{equation}
E_{xc}^{\text{semi-local}} = \int F(n(\vec{r}), |\nabla n(\vec{r})|) \, d^3\vec{r}.
\end{equation}

Approximating $E_{xc}$ in this form is called the generalized gradient approximation
\mbox{(GGA)}. A typical form for the GGA is given by the popular functional of Perdew,
Burke, and Ernzerhof (PBE), who write it as\textsuperscript{25}

\begin{equation}
E_{xc}^{\text{PBE}} = \int n(\vec{r}) \epsilon_{xc}^{\text{UEG}} G_{\text{PBE}}(n(\vec{r}), |\nabla n(\vec{r})|) \, d^3\vec{r},
\end{equation}

that is, as the LDA times an \textit{enhancement factor} $G$, which depends on the density
and its gradient at each point $\vec{r}$. The enhancement factor determines the behavior of
the functional away from the LDA, and selection of a precise form gives rise to the
many different flavors of the GGA.

Even further refinement has been made by allowing $F$ to depend on the charge
density, its gradient, and the local kinetic energy density as in

\[ E_{\text{xc}}^{\text{meta-GGA}} = \int F(n(\vec{r}), |\nabla n(\vec{r})|, |\nabla \phi(\vec{r})|^2) d^3\vec{r}. \] (2.17)

Such functionals are known as meta-GGA and serve as some of the most accurate functionals to date, although their construction is not without controversy.\textsuperscript{26} The prime advantage of the meta-GGA formulation is that it casts the exchange-correlation energy into a form that is implicitly non-local in the density. This is accomplished by utilization of the Kohn-Sham orbitals within the functional.

### 2.3.5 The Kohn-Sham Potential

The potential that goes into the Schrödinger equation for a Kohn-Sham DFT calculation is not the true potential. Since the energy is written as a functional of the density, the potential is the functional derivative of that functional with respect to the density. That is,

\[ v^{KS} = \frac{\delta E^{KS}[n(\vec{r})]}{\delta n(\vec{r})}. \] (2.18)

Optimization with respect to this potential guarantees that the Kohn-Sham orbitals found will be variational with respect to the density; an infinitesimal change in the density will yield no change in the overall energy. This is a desirable property to have since the energy found in this way yields a rigorous upper-bound on the ground-state energy. As more basis functions are added, more degrees-of-freedom are added to the wave function and the energy necessarily decreases.

When developing functionals one must be careful that the functional derivative with respect to the density can be obtained, so the functional can be used in a self-consistent calculation. Also, the functional derivative is required for nuclear forces and some other linear-response properties.
2.3.6 The Kohn-Sham Orbitals

The orbitals generated in a Kohn-Sham DFT calculation are those corresponding to a non-interacting system with the same total density as the real system. As such, they have little inherent meaning. The only exception to this is the eigenvalue (energy) associated with the highest-occupied orbital of a finite system. Since the density of a Kohn-Sham calculation is, by construction, equal to that of the true density, the eigenvalue of the highest-occupied Kohn-Sham orbital is correct. This is true because the Kohn-Sham state corresponding to this eigenvalue dominates the long range tail of the density, which is correct by construction.

The Kohn-Sham orbitals are of use in only two places within DFT. The first is in the kinetic energy term for the non-interacting system

\[ T^{KS} = -\frac{1}{2} \sum_i \langle \psi_i | \nabla^2 | \psi_i \rangle = \frac{1}{2} \sum_i \int |\nabla \psi_i(\vec{r})|^2 d^3\vec{r}. \]  

The other place where the Kohn-Sham orbitals may be of use is in modern meta-GGA functionals. As already discussed, such functionals take the kinetic energy density into account when calculating the exchange-correlation interaction.
van der Waals interactions are non-specific, attractive interactions that occur between dynamically polarizable charge distributions. Their prime importance to this work is in systems made of atoms, where the electron clouds around each nucleus can distort, giving rise to an attractive force between atoms. Such forces have been known and well understood for quite some time, but their importance within chemical physics is less understood.

3.1 Physical Origins in Atoms

The electron cloud around the nucleus of an atom is a dynamic entity. It is constantly responding and reacting to both external and internal forces (e.g. fields of other electrons, external fields, nuclear motions). When two atoms are brought together, these fluctuations can correlate, resulting in a net attractive force that draws the two atoms together. The attraction can be thought of as arising from multipole moments set up by the fluctuating electron clouds. This simple physical picture is the basis of the $1/r^6$ dependence of the van der Waals interactions in the asymptotic limit. One can expand the energy of two physically separated, polarizable charge distributions
\[ E = -\frac{C_6}{r^6} - \frac{C_8}{r^8} - \frac{C_{10}}{r^{10}} - \cdots, \] (3.1)

where each term arises from an induced multipole of some order on one distribution interacting with an induced multipole of some order on the other. In Equation 3.1 the \( C_6/r^6 \) term arises from the dipole-dipole interaction, the \( C_8/r^8 \) term arises from a dipole-quadrupole interaction and so forth.

3.2 vdW Interactions in DFT

The explicit inclusion of van der Waals interactions within DFT does not have a particularly long history. Even a decade ago it was thought that van der Waals interactions were too weak to play any significant role in most crystals. Even if they were thought important, the theoretical foundation on which to treat them was not yet developed. Recent work, however, has shown that van der Waals effects are paramount to the correct description of numerous materials, including those for which few would have suspected van der Waals effects to play a role.\(^2\),\(^29\),\(^30\) The ability to calculate these effects accurately within DFT is a relatively recent occurrence, and the methods involved enjoy active, ongoing development.\(^31\)–\(^35\)

3.2.1 Lack of vdW in Standard Approximations

Since the Hohenberg-Kohn theorems state that the ground-state charge density is a basic variable and all properties of the system can be calculated exactly from it, why are van der Waals interactions not automatically included in DFT? The answer lies in the approximations made within exchange-correlation functionals.

As discussed in the previous chapter, most modern exchange-correlation functionals in DFT are local or semi-local in nature; the contribution of a point in the density, \( n(\vec{r}) \), to the exchange-correlation energy depends only on an infinitesimal
neighborhood around $\vec{r}$. This can be written as

$$E_{\text{semi-local}}^{\text{xc}} = \int F\left(n(\vec{r}), \nabla n(\vec{r}), \nabla^2 n(\vec{r}), \ldots \right) d^3\vec{r},$$ \hspace{1cm} (3.2)

where the contribution to the exchange-correlation energy from any point is a function of the charge density, its first derivative, second derivative, etc. \textit{at that same point}. In other words, the (semi)-local functionals utilize a single spatial integral over three dimensions.

If taken to sufficiently high order, an expression like that in 3.2 should yield the correct result. However, in reality we do not know how the functional depends on the higher-order terms in the expansion, nor can we hope to include more than the first few. Keeping only a few terms in the expression means high-order (long ranged) effects will be missed. In addition, densities \textit{in silico} don’t necessarily behave as their continuous-function counterparts. A continuous charge density never goes truly to zero (except at nodes in the wave function), but computed densities routinely reach zero or, even worse, become negative. In practice, an expression like that in Equation 3.2 is unlikely to correctly account for long-ranged effects occurring in the low-density tails of the charge distributions.

To combat this problem, one could write the energy functional explicitly as a non-local functional of the density, as in

$$E_{\text{xc}}^{\text{non-local}}[n(\vec{r})] = \int \int F(n(\vec{r}_1), n(\vec{r}_2)) d^3\vec{r}_1 d^3\vec{r}_2,$$ \hspace{1cm} (3.3)

where the functional now depends on two arbitrary points in the density simultaneously, and, as such, is written as a double spatial integral. This effectively includes high-order effects without needing to go to high-order in the expression in Equation 3.2. The function $F$ can be thought of as the density at points $\vec{r}_1$ and $\vec{r}_2$ times a kernel function that gives the correlation interaction of the densities at those points.
This is the approach taken by the van der Waals density functional, discussed next.

### 3.2.2 The van der Waals Density Functional (vdW-DF)

All the functionals discussed thus far have been local with respect to the density, meaning that each functional’s dependence on the density at a point in space is limited to an infinitesimal neighborhood about that point. Another approach is to allow the functional to be explicitly non-local with respect to the density. One way to do this is to write

$$E_{xc}^{\text{non-local}}[n(\mathbf{r})] = \frac{1}{2} \int \int n(\mathbf{r}_1) \Phi(\mathbf{r}_1, \mathbf{r}_2) n(\mathbf{r}_2) \, d^3r_1 \, d^3r_2,$$

where the functional now depends explicitly on two density points simultaneously. This is a special case of the non-local functional given in Equation 3.3. The kernel function $\Phi(\mathbf{r}_1, \mathbf{r}_2)$ determines how the two points $\mathbf{r}_1$ and $\mathbf{r}_2$ interact to yield the exchange-correlation density at the point $(\mathbf{r}_1, \mathbf{r}_2)$.

The kernel function was first successfully approximated for arbitrary systems by Dion et al., when, starting from the adiabatic-connection and employing some approximations, they expressed it as a function of the variables $d(\mathbf{r}_1, \mathbf{r}_2)$ and $d'(\mathbf{r}_1, \mathbf{r}_2)$, as

$$\Phi(d, d') = \frac{2}{\pi^2} \int a^2 \int b^2 W(a, b) T(a, b, d, d') \, da \, db,$$

where

$$W(a, b) = \frac{1}{a^3 b^3} [(3 - a^2)b \cos(b) \sin(a) + (3 - b^2)a \cos(a) \sin(b) + (a^2 + b^2 - 3) \sin(a) \sin(b) - 3ab \cos(b)].$$
and

\[ T(a, b, d, d') = \left[ \frac{1}{\alpha + \beta} + \frac{1}{\gamma + \omega} \right] \left[ \frac{1}{(\alpha + \gamma)(\beta + \omega)} + \frac{1}{(\alpha + \omega)(\gamma + \beta)} \right], \quad (3.7) \]

with

\[ \alpha(a, d) = \frac{a^2}{2 \left[ 1 - e^{-\frac{4\pi}{9} d^2} \right]} \]
\[ \beta(b, d) = \frac{b^2}{2 \left[ 1 - e^{-\frac{4\pi}{9} d^2} \right]} \]
\[ \gamma(a, d') = \frac{a^2}{2 \left[ 1 - e^{-\frac{4\pi}{9} (d')^2} \right]} \]
\[ \omega(b, d') = \frac{b^2}{2 \left[ 1 - e^{-\frac{4\pi}{9} (d')^2} \right]} . \quad (3.8) \]

The variables \( d \) and \( d' \) are defined as

\[ d = |\vec{r}_1 - \vec{r}_2| \left[ -\frac{4\pi}{3} \epsilon_{xc}^{\text{LDA}} n(\vec{r}_1) + Z_{ab} \frac{\left| \nabla n(\vec{r}_1) \right|^2}{108\pi^2 n(\vec{r}_1)^3} \right] \quad (3.9) \]

and

\[ d' = |\vec{r}_1 - \vec{r}_2| \left[ -\frac{4\pi}{3} \epsilon_{xc}^{\text{LDA}} n(\vec{r}_2) + Z_{ab} \frac{\left| \nabla n(\vec{r}_2) \right|^2}{108\pi^2 n(\vec{r}_2)^3} \right], \quad (3.10) \]

with \( \epsilon_{xc}^{\text{LDA}} \) being the exchange-correlation potential of some accompanying LDA formulation. The factor of \( Z_{ab} = 0.8491 \) in the definitions of \( d \) and \( d' \) is essentially a fitting parameter that can be tuned to provide maximum accuracy with respect to some reference (see for example Reference 34).

The above definition of \( \Phi(\vec{r}_1, \vec{r}_2) \) makes evaluation of the kernel computationally expensive. However, the explicit position-dependence comes only in the distance, \( |\vec{r}_1 - \vec{r}_2| \), so the kernel function can be calculated once in advance and stored for later lookup. Generation of the table can be made very fast because each table value is
independent, meaning the problem is embarrassingly parallel. In practice, the kernel function is calculated and stored on a mesh of points. During a DFT calculation, some form of interpolation is done to evaluate the kernel at arbitrary points. This need to store a large file of tabular data is one of the prime drawbacks of the vdW-DF functional.

One of the reasons for the vdW-DF approach’s success is that it did not try to write the entire exchange-correlation functional as a non-local functional. Instead, it utilized existing local and semi-local functionals and simply added a non-local correction to them. For this reason, the interpretation of the non-local piece of the vdW-DF is hazy. It is not simply the van der Waals contribution to the energy. In fact, since LDA almost always overbinds systems, the vdW-DF non-local contribution is invariably positive, in contrast with the always-negative van der Waals energy. Extraction of the van der Waals energy can be accomplished approximately by comparing energies using the non-local functional to those with this term switched off, but even then the ground is dangerous. This is because turning on the non-local vdW-DF has the effect of both (i) changing the energy associated with a given density and (ii) changing the actual ground-state density itself. It is therefore hard to interpret the energies given by the vdW-DF directly. This is simply one drawback of its use compared with explicit $1/r^6$ correction terms, though it does reduce to a $1/r^6$ distance dependence in the asymptotic limit.

In the original vdW-DF approach of Dion et al., the non-local part of the correlation functional was written

$$E_{\text{xc}}^{\text{non-local}}[n(\vec{r})] = \frac{1}{2} \int \int n(\vec{r}_1) \Phi(\vec{r}_1, \vec{r}_2) n(\vec{r}_2) d^3\vec{r}_1 d^3\vec{r}_2,$$  \hspace{1cm} (3.11)

with the kernel function $\Phi(\vec{r}_1, \vec{r}_2)$ already discussed. This form requires the evaluation of a double integral over 3-dimensional space (i.e. a six-dimensional integral), making
evaluation of the vdW-DF computationally demanding compared with previous GGA functionals. A technique proposed by Román-Pérez and Soler solved this problem in 2009. In this approach they use the convolution theorem to turn the double integral over functions in 3-dimensional space in Equation 3.11 into a single integral over their Fourier transforms. The Fourier transform is already an integral part of plane-wave-based DFT codes, so they are relatively cheap to obtain. This effectively makes the algorithm $O(N \ln(N))$ rather than $O(N^2)$, placing it on par with standard gradient-corrected functionals.

In order for the convolution theorem to hold, the kernel must have a dependence on $\vec{r}$, only through the magnitude $|\vec{r}| = r$. Román-Pérez and Soler achieved this by discretizing the kernel over a mesh of points in “$q$-space”, defined in the original work of Dion et al. as

$$q_i = -\frac{4\pi}{3} \epsilon_{xc}^{\text{LDA}} n(\vec{r}_i) + Z_{ab} \frac{|\nabla n(\vec{r}_i)|^2}{108\pi^2 n(\vec{r}_i)^3}.$$ (3.12)

One may then write $\Phi(\vec{r}_1, \vec{r}_2) = \Phi(q_1, q_2, r_{12})$ for any particular $q_1(n(\vec{r}_1), |\nabla n(\vec{r}_1)|)$ and $q_2(n(\vec{r}_2), |\nabla n(\vec{r}_2)|)$ and the associated distance $|\vec{r}_1 - \vec{r}_2| = r_{12}$, which can be interpolated as

$$\Phi(q_1, q_2, r_{12}) = \sum_{\alpha,\beta} \phi(q_{\alpha}, q_{\beta}, r_{12}) P_{\alpha}(q_1) P_{\beta}(q_2),$$ (3.13)

where $P_{\alpha}$ and $P_{\beta}$ are interpolating polynomials, usually cubic splines, and the mesh of points $q_i$ is chosen to give an accurate interpolation. Typically 20 values are used distributed over a logarithmic mesh, an approach that can be justified by the form of the kernel function. This gives 400 total functions $\phi(q_{\alpha}, q_{\beta}, r)$, which are further interpolated from a mesh of around 1000 values of the scalar variable $r$. This kernel function and the second derivatives required for its interpolation can be precomputed once-and-for-all and stored in a lookup table for use during a computation.
Román-Pérez and Soler go on to define $\Theta_\alpha(\vec{r})$ as

$$\Theta_\alpha(\vec{r}) = n(\vec{r}) P_\alpha(q(n(\vec{r}), |\nabla n(\vec{r})|)) ,$$  

(3.14)

with $P_\alpha$ being the interpolating polynomials of Equation 3.13. With this definition, one can then write,

$$E_{xc}^{\text{non-local}}[n(\vec{r})] = \frac{1}{2} \iint n(\vec{r}_1) \Phi(\vec{r}_1, \vec{r}_2) n(\vec{r}_2) d^3 \vec{r}_1 d^3 \vec{r}_2$$

$$= \frac{1}{2} \sum_{\alpha,\beta} \iint \Theta_\alpha(q_1) \phi_{\alpha,\beta}(r_{12}) \Theta_\beta(q_2) d^3 \vec{r}_1 d^3 \vec{r}_2$$

$$= \frac{1}{2} \sum_{\alpha,\beta} \int \tilde{\Theta}_\alpha^*(\vec{k}) \tilde{\phi}_{\alpha,\beta}(k) \tilde{\Theta}_\beta(k) d^3 \vec{k} ,$$  

(3.15)

where tildes indicate Fourier transformed functions. Thus, the non-local correlation functional is transformed into a single integral over Fourier transforms. This approach is vastly superior in speed to the more straightforward double integral approach and is the method of choice for vdW-DF implementations within a plane-wave code.

### 3.2.3 vdW-DF Within Quantum-Espresso (QE)

Quantum-Espresso is a suite of Fortran programs written to solve the electronic-structure problem within molecules and crystals. It uses a plane-wave basis set and utilizes pseudopotentials to represent the inner core of atoms. Many local and semi-local exchange-correlation functionals are available within QE.

The success of the vdW-DF led us to program an in-house copy of the functional within the open-source QE package. This copy was used for most of the vdW-DF computation in this work. The code, with some additions, later made its way into the official release of QE and is now part of the standard distribution. Some of the calculations in this work were done using the official release version 4.3.1.
Chapter 4

Practical Considerations for Computation

The previous two chapters discussed the basic theory behind quantum-chemistry and density functional theory (DFT) calculations including the treatment of van der Waals interactions within Kohn-Sham DFT. (Explicit inclusion of van der Waals interactions within quantum-chemistry calculations is not necessary since post-Hartree-Fock methods do not miss van der Waals effects the way (semi)-local DFT does.) The following part of this dissertation discusses the application of DFT and quantum-chemistry wave-function methods to various interesting systems in which van der Waals interactions play a key role. This chapter deals with a few practical considerations and details regarding the calculations that were performed.

4.1 Quantum Chemistry Considerations

Computational quantum chemistry (otherwise known as wave-function methods) carried out in this work utilized two main programs—Gaussian \(^ {37}\) and NWchem. \(^ {38}\) Gaussian is a commercial package that is one of the most used quantum chemistry programs. NWchem is an open-source code created at Pacific Northwest National Lab. Both of the codes operate similarly from a user’s perspective, so they will be discussed as one.
4.1.1 Basis Sets

The basis sets used in most wave-function based codes are atom centered, hydrogenic (hydrogen-like) atomic orbitals. These consist of an angular part and a radial part, as discussed in Section 2.1.2. The angular part is generally comprised of spherical harmonics while the radial part is generated by different approaches, depending on the code.

Both Gaussian and NWchem use Gaussian Type Orbitals (GTO) for their calculations. To form a GTO, one attempts to approximate the true form of a hydrogenic radial wave function by way of a sum of Gaussian functions. This is advantageous because integrals involving the actual hydrogenic orbitals must be done numerically and are quite costly. When Gaussian functions are used, the integrations are substantially easier and can be done much faster. Expanding a hydrogenic orbital in a set of Gaussians is a good approximation, even a relatively small distance from the nucleus.

Atom-centered basis functions are well-suited for treating molecules because they reside on the atoms themselves and, as such, do not waste computational power attempting to recreate the wave function in regions of empty space far from the molecule. To be of use, there must be at least enough basis functions (orbitals) to house all the electrons of the system. In practice, such a minimal basis set is insufficient because there is not enough freedom to distort basis functions for effects such as polarization.\textsuperscript{14} The standard approach is to determine the minimum basis set required to house all electrons, then use some multiple of that number. For example, a hydrogen atom needs only a 1s orbital to treat its one electron. If only a single 1s orbital were used however, polarization of the hydrogen atom would not be possible. Adding a second s orbital allows the expansion more freedom in choosing the electron’s placement. Also, adding a p orbital allows for polarization effects since the basis set now has a non-spherical basis function available for use. Basis sets that use two
basis functions for each required orbital are called double zeta (zeta referring to the parameter in the exponential of the hydrogenic wave function. See Section 2.1.2). When three basis functions per orbital are used the basis set is called triple zeta. Basis sets up to sextuple zeta are fairly common for light elements but, in practice, are rarely used. Partly, this is because when large numbers of atom-centered basis functions are used they tend to become linearly dependent, making their use difficult. All quantum-chemistry calculations done in this work used at least double zeta basis sets and triple zeta when they were affordable.

Another important aspect to atom-centered basis sets, especially in systems where long ranged effects (e.g. van der Waals interactions) are expected to play an important role is the introduction of diffuse functions. Diffuse functions are standard hydrogenic orbitals that have lowered values of their exponents to make them less spatially localized. This allows freedom for the atomic wave functions of separated atoms to overlap somewhat and affect each other. Most of the calculations done in this work utilized diffuse functions to help capture van der Waals effects.

Unfortunately, all atom-centered basis functions suffer from a side-effect of the variational principle called basis set superposition error (BSSE). When two atoms are close enough to interact, their basis functions will overlap. When the quantity of interest is the difference in energy between two infinitely-separated monomers (A and B) and an interacting configuration (AB), one can write

\[ \Delta E = E_{AB}(AB) - E_A(A) - E_B(B) \]

where subscripts denote the basis set used and terms in parentheses represent the system that was computed. The problem is that the energy \( E_{AB}(AB) \) is artificially lowered because the basis functions on separate atoms are not orthogonal. The description of the wave function of one monomer is accidentally improved because some
basis functions from the other monomer were available to it. This must lower the energy according to the variational principle. The energy computed as in Equation 4.1 suffers from BSSE in which the superposition of atom-centered basis sets caused an unbalanced lowering of the dimer relative to the isolated monomers.

The simplest solution to the problem is to apply the counterpoise method where the energies of each monomer are calculated using the full basis of the dimer—for example, $E_{AB}(A)$. If one writes

$$\Delta E = E_{AB}(AB) - E_{AB}(A) - E_{AB}(B) \quad (4.2)$$

instead of Equation 4.1, then the BSSE is corrected for by treating the isolated monomers with the full basis that is available to them in the dimer. In all calculations where it was necessary, the BSSE was accounted for by using the counterpoise method given by Equation 4.2.

### 4.1.2 Atomic Relaxation

Wave-function methods scale heavily with system size—$\mathcal{O}(N^5\sim N^7)$ for the most common methods. This makes full relaxation of large molecular systems difficult.

When two isolated molecules are brought together, each will alter its geometry somewhat in response to the other molecule. We could take our notation and add a superscript, denoting the geometry at which the energy is calculated. For example, a superscript of $A$ indicates that the calculation is to be performed at the equilibrium geometry of subsystem $A$. Now, the binding energy equation ideally takes the form

$$\Delta E = E_{AB}^{AB}(AB) - E_{AB}^{A}(A) - E_{AB}^{B}(B), \quad (4.3)$$

with the superscript convention mentioned above. In Equation 4.3, each monomer is calculated in its fully-relaxed state and the dimer is also residing in its fully-relaxed state.
state. This is an expensive calculation, however, because it requires full relaxation of all molecular species. A less accurate but more attainable approach, is to relax each monomer and then bring it rigidly into the dimer in the correct orientation. This saves the relaxation of the full dimer. In practice, the monomer relaxations are generally done in the monomer-only basis, but the counterpoise corrected energy still uses the full dimer basis.

4.2 Computational Density Functional Theory

4.2.1 Quantum-Espresso

Quantum-Espresso\textsuperscript{6} (QE) is a suite of Fortran programs designed to calculate the electronic-structure of molecules and crystals. It is open-source and freely distributed. It also enjoys active development by both the community and a tight-knit group of primary developers. Among other things, QE can perform DFT calculations within the Born-Oppenheimer approximation. It uses a plane-wave basis set with pseudopotentials in place of atoms.

Basis Set

QE uses a plane-wave basis set wherein the system’s wave function is expanded in a set of functions of the form \( Ae^{i((\vec{k}+\vec{G}) \cdot \vec{r})} \). This type of basis set has several advantages over its atom-centered counterparts: (i) a single number, the plane-wave cutoff, determines the size of the basis set, (ii) the functions, when taken over a unit of periodicity, are automatically orthogonal so there is no basis set superposition error, and (iii) plane-waves are periodic, meaning periodic structures such as crystals can be treated naturally with them.

In the calculation of a molecular system, one places the molecules in a box of some predetermined size. Because of the periodic nature of the plane-wave basis,
the wave function outside of this box is forced to be a translational replica of the one in the box. Thus, in molecular systems the molecules are repeated throughout space periodically on a lattice (generally this lattice is chosen to be cubic). The size of the box in which the molecules are placed must be large enough to prevent significant interaction of these periodic images. In practice, the size of the box is treated as a convergence parameter to be checked at the start of any calculations on a new species. The optimal amount of space between periodic images is a matter of debate, but around 10 Å generally gives reasonable results. A larger box is desirable for systems with a large dipole moment, as these can interact over significant ranges.

Another subtle side effect of using periodic boundary conditions is that charged systems cannot be treated directly. The problem is that the charge is also periodically repeated throughout space. This gives an infinite amount of interacting charge. Since this charge is all of the same sign, the energy becomes infinite. To combat this problem, calculations of charged systems generally use either counterions to balance the charge or a jellium background. In either case, care must be taken to ensure that the energies calculated are realistic for the system of interest and do not simply reflect the choice of charge compensation.

**Pseudopotentials**

The compact nature of the orbitals within a small radius of the core of an atom coupled with the requirement that they be orthogonal to outer states makes them difficult to represent in a plane-wave basis. Typically, one might have to increase the plane-wave cutoff by an order of magnitude or more to properly capture the fast oscillations of the orbitals near the core. To combat this effect, pseudopotentials are often used in plane-wave codes. The pseudopotential takes away the strong Coulomb attraction of the atomic nucleus and replaces it with a softer potential. This, in turn, makes the wave function a smoother function in space, requiring fewer plane-waves to
properly represent it. The pseudopotential used must, of course, conform to certain constraints for this to be a viable approximation.

Several different types of pseudopotentials exist. The primary difference between the types of pseudopotential are the exact parameters used in their construction and the underlying constraints they are forced to satisfy. Generating pseudopotentials can be quite tricky, and great care must be taken in their construction to produce accurate, transferable pseudopotentials. A pseudopotential is generated for a given element by first performing an all-electron calculation on the free atom. In general, a pseudopotential must produce pseudo-valence wave functions that are identical to their all-electron counterparts outside a chosen cutoff radius $r_c$. The cutoff radius must be chosen carefully. Too large a value makes the pseudopotential require less plane-waves to model valence electrons but only at a loss of transferability. Too small a $r_c$ yields little benefit over use of the full $1/r$ potential, as many plane-waves will still be required to accurately model the wave function. Once the cutoff radius is chosen, the radial Kohn-Sham equation is solved to produce a set of states whose wave functions match the all-electron wave functions beyond $r_c$ and whose eigenvalues are identical to the all-electron case. Norm-conserving (NC) pseudopotentials are further required to produce pseudized wave functions with the same norm as the all-electron wave functions. This guarantees that scattering properties are reproduced correctly and that the charge in each pseudo-wave function is correct. Ultrasoft (US) pseudopotentials achieve this by instead adding charge augmentation functions within the core region to recover the correct charge.

The pseudopotentials used in this work were generally of the ultrasoft variety. These require fewer plane-waves to adequately model the wave function. In this work, the cutoffs chosen for use with the US pseudopotentials were generally higher than would normally be used in conjunction with US pseudopotentials. This was done to allow greater accuracy in modeling the valence wave functions to increase
the usefulness of their representation. Ideally, all pseudopotentials would have been
generated using the vdW-DF, but general pseudopotential generation codes do not
yet have this capability. For this reason, pseudopotentials generated with the PBE
functional were used. It is not clear how much of an effect the vdW-DF will have on
an atomic pseudopotential since van der Waals interactions are generally thought of
as occurring between separated atoms rather than within a single atom.

**Functionals Used**

The choice of functional in DFT is paramount to capturing the effects that are impor-
tant for a given system. Since van der Waals interactions were the general quantity of
interest in the work herein, all calculations were done with the vdW-DF. The vdW-
DF must be paired with an appropriate local exchange-correlation functional. In the
work herein, the exchange functional was taken as Slater local exchange augmented
with a revised PBE gradient correction.\(^39\) The local correlation used was the func-
tional of Perdew and Wang.\(^40\) Often, for comparison purposes calculations were also
done with an LDA functional (generally Slater exchange with Perdew-Wang local
correlation) and a GGA functional (generally the PBE\(^25\) functional). These two local
functionals (discussed in Section 2.3.4) were selected because they represent two of
the most common choices for physicists and chemists using local functionals for their
DFT studies.

**4.2.2 NWchem**

The basis sets used in NWchem for its DFT modules are identical to those used for its
quantum chemistry functionality. The same considerations of BSSE and suitability
of the basis apply.
Functionals Used

One key feature of NWchem is its large number of available exchange and correlation functionals, and the ease with which they can be combined in complex ways. The vdW-DF has not yet been implemented in NWchem (or any other atom-centered basis code), but there are a wide range of local, semi-local, and meta-GGA functionals to choose from. In this work, DFT within NWchem was mainly used as a survey of different functionals.
Part II

Applications
Chapter 5

van der Waals Interactions in H₂O Systems

There is, perhaps, no more important molecule to understand than water. It makes up a large fraction of the surface of the Earth and the majority of life as we know it. Despite this, first-principles approaches to model the properties of water suffer from some serious limitations in their abilities to accurately model important properties. Vibrational frequencies, geometries, dipole moments, binding energies, self-diffusion coefficients, the radial distribution function, and even the phase diagram are incorrectly predicted by most DFT methods. The high-level quantum-chemistry methods discussed in Section 2.2 can correctly predict many properties of small water clusters, but their poor scaling limits their usefulness to clusters of no more than 5–10 water molecules, far too few to extend predictions to bulk-like water. Density functional theory is capable of treating much larger systems, and can handle systems that mimic bulk behavior, but the common functionals typically used miss some important physics and render the predictions poor.

In this work, we use the vdW-DF to calculate properties of small water clusters, \((\text{H}_2\text{O})_n\) with \(n = 1–5\) and hexagonal ice \(\text{I}_h\). We demonstrate how inclusion of van der Waals interactions can greatly improve the predictive power of DFT with respect to these systems.
5.1 Water as a Chemical System

The water molecule is fairly simple as molecules go, containing only three atoms and 10 electrons. As such, the properties of a single water molecule are fairly well understood. This can be attributed both to the ability of high-level quantum chemistry methods to treat such a small system and to the presence of only covalent bonds in the system, which can be treated relatively well by standard DFT functionals.

Adding more water molecules to the system complicates things immensely. Now, the system is no longer comprised purely of covalent bonds since water molecules can engage in hydrogen bonding. Hydrogen bonds are a non-local effect in which a hydrogen covalently bonded to a highly electronegative atom obtains a partial positive charge. This can then interact with a lone electron pair on another atom setting up an interaction that can be quite strong, perhaps 5–10 kcal/mol. As will be demonstrated in the following, local and semi-local functionals show a systematic inability to treat such an interaction, and this failure permeates to the prediction of a host of water’s properties.

5.2 Water in the Literature

Owing to the importance of developing a good understanding of the bulk behavior of water, numerous computational studies have been carried out on both water clusters and bulk water. The most successful of these, in terms of predicting macroscopic behavior, come from classical force-field approaches.\textsuperscript{41–44} Such methods allow for computation on very large systems and for very long times, effectively removing finite size and sampling errors from the calculations. These approaches can obtain accurate predictions of most macroscopic properties such as the phase diagram, self-diffusion coefficients, and the radial distribution function. However, the fact that these models are generally parameterized to get macroscopic properties correct limits
their usefulness in elucidating new physics and developing an understanding of water as a chemical system.

Much of what we understand today about water’s properties comes from high-level quantum-chemistry calculations. These have investigated small water clusters \((\text{H}_2\text{O})_n\) with \(n\) up to about 6. The geometries,\(^{45,46}\) binding energies,\(^{45,47,48}\) vibrational properties,\(^{46}\) and electrostatic characteristics\(^{49}\) of these molecules are predicted well by such methods. However, as discussed in Section 2.2, the poor scaling of these methods with respect to system size renders them incapable of treating bulk-like water.\(^{17}\) This deficiency has led to the investigation of larger aggregates of water using density functional theory.

It has been known for quite some time that DFT, utilizing standard functionals, does a poor job of describing water in the bulk. The oxygen-oxygen radial distribution function, which describes the conditional probability of finding an oxygen at a particular radius given that there is one at the origin, shows a distinct over-structuring of water.\(^{29,50-55}\) That is, the first coordination shell is substantially overpopulated using most functionals. This result has been observed by many groups using different codes, functionals, and approaches. Further, the self-diffusion coefficient, which describes how easily a water molecule can diffuse through the bulk, is generally predicted to be several times too small with standard functionals.\(^{29,53,55}\) Even more dramatic, Sit and Marzari\(^{55}\) carried out careful molecular dynamics simulations to determine the melting point of ice within the PBE functional. Their results placed the melting point somewhere between 375 and 400 K, alarmingly far from the known experimental value.

This failure of DFT to correctly predict properties of water is not limited to the bulk. In the same study, Sit and Marzari\(^{55}\) calculated the vibrational frequencies of the water dimer with the PBE functional. They found that some modes were predicted accurately relative to experiment, but some showed errors of 25% or more.
They proposed, as have others, that improper treatment of van der Waals interactions within the PBE functional might be partly to blame for the poor results.\textsuperscript{29,53,55} This assessment was partially corroborated when a recent study\textsuperscript{56} found that the prediction of the bulk modulus, which describes the energetic cost of uniform compression of a solid, of ice is substantially improved when the vdW-DF is used rather than standard semi-local approximations. Further, it has been noted that inclusion of van der Waals interactions, even in a semi-empirical manner, improves the over-structuring of water evident in the oxygen-oxygen radial distribution function.\textsuperscript{29,53}

### 5.3 Aim of this Work

The work described in this chapter was undertaken to determine if proper inclusion of van der Waals interactions might resolve some of the difficulties in predicting water properties with density functional theory. In particular, we sought to examine the error in vibrational frequencies of small water clusters and the predicted melting point of ice I\textsubscript{h} to determine if van der Waals effects play an important role in these properties.

### 5.4 Computational Details

All DFT calculations performed in this work were carried out using PWscf within the Quantum-Espresso package. Ultrasoft pseudopotentials were used with plane-wave and charge-density cutoffs of 35 Ry and 420 Ry, respectively. A self-consistency convergence criterion of $1 \times 10^{-10}$ Ry was used to ensure accurate energies and forces. Forces were considered converged when each component of each force was less than $1 \times 10^{-5}$ Ry/bohr in the water clusters and $1 \times 10^{-4}$ Ry/bohr for ice I\textsubscript{h}. Unit cell parameters for ice I\textsubscript{h} were relaxed until the residual pressure was less than 1 kbar. Interactions between periodic images were minimized by guaranteeing a separation of
at least 10 Å between any atom and any atoms in a neighboring cell. For comparison purposes, three functionals were used for all calculations: LDA, PBE, and vdW-DF.

For the wave-function based calculations, Møller-Plesset perturbation theory calculations were performed within the Gaussian quantum-chemistry package employing Dunning’s correlation consistent triple zeta basis set including diffuse functions (aug-cc-pVTZ). It has been shown that this basis set is sufficient to obtain relatively converged properties of water clusters, and tests with the larger quadruple zeta, aug-cc-pVQZ basis set confirmed only minimal changes in the properties of interest here. Additionally, the MP2 binding energies obtained herein were all within 5% of those reported by Santra et al., who extrapolated their results to the complete basis-set limit. Counterpoise corrections proved negligible for some of properties of interest here, but in testing they did alter vibrational frequencies by as much as 6%, so counterpoise corrections are included in all calculations performed in this work.

Vibrational frequencies for the DFT methods were calculated within the harmonic approximation. The dynamical matrix was built by displacing each atom in each spatial dimension by ±0.0025, ±0.005, ±0.0075, and ±0.01 Å and using a 9-point formula to determine the first derivative of atomic forces (i.e. the second derivative of the energy with respect to atomic displacements). Vibrational frequencies for the MP2 method were calculated directly by the Gaussian code used. Other properties were calculated from converged geometries or charge densities obtained within the DFT or MP2 runs.

### 5.5 Vibrational Frequencies

The vibrational frequencies predicted by LDA, PBE, and vdW-DF for the water monomer are shown in the top panel of Figure 5.1. This figure gives the vibrational frequencies (reported as a wavenumber in cm$^{-1}$) of each mode using the three func-
Figure 5.1: Vibrational frequencies for the water monomer, dimer, and trimer as predicted by LDA, PBE, and vdW-DF and compared with experimental values. The vertical axis is an arbitrary mode index and the horizontal axis gives the wavenumber of a mode in cm⁻¹. The gray box at left indicates the region of low frequency modes that were left out due to numerical difficulties with the computation of such low-frequency modes. The vertical line represents the split between inter-molecular and intra-molecular modes. Several important dimer modes, which will be discussed, are labeled in the figure. Figure reprinted with permission from Reference 4 © American Physical Society, 2011.

Since the water monomer is made up entirely of covalent bonds, all DFT methods do a reasonable job at predicting the vibrational frequencies for this system. This can be clearly seen in the figure. When more molecules are added, however, the situation changes. Hydrogen bonds present between the molecules alter the effective force constants governing the vibrational frequencies. The different functionals have varying degrees of success in modeling these weak interactions and there is a concomitant spread in the predicted frequencies from the various methods. This spread is most evident in the
high-frequency region of the inter-molecular modes (i.e. modes corresponding to relatively rigid molecular motions with respect to one another) and the lower-frequency region of intra-molecular modes (i.e. modes corresponding to oscillations within one or more molecules). This can be seen in the dimer and trimer panels of Figure 5.1. In particular, LDA and PBE tend to overestimate the frequency of the low-frequency modes and underestimate the frequency of higher-frequency modes. The vdW-DF also tends to overpredict the frequencies of intra-molecular modes but also tends to overpredict the frequencies of inter-molecular modes in most cases. There are some modes, most notably those around 1600 cm$^{-1}$, which correspond to angle flexes within molecules, that are predicted well by all methods.

For completeness, Figure 5.3 gives histograms of the error in vibrational frequencies with respect to MP2 calculations for each of the three functionals used here. The trends visible in the specific frequency plots show up in the histograms as a bi-
Figure 5.3: Histograms of errors in vibrational frequencies with respect to MP2 calculations for (top) LDA, (middle) PBE, and (bottom) vdW-DF. Note that LDA shows a strong bi-modal distribution with a large spread, corresponding to the overestimation of inter-molecular frequencies and an underestimation of intra-molecular frequencies. PBE also exhibits a bi-modal distribution but it is less pronounced and with less spread. The vdW-DF results do not exhibit a strong bi-modal distribution and tend to be clustered relatively tightly around 0% error, though with a slight overall tendency to overestimate frequencies. Figure reprinted with permission from Reference 4 © American Physical Society, 2011.

modal distribution. LDA shows a strong bi-modal distribution in errors, with some centered a little under zero error and another group centered near 40%. There is also a wide spread in the distribution of the LDA results. Results from PBE also show a bi-modal distribution but with less variance and a smaller separation between peaks. The vdW-DF results do not exhibit the same bi-modal character as the other methods, and the errors are clustered much more tightly around 0%.

The trends visible in the histograms in Figure 5.3 and in Figures 5.1 and 5.2 are not constrained to small water clusters but continue into bulk ice I$_h$. Figure 5.4 shows the vibrational frequencies calculated with LDA, PBE, and vdW-DF for
Figure 5.4: Predicted vibrational frequencies for ice I$_h$ by LDA, PBE, and vdW-DF. Again, the vertical axis is an arbitrary mode index and the horizontal axis gives the mode frequency in cm$^{-1}$. Note the substantial splitting between the methods for the high-frequency inter-molecular modes and the low-frequency intra-molecular modes. Also note that, as with the smaller water clusters, the angle flex mode is obtained accurately by all methods. Figure reprinted with permission from Reference 4 © American Physical Society, 2011.

standard hexagonal ice I$_h$. The same trends are apparent, with a large splitting between the methods especially on higher-frequency inter-molecular modes and the lower-frequency intra-molecular modes.

A careful examination of the prototypical water dimer can elucidate the reason for the observed trend in predicted vibrational frequencies. Figure 5.5 shows the charge density plotted on a line between a covalently bonded oxygen and hydrogen atom (solid line) and a hydrogen bonded oxygen and hydrogen atom (dashed line). LDA, PBE, and vdW-DF all predict similar charge density distributions for the covalently
bonded pair. This is consistent with the reasonable ability of all methods to obtain accurate properties for covalently linked molecules. There is substantial difference (by as much as a factor of 2) in the predicted charge density along the hydrogen bonded path, however. All methods place the bulk of the charge density nearer the oxygen atom, but LDA and PBE each place more charge density in the interstitial region. This tends to strengthen the hydrogen bond interaction as predicted by LDA and PBE compared with vdW-DF.

Armed with the knowledge that LDA and PBE artificially strengthen the hydrogen bond, we can understand the trends visible in Figures 5.1–5.4. Returning to the dimer...
as a prototypical case, Figure 5.6 shows the total energy as a function of oscillation along the particular modes labeled in the dimer portion of Figure 5.1. The figure also shows how this energy is partitioned into contributions coming from the change in geometry of each monomer and the changing interaction energy between them. This partitioning was performed as follows.

The change in energy of any dimer configuration relative to the equilibrium geometry can be written

\[ \Delta E_{\text{total}} = \Delta E_{M1} + \Delta E_{M2} + \Delta E_{\text{Int}}, \]  

(5.1)

where \( \Delta E_{M1} \) and \( \Delta E_{M2} \) are the strain energies in monomers one and two and \( \Delta E_{\text{Int}} \) is the change in their interaction energy. As the system is forced a small distance along a particular mode, the individual terms in Equation 5.1 can increase, decrease, or remain unchanged, depending on whether they enhance, inhibit, or are irrelevant to the change in energy for small excitations along the mode. For the plots in Figure 5.6, displacements were made along normalized eigenvectors up to a maximum displacement of 0.1 times the eigenvector, and the components of the energy according to Equation 5.1 were calculated.

Mode \( \alpha \) is an inter-molecular mode in which monomer 1 flexes and rocks relative to the largely stationary monomer 2. The force constant for this particular mode is relatively small, as can be seen in the \( E_{\text{total}} \) curve for mode \( \alpha \) in Figure 5.6(a). The motion of mode \( \alpha \) changes the hydrogen bonding geometry appreciably. Since each method overpredicts the strength of the hydrogen bond by some amount, the force constants for this mode are also overpredicted. The overprediction of the vibrational frequency for mode \( \alpha \) within LDA and PBE results from the insufficient treatment of the hydrogen bond.

The same arguments hold for the dimer mode \( \gamma \), which consists of a symmetric
stretch in monomer 1 coupled with a relatively stationary monomer 2. The stretch-
ing of the hydrogen participating in the hydrogen bond changes the hydrogen bond
gometry dramatically, resulting in the poor prediction of the frequencies from LDA
and PBE.

The dimer modes $\beta$ and $\delta$ correspond to modes in which the hydrogen bonding
gometry is relatively unaffected. The relative spread in mode oscillation energies is
quite small, resulting in good prediction of mode frequencies by all functionals.

5.6 Other Physical Properties

Vibrational frequencies are not the only property whose DFT description can be
improved with proper inclusion of van der Waals interactions. Figure 5.7 shows a
systematic improvement in the binding energies, oxygen-oxygen separation distance,
and dipole moments of small water clusters and ice $I_h$ when using vdw-DF instead
of LDA or PBE. As can be seen in the figure, LDA and PBE tend to overpredict the
binding energy of all the small water clusters and ice. In addition, they underpredict
the oxygen-oxygen separation distance. Both of these results are consistent with the
overestimation of the hydrogen bond strength that is elucidated in Figure 5.5. Figure
5.7 also shows that vdw-DF does a better job at predicting dipole moments of the
small water clusters as compared to experiment and MP2 calculations. This may be a
result of a more accurate distribution of charge throughout the bonding region when
using the vdw-DF.

5.7 Melting Point Estimate of Ice $I_h$

The computational resources to accurately calculate the melting point of ice using
density functional theory were out of reach of the current project, particularly since
the vdw-DF has not yet been implemented in an efficient molecular dynamics code.
Nevertheless, a rough estimate of the melting point can be made as follows.

The change in Gibbs free energy of a process ($\Delta G$) is defined as $\Delta G = \Delta H - T \Delta S$, where $\Delta H$ and $\Delta S$ are the changes in enthalpy and entropy, respectively during the process and $T$ is the absolute temperature. At the melting point of a material, the change in Gibbs free energy for the solid-liquid phase transition is zero. Thus, if one knows the change in enthalpy and entropy upon melting, the melting temperature can be calculated. To estimate $\Delta H$, a classical TIP4P molecular dynamics simulation of 64 water molecules at 300 K was carried out. The total simulation time was 5 ns, the final nanosecond of which (in 0.5 ps steps) was used for analysis, resulting in 2000 total structures analyzed. The classical simulation was used merely to produce an ensemble of configurations consistent with liquid water just above its melting point, something TIP4P is known to do well. The total energy of each of the 2000 configurations was then calculated via DFT using each of the three functionals. The expectation value of the cohesive energy for the liquid-like state minus that of the ice structure gives an estimate of $\Delta H$ for melting under a particular functional. (Technically, this gives the change in internal energy, but the small volume change for the solid-liquid transition means that P-V work can be safely neglected for any reasonable pressure.) This is calculated as

$$\langle E \rangle = \frac{\sum_i E_i e^{\frac{E_i}{k_B T}}}{\sum_j e^{\frac{E_j}{k_B T}}},$$

(5.2)

where the sums over $i$ and $j$ run over all of the 2000 structures.

At the melting point, the change in Gibbs free energy is zero. Thus, we can write

$$\Delta H_{\text{PBE}} = T_{\text{PBE}} \Delta S_{\text{PBE}} ,$$

(5.3)

and

$$\Delta H_{\text{vdW-DF}} = T_{\text{vdW-DF}} \Delta S_{\text{vdW-DF}} .$$

(5.4)
Using our PBE value of $\Delta H_{PBE} = 33.4$ kJ/mol and the 375–400 K melting temperature found by Sit and Marzari, we can estimate the change in entropy for the melting process to be $\Delta S_{PBE} = 83.5–89.02$ kJ/mol. Although this result was calculated with the PBE functional, it is not hard to see that it is universal to the three functionals since (1) all functionals started with essentially the same (proton ordered) ice structure and (2) the ensemble of configurations in the liquid state was identical for the three functionals. Thus, we can use this value of $\Delta S$, along with our calculated vdW-DF value of $\Delta H_{vdW-DF} = 24.55$ kJ/mol to obtain an approximate vdW-DF melting point, $T_{vdW-DF}$, between 276 and 294 K, tantalizingly close to the experimental value. This estimate is very approximate and should not be used as a substitute for careful molecular dynamics simulations to determine the melting point more precisely, but it does hint that the over-binding present in PBE may be responsible for the high melting point of ice under this functional, and that this may be corrected somewhat by a proper treatment of van der Waals interactions.

5.8 Conclusions

It is clear that a proper inclusion of van der Waals interactions systematically improves the description of water within DFT, both in small clusters and in bulk-like liquid and ice. The improvement is not perfect, however, and it is interesting to note that significant work done outside of the Born-Oppenheimer approximation suggest that quantum nuclear effects for the hydrogens may play an important role in both the static and dynamic properties of water.\textsuperscript{58–61} Calculations including these effects could not be carried out here, but they do provide promise of the ability of DFT, when used with an appropriate van der Waals functional, to ultimately predict accurate properties for water-based systems, resolving the long-standing failure of DFT within such systems.
Figure 5.6: Total energy as a function of oscillation distance along various modes as measured by a dimensionless progress variable. Also shown are the energy contributions from each monomer ($E_{M1}$ and $E_{M2}$) and the interaction energy ($E_{Int}$). The pictures on the top of each set of plots show the modes being explored. The mode labels correspond to the modes labeled in Figure 5.1. The modes in (a) are examples of modes which exhibit a spread in frequency predictions between the three functionals. The modes in (b) are examples of modes whose frequencies are relatively well predicted by all functionals. Figure reprinted with permission from Reference 4 © American Physical Society, 2011.
Figure 5.7: Systematic improvement in the prediction of water properties when using vdw-DF over LDA or PBE. (a) The binding energy of small water clusters and ice I$_h$ as calculated by LDA, PBE, and vdw-DF compared with MP2 calculations. (b) mean oxygen-oxygen separation as calculated by the three functionals compared with experiment and MP2 calculations. (c) Dipole moment as calculated by the three functionals compared with MP2 calculations. Figure reprinted with permission from Reference 4 © American Physical Society, 2011.
Chapter 6

van der Waals Interactions in Mg(BH₄)₂

Mg(BH₄)₂ has attracted attention recently as a potential hydrogen storage material for automobile use. Despite this interest, there has been much debate in the literature regarding the identity of the low-temperature phase of Mg(BH₄)₂. Experimentalists using X-ray and neutron diffraction were able to determine the space group for the low-temperature phase, but numerous attempts to calculate it within DFT converged on wrong phases. In this work, we were able to align theory and experiment by showing that van der Waals interactions play a role in determining the low-temperature phase of the material. It is not surprising that this was missed in previous work, since the vast majority of the interactions within Mg(BH₄)₂ are covalent (the hydrogen atoms are covalently bound to the boron) and electrostatic (the magnesium atom has a partial positive charge and the BH₄ groups have a partial negative charge). When van der Waals interactions are included, either through first-principles or a semi-empirical correction to DFT, the experimentally observed structure is lowered in energy relative to previously reported potential ground-state phases.
6.1 Hydrogen Storage

The demand for cleaner and more sustainable energy sources has led to interest in hydrogen as an alternative to hydrocarbon fuels. Hydrogen for automobiles can be produced from electrolysis of water and either burned in an internal combustion engine or used in a fuel cell. Under ambient conditions pure hydrogen is a gas with a large volume. Storing enough hydrogen in gaseous form to travel for any appreciable distance in a car would require approximately 45 m$^3$ of hydrogen storage space.\textsuperscript{62} Compression of hydrogen into a liquid takes extreme pressures that are difficult to achieve in a lightweight mobile system. For this reason, scientists are looking into materials capable of storing hydrogen reversibly. Ideally, these materials can uptake hydrogen to a high mass-percentage, store it stably under ambient conditions, and release it easily under relatively mild conditions.

Good hydrogen storage materials must satisfy a number of practical constraints. The material must be light, with much of its mass being attributed to the hydrogen it stores. A heavy material will be too costly to carry around, leaving less residual energy to drive the vehicle. Additionally, it must be able to uptake hydrogen easily, store it stably, and release it again on demand. This reversible storage of hydrogen requires a delicate balance of hydrogen binding energy with environmental conditions. If the hydrogen binds too strongly to the material, it will not be able to be removed efficiently for use in the vehicle. If it binds too weakly, it may leak out before it is ready to be used.

Mg(BH$_4$)$_2$ has attracted attention as a hydrogen storage material because it is capable of storing a large amount of hydrogen—14.9% by mass. The hydrogen in Mg(BH$_4$)$_2$ is covalently bound to boron atoms, making the material extremely stable under ambient conditions. The material does not release hydrogen until temperatures reach 573 K,\textsuperscript{63} so removing hydrogen is difficult. This has led some to propose destabilization of the material by mixing it with other hydrides\textsuperscript{64-66} or by alloying it...
specifically with other metal borohydrides. To perform any type of destabilization, however, the low-temperature \((T \lesssim 400 \text{ K})\) phase must be known and understood. The next section discusses previous attempts in the literature to answer this question.

### 6.2 The Debate Over \(\text{Mg(BH}_4\text{)}_2\) in the Literature

The phase diagram of \(\text{Mg(BH}_4\text{)}_2\) is of great importance if it is to be used as a hydrogen storage material. In particular, a good understanding of the low-temperature phase of the material is needed. The low-temperature phase of \(\text{Mg(BH}_4\text{)}_2\) has been hotly debated in the literature for half a decade. An early study of \(\text{Mg(BH}_4\text{)}_2\) by Nakamori et al. attempted to determine the \(T=0 \text{ K}\) ground state of the material. Density functional theory was used to study a range of metal borohydrides including \(\text{Mg(BH}_4\text{)}_2\). In particular, the PBE functional was used along with a primitive search based on analogous compounds for low lying structures. This study identified two candidate structures as possible ground states. The most stable structure found was a monoclinic phase with space group \(\text{P2/c}\). Also identified as a low energy structure was a trigonal phase of space group \(\text{P}^3\text{m}_1\).

Still in 2006, Vajeeston et al., also using density functional theory with the PBE functional, found a different ground-state structure for \(\text{Mg(BH}_4\text{)}_2\). In their study, 28 candidate structures were tested for the lowest energy configuration. The structures calculated were largely taken from a list of known ground states of related compounds. This study predicted the ground state to be of \(\text{Pmc}2_1\) symmetry, at odds with the predictions of Nakamori et al.

In 2007 the first serious experimental measurements were undertaken by \v{C}ern et al. to determine the spacegroup of \(\text{Mg(BH}_4\text{)}_2\). X-ray and neutron diffraction were performed on a polycrystalline powdered sample of the material. This study found, in contrast to the previous theoretical studies, a hexagonal phase with a space group of...
P6$_1$ for the Mg(BH$_4$)$_2$ low-temperature phase. A second study in the same year used single-crystal X-ray diffraction to confirm the P6$_1$ structure as the low temperature phase, which transforms to a Fddd phase above 453 K.\textsuperscript{63} This high-temperature orthorhombic phase was stable up to 573 K after which it decomposed with hydrogen release.

In 2008, Dai, Sholl, and Johnson performed a DFT relaxation of the unit cell given experimentally by X-ray powder diffraction studies.\textsuperscript{71} They found that the P6$_1$ structure reported in the literature changed to a P6$_1$22 space group when all degrees-of-freedom were allowed to relax within the chosen DFT framework. In the same year, Ozolins, Majzoub, and Wolverton, again using DFT, predicted the Mg(BH$_4$)$_2$ ground state to be of I\textbar m2 symmetry.\textsuperscript{72} This result was based on a systematic search for low energy crystal structures.

In 2009, Voss et al. reported that the I\textbar m2 structure predicted by Ozolins, Majzoub, and Wolverton was dynamically unstable, owing to the existence of imaginary vibrational modes, and proposed a novel F222 structure as the true ground state of Mg(BH$_4$)$_2$.\textsuperscript{73} In the same year, Filinchuk, Čern, and Hagemann repeated their X-ray diffraction study of Mg(BH$_4$)$_2$ using a single-crystal technique, finding that the low-temperature $\alpha$ phase is of P6$_1$22 symmetry.\textsuperscript{74} This finding effectively ended the argument over the experimental structure of Mg(BH$_4$)$_2$ and opened the door for DFT studies to explain the discrepancy between experiment and theory and even between different theoretical results.

### 6.3 Aim of this Work

It was this discrepancy between experiment and theory (and even within theory itself) that we sought to explain with our study of the Mg(BH$_4$)$_2$ system. We believed the discrepancy to arise from the lack of proper inclusion of van der Waals interactions
within the previously conducted DFT studies. The goal of the research was to ascer-
tain the role of van der Waals interactions within Mg(BH$_4$)$_2$ and to determine if they
may be responsible for the inability of DFT to correctly predict the experimentally
observed low-temperature phase.

### 6.4 Methods of Study

In order to settle the longstanding debate about the nature of the low-temperature
ground-state structure of Mg(BH$_4$)$_2$ density functional theory was used in conjunc-
tion with several different functionals. Calculations were performed with LDA and
PBE functionals (these are discussed in Section 2.3.4). In addition, two methods
for including the effects of van der Waals interactions were employed. The first of
these was the vdW-DF, already discussed in Section 3.2.2. Also employed was the
semi-empirical approach of Grimme$^{21,75}$ (dubbed PBE-D when used with the PBE
functional), which expresses the van der Waals energy of a collection of atoms as

$$ E_{vdW} = -s_6 \sum_{I<J} f_{damp}(R_{IJ}) \frac{C_{6}^{IJ}}{R_{IJ}^6}, $$ \hspace{1cm} (6.1)

where $s_6$ is a parameter used to scale the interaction for a particular exchange-
correlation functional, $C_{6}^{IJ}$ is an empirically-derived constant describing the van der
Waals interaction between atoms $I$ and $J$, $R_{IJ}$ is the distance between atoms $I$ and
$J$, and the sum runs over all pairs of atoms. The damping function $f_{damp}(R_{IJ})$ is
given by

$$ f_{damp}(R_{IJ}) = \frac{1}{1 + e^{-\alpha \left( \frac{R_{IJ}}{R_0} - 1 \right)}}, $$ \hspace{1cm} (6.2)

with $\alpha$ being a scaling constant. It removes the unphysical short-ranged behavior
of a $1/r^6$ interaction and transitions smoothly from 0 to 1 at some characteristic
lengthscale, set by $R_0$. Typically, $R_0$ is chosen to be the sum of van der Waals radii for the two atoms involved.

The PBE-D approach is a post-processing procedure that treats the van der Waals interaction as a classical addition to the quantum-mechanical energy of the system, arising from the polarizability of the electron cloud around each nucleus. As a semi-empirical method, the transferability of PBE-D is lower than might be expected for a truly ab initio method. As such, it has been re-parameterized many times to apply to different chemical situations. One re-parameterized version (dubbed PBE-D*) was created for use in solid-state applications.\textsuperscript{75,76} Both PBE-D and PBE-D* were used in this work. The parameters used for each are collected in Table 6.1.

Calculations using the local density approximation and those required by the phonon calculations used the Vienna Ab Initio Simulation Package (VASP).\textsuperscript{77} All other PBE, PBE-D, PBE-D*, and vdW-DF calculations were carried out with a modified version of PWscf.\textsuperscript{6} Full relaxations including atomic positions and cell parameters were performed for all structures. An energy cutoff of 500 eV was employed with Monkhorst-Pack\textsuperscript{78,79} k-point meshes of about 0.03 Å\(^{-1}\) throughout the Brillouin zone.

### 6.5 Crystalline Mg(BH\(_4\))\(_2\) at T=0 K

In order to compare energies of potential low-energy structures of Mg(BH\(_4\))\(_2\), a search space must be defined. A set of 36 structures were chosen on which to perform
calculations. All the structures chosen were predicted ground states of Mg(BH\(_4\))\(_2\) or closely related (mostly borohydride) compounds. These structures ranged in size from 11 atoms per unit cell to the high temperature β phase of Mg(BH\(_4\))\(_2\) consisting of 704 atoms per unit cell. To normalize the energies of various polymorphs, all energies in this section are reported in meV/BH\(_4\), though the “/BH\(_4\)” will be omitted for clarity.

**LDA**

Calculations using the local density approximation predict a number of phases lower in energy than the α phase of Mg(BH\(_4\))\(_2\), the lowest of these is of I\(_{4\!1}/acd\) symmetry and lies 22 meV below the α phase. The experimental β phase lies 49 meV above the α phase as predicted by LDA.

**PBE**

The lowest-energy structure found from our PBE calculations are consistent with the prediction of the F222 ground state by Voss et al.\(^{73}\) PBE places this structure 20 meV below the α phase. The I\(_{4m2}\) structure predicted by Ozolins, Majzoub, and Wolverton\(^{72}\) lies just above this in our calculations. These structures are too close in energy to be resolved by our methods. However, the existence of both of these phases below the α phase within the PBE approximation is consistent with the literature. These two structures are the only ones in our set that PBE predicts to be lower in energy than the α phase. The high-temperature β phase is predicted by PBE to lie 37 meV above the α phase at T=0 K.

**PBE-D**

The original PBE-D method of Grimme was developed and parameterized for molecules, and it is known to perform less adequately for solids.\(^{76}\) This was confirmed in
Figure 6.1: van der Waals energies as calculated via PBE-D* broken into components coming from BH$_4$-BH$_4$ interactions (red circles), BH$_4$-Mg interactions (black squares), and Mg-Mg interactions (blue triangles). Reprinted with permission from Reference 2 © American Physical Society, 2011.

the present case where PBE-D predicts a number of structures to be lower in energy than the $\alpha$ phase of Mg(BH$_4$)$_2$. The lowest-energy structure lies 27 meV below the $\alpha$ phase as predicted by PBE-D and there exist 5 structures each lying 23 meV below the $\alpha$ phase.

**PBE-D***

The re-parameterized PBE-D* was found to perform much more satisfactorily for solid Mg(BH$_4$)$_2$. PBE-D* predicts the lowest-energy polymorph to be the experimentally-determined $\alpha$ phase, however, the lowest-energy prediction from LDA, with $I4_1/acd$ symmetry is nearly degenerate with it. The high-temperature $\beta$ phase is predicted to be 56 meV above this in energy.

The atomic pairwise form of Equation 6.1 allows the dispersion contributions from different groups to be analyzed. Figure 6.1 shows the contributions to the total van der Waals energy coming from BH$_4$-BH$_4$ interactions, BH$_4$-Mg interactions, and Mg-Mg interactions. As can be seen in the figure, it is predominantly the BH$_4$
molecules that participate in van der Waals interactions, both with each other and with Mg atoms. Magnesium atoms have very little dispersion interaction with other magnesium atoms. This is expected, as the magnesium ion is quite small and has a partial positive charge.

**vdW-DF**

Using the vdW-DF one of the predicted lowest-energy structures is a P6\(_{1}22\) phase, in agreement with experiment. Another closely related phase with P3\(_{1}12\) symmetry is nearly degenerate with it and the two phases cannot be resolved at the level of calculation performed here. The high-temperature \(\beta\) phase is predicted by vdW-DF to lie about 62 meV above the \(\alpha\) phase.

### 6.6 Mg(BH\(_{4}\))\(_{2}\) at Finite Temperature

The T=0 K ground-state energy is important for a full understanding of the behavior of Mg(BH\(_{4}\))\(_{2}\), but a description of the material at finite temperature is also critical. The contribution of vibrational degrees-of-freedom to the Helmholtz free energy at finite temperature were calculated as\(^{80}\)

\[
\Delta G_{phon} = k_B T \int_0^\infty \ln \left( 2 \sinh \left( \frac{\hbar \omega}{2 k_B T} \right) \right) n(\omega) d\omega ,
\]

(6.3)

where \(n(\omega)\) is the phonon density of states computed by finite displacements of atoms within a supercell. Calculations of this type were carried out with the PHON code coupled to the VASP.

Figure 6.2 shows both the zero temperature energy predictions (referenced to the \(\alpha\) phase) and the high-temperature behavior of several polymorphs as predicted by both PBE and PBE-D\(^*\). It is interesting to note that neither of these methods predict the experimentally observed \(\beta\) phase to be the most stable at elevated temperature.
Figure 6.2: Predicted energies of various polymorphs of Mg(BH₄)₂ using several different approaches. b) Total energies at T=0 K of the 36 polymorphs tested using the five different choices of energy functional. a) The effects of finite temperature as calculated by PBE. c) The effects of finite temperature as calculated by PBE-D*. d) A comparison of the relaxed-cell densities between PBE-D* and vdW-DF. Reprinted with permission from Reference 2 © American Physical Society, 2011.

This may in part be due to the rather crude approximation of assuming harmonic excitations of phonon modes at high temperature. Anharmonic effects are likely at such elevated temperature. It should also be noted, however, that inclusion of the zero-point energy did not move any structures below the α phase within the PBE-D* method.

Also shown in Figure 6.2(d) are the computed densities of each polymorph with both PBE-D* and vdW-DF. The vdW-DF densities are generally lower than those of PBE-D*, which is consistent with the general overestimation of interaction distances present in the original vdW-DF.
6.7 Conclusions

From the data generated here, it is evident that van der Waals interactions play a role in determining the precise polymorph that is most stable at a given temperature. The inability of standard DFT to predict the experimentally observed phase as the lowest in energy without inclusion of van der Waals effects is testament to this. However, it should not be overlooked that the overwhelming majority of the energy in this system does come from covalent and electrostatic interactions. These provide the bulk of the effect with van der Waals interactions playing a small but important part in determining the energetic ordering of polymorphs. This is a case where weak van der Waals interactions, when taken over a large number of interacting sites, can make a difference in unexpected ways.
Chapter 7
Phenaleny1 and Closed Shell Analogues

The phenalenyl molecule is of great interest to chemistry because of its somewhat anomalous binding properties. Phenaleny1 molecules, when brought together in a face-on $\pi$-stacked fashion, engage in so called 2-electron/multi-center bonding, where 2 electrons are shared among 12 (or 14) atoms forming a weak but significant chemical bond that holds the dimer together. Such bonds are a hybrid, having some covalent character and some characteristics of van der Waals interactions. Phenaleny1 is of interest to materials science because when properly linked it can be formed into molecular crystals with tunable electric, magnetic, and optical properties. Molecular crystals of appropriately linked phenalenyl molecules have been made as insulators, semi-conductors, and conductors, depending on the precise form of the linker and even the presence or absence of light during the crystallization process. A single $\pi$-stacked dimer has been predicted to conduct electricity if the monomers are brought close enough together, and even the single monomer holds promise as a molecular conductor. Its great utility, coupled with the difficulty in treating it accurately (as will be discussed shortly) makes the phenalenyl molecule an interesting target of investigation.

Phenaleny1 (hereafter referred to as C-Phy) has interesting binding characteristics
Figure 7.1: The phenalenyl molecule. The sites labeled $\alpha$ and $\beta$ (and their symmetry equivalent counterparts) are important for binding.

when engaging in $\pi$-stacked binding with another C-Phy. One can also replace the central carbon atom of C-Phy with either a boron atom (forming B-Phy) or a nitrogen atom (forming N-Phy). These two species differ mainly in the number of electrons within the molecule, B-phy having 86, C-Phy 87, and N-Phy 88 electrons. Despite their similarity, their binding characteristics are completely different, both from C-Phy and from each other. This makes these closed-shell analogues interesting to study in their own right.

### 7.1 The Phenalenyl (C-Phy) Molecule

Phenalenyl (Figure 7.1) is a planar molecule that can be most easily visualized as a truncated graphene sheet comprised of three aromatic rings terminated by hydrogen atoms. One of the most important aspects of this molecule is its single unpaired electron, which makes C-Phy a neutral radical hydrocarbon. This unpaired electron complicates the treatment of the system because it renders spin-polarization effects important. The lone unpaired electron in C-Phy resides in a singly occupied molecular orbital (SOMO) that is concentrated on the $\alpha$ carbons. This orbital looks much like a typical p-type orbital centered on each $\alpha$ carbon, with lobes extending above and below the plane of the molecule, as shown in Figure 7.2.
Figure 7.2: The singly occupied molecular orbital (SOMO) of C-Phy. Blue and red represent the sign of the wave function.

7.2 The C-Phy\textsubscript{2} $\pi$-Dimer

7.2.1 Experimentally

Much work has been done experimentally regarding \textit{C-Phy}\textsubscript{2} and derivatives. In solution, C-Phy can form two types of dimers, the $\pi$-stacked dimer which is of general interest, and a less interesting covalently linked $\sigma$-dimer, which tends to form long chains of the molecule. Experimentally, $\sigma$-dimerization is prevented by adding bulky groups (most commonly tert-butyl groups) to the $\beta$ carbons of C-Phy, effectively blocking the covalent linking.\textsuperscript{97} Most of the work that has been carried out on the $\pi$-stacked \textit{C-Phy}\textsubscript{2} dimer includes these groups, though owing to their size they are rarely included in computational studies of the molecule. It has been argued that this approach is valid and that the tert-butyl groups do not participate strongly in the chemistry.\textsuperscript{98}

The individual monomers in \textit{C-Phy}\textsubscript{2} are known to bind in a staggered conformation (monomers rotated 60° relative to each other), giving the overall molecule a $D_{3h}$ symmetry.\textsuperscript{84,97} This has been found experimentally, and is corroborated by computational studies (including the one presented here), lending confidence to the assertion that the bulky tert-butyl groups do not participate significantly in the chemical binding.\textsuperscript{98} One of the more interesting aspects of the system is the close contact
exhibited by the two monomers of C-Phy$_2$. The precise distance between monomers depends somewhat on which groups are attached to the outer rings, but the distance between the monomers generally falls in the range 3.2–3.3 Å, significantly under the expected 3.4 Å, which is the sum of van der Waals radii for two carbons.$^{82,98}$ The reason for this close binding contact will be discussed shortly. The measured binding energy for the dimer depends somewhat on the solvent in which it is dissolved, but it has been measured as $-7.5$ kcal/mol in hexane$^{84}$ and $-8.8$ to $-9.5$ kcal/mol in dichloro-methane.$^{84,98}$

7.2.2 Techniques Required to Treat C-Phy$_2$

Computationally

Quantum Chemistry

Typical quantum-chemistry methods (as discussed in Section 2.2) start with the Hartree-Fock approach, which assumes the total molecular wave function can be written as a single Slater determinant. This is a poor starting point for C-Phy, whose ground-state wave function does not exist as an eigenfunction of the total spin operator, $S^2$. Multi-reference methods, which start with a reference wave function that is a linear combination of Slater determinants, are required to properly treat C-Phy and the π-stacked C-Phy$_2$ dimer. It has been argued that an adequate treatment of the ground-state wave function in C-Phy$_2$ can be achieved by taking as the reference wave function a linear combination of the Slater determinants arising from all combinations of the two highest-energy electrons populating the two highest-energy molecular orbitals.$^{98}$ This is typically denoted CASSCF(2,2) for complete active space self-consistent field with the specified electronic excitations.

Such multi-reference methods are relatively new within quantum-chemistry codes, but systems which necessitate their use are not uncommon in chemistry. The canon-
ical example of this is the dissociation of the H\textsubscript{2} molecule where a single determinant reference wave function fails to adequately describe this dissociation because it gives significant weight to a state in which both electrons remain on one hydrogen. With a multi-reference wave function, this solution is rightly deemed unsuitable, and proper weight is given to solutions in which each hydrogen takes with it one electron, keeping them both neutral.

The ability to use high-level correlation methods (e.g. coupled cluster) with multi-reference wave functions is lacking in most quantum-chemistry codes, although MP2 correlation can sometimes be used in such cases. The quantum chemistry calculations presented in this chapter used a CASSCF(2,2) reference wave function coupled with MP2 correlation. These calculations were performed as an independent reference against which to compare DFT calculations.

Density Functional Theory

It has already been discussed in Section 2.3.4 that special care needs to be taken to properly include van der Waals effects within DFT. The vdW-DF was designed with this in mind. However, no spin-polarized version of the functional exists. Since both spin-polarization and van der Waals effects need to be included to properly treat C-Phy\textsubscript{2}, an approximation had to be made to adequately treat the system within DFT.

We begin, as in the derivation of the vdW-DF, by writing the exchange correlation functional as $E_{\text{xc}}[n(\vec{r})] = E_{\text{xc}}^{\text{local}}[n(\vec{r})] + E_{\text{xc}}^{\text{nl}}[n(\vec{r})]$. (Here, local is used to mean either local or semi-local.) The approach used here makes the simple assumption that the non-local piece of the correlation density functional, $E_{\text{xc}}^{\text{nl}}[n(\vec{r})]$, does not depend explicitly on spin. Under this assumption, the density used to evaluate $E_{\text{xc}}^{\text{nl}}$ is simply the total density, given by $n(\vec{r}) = n_{\uparrow}(\vec{r}) + n_{\downarrow}(\vec{r})$, where $n_{\uparrow}(\vec{r})$ is the spin-up charge density and $n_{\downarrow}(\vec{r})$ is the spin-down charge density. The effects of spin-polarization
are still fully accounted for in the local piece of the functional by use of the local spin density approximation. In order to obtain forces and self-consistent energies, the Kohn-Sham potential for this functional is required. This can be derived as follows.

We write the non-local correlation functional as

\[ E_{xc}^{nl}[n(\vec{r})] = E_{xc}^{nl}[n_\uparrow(\vec{r}) + n_\downarrow(\vec{r})] \]  

(7.1)

Written in this way, it is easy to see that the non-local exchange-correlation potential for the spin-up density, which is the functional derivative of the energy with respect to the spin-up density, can be written as

\[
\nu_{xc}^{nl}[n_\uparrow(\vec{r})] = \frac{\delta E_{xc}^{nl}[n(\vec{r})]}{\delta n_\uparrow(\vec{r})} \cdot \frac{\delta n_\uparrow(\vec{r})}{\delta n(\vec{r})} = \frac{\delta E_{xc}^{nl}[n(\vec{r})]}{\delta n(\vec{r})} \cdot \frac{\delta [n_\uparrow(\vec{r}) + n_\downarrow(\vec{r})]}{\delta n_\uparrow(\vec{r})} = \frac{\delta E_{xc}^{nl}[n(\vec{r})]}{\delta n(\vec{r})},
\]

(7.2)

with a similar derivation for \( n_\downarrow(\vec{r}) \). That is, the total Kohn-Sham potential for each spin-density channel is just what it would be for the total density. Armed with this approximation, the vdW-DF can now be tested in systems in which spin-polarization effects are important.

### 7.2.3 Binding Characteristics

When two C-Phy molecules are brought together face-on (see Figure 7.3), they form a strong \( \pi \)-stacking interaction that holds the dimer together. The interaction is different from more conventional \( \pi \)-stacking situations in that it is stronger, at shorter distance, and has a strong angular dependence. All of these characteristics stem from
Figure 7.3: (a) Bonding and (b) anti-bonding orbital formed from the SOMO-SOMO overlap of two C-Phy monomers. Both orbitals were calculated using unrestricted Hartree-Fock theory and are shown for the preferred staggered conformation.

Figure 7.4: Rotational energy scan of C-Phy$_2$ with an inter-monomer separation of 3.3 Å. Note the strong preference for a relative rotation angle of 60° indicative of the formation of a 2-electron/multi-center bond. This rotational preference is predicted by both density functional theory and MP2.

the formation of a 2-electron/multi-center bond.$^{82,83}$ This bond originates when the singly occupied molecular orbitals (SOMO) of the two molecules overlap to form a bonding orbital and a corresponding anti-bonding orbital. Since each SOMO has only one electron, there are only two electrons to fill these two orbitals so only the lower-energy bonding orbital is filled. This bond is weaker and longer than a traditional covalent bond.
Rotational Energy Scan

When the monomers of C-Phy$_2$ are rotated with respect to each other, they yield an energy profile which exhibits a strong rotational preference for the 60° rotation angle (see Figure 7.4), corresponding to the staggered conformation. If only $\pi$-stacking and van der Waals interactions were at play, a relatively flat energy profile would be expected, especially far from the eclipsed conformation. The strong rotational preference is a consequence of the 2-electron/multi-center bond which binds each $\alpha$ carbon on one monomer to the $\alpha$ carbon directly above it on the other monomer. This bond also forms at an angle of 0° because the $\alpha$ carbons are also on top of each other in this fully eclipsed conformation. When the monomers are rotated away from 0°, this bond is strained. The bond breaks completely at 30° and is reformed as the rotation angle exceeds 30°. The 60° conformation is energetically favored because the 2-electron/multi-center bond is fully formed, but there is less steric overlap than in the eclipsed 0° conformation. This is true even in the absence of the bulky tert-butyl groups that are present in experiment.

In the computer, the formation of the 2-electron/multi-center bond can be prevented by disallowing electron pairing near the Fermi level. This forces one electron to remain in the bonding orbital and one to be promoted to the anti-bonding orbital,
Figure 7.6: Binding energy with respect to monomer separation for (left) C-Phy at a rotation angle of 60°, (center) N-Phy at a rotation of 30°, (right) B-Phy at a rotation of 30°. The MP2 curves plotted here used either the 6-31G* basis or the 6-31++G** basis, which tended to give a deeper binding well.

effectively removing the bond. This situation is easily forced in the computer by requiring a total spin of two Bohr magnetons in the system. The rotational energy profile for this situation is shown in Figure 7.5. The profile here is what would be expected for a system which binds only by \(\pi\)-stacking and van der Waals interactions. It exhibits a strong dislike of the eclipsed 0° conformation but little particular preference for any other angle.

**Dissociation Energy Scan**

The binding energy as a function of monomer separation is shown in Figure 7.6. As the curve shows, the vdW-DF predicts a binding energy of \(-14.6\) kcal/mol at a separation of 3.31 Å in excellent agreement with experiment. The MP2 curve shows a much deeper binding energy of \(-30.9\) kcal/mol at the shorter separation of 2.94 Å.
Spontaneous Magnetization

Although the energy of C-Phy$_2$ is lowest when the total magnetization is zero, corresponding to the anti-ferromagnetic case, it is interesting to investigate the presence of spontaneous local magnetization. The integrated local magnetization is defined as $\int |n_\uparrow(\vec{r}) - n_\downarrow(\vec{r})|d^3\vec{r}$. That is, the integral over all space of the absolute value of the

Figure 7.7: Plots of the integrated local magnetization defined as $\int |n_\uparrow(\vec{r}) - n_\downarrow(\vec{r})|d^3\vec{r}$ in bohr magnetons as a function of (a) inter-monomer separation at a rotation angle of 60° and (b) relative monomer rotation angle at a separation of 3.3 Å. The vertical line in (a) indicates the vdW-DF predicted optimum separation of 3.31 Å.

The binding energy difference is not unexpected since MP2 is known to over-bind, particularly in situations with significant $\pi$-stacking interactions. In addition, the MP2 values showed a large dependence on the basis set in going from the 6-31G* basis to the 6-31++G** basis. This likely means that the MP2 results are not yet fully converged with respect to basis set, and a set of triple zeta quality would probably improve the results. Unfortunately, the poor scaling of MP2 with system and basis set size makes it unfeasible to use a larger basis set on this system. In any event, the MP2 results are at least in qualitative agreement with experiment, showing significant binding at a distance near 3.2 Å.
difference between the up-spin charge density and the down-spin charge density. This quantity is a measure of the total spatial difference between the up and down spin densities and a non-zero value indicates that spin-polarization effects are important. Figure 7.7 shows this quantity plotted as a function of the inter-monomer separation (Figure 7.7(a)) and relative rotation angle (Figure 7.7(b)). As can be seen in the figure, at a rotation angle of 60° magnetization develops when the monomers are separated by a distance of about 3.4 Å, reaching full saturation by around 4.5 Å. At a fixed separation of 3.3 Å, below the onset of local magnetization for a 60° orientation, rotation of the monomers to an angle of 30° also saturates the local magnetization. The vertical line in Figure 7.7(a) indicates the optimum 3.31 Å separation as calculated by the vdW-DF and shows that magnetization has not developed at this separation and the optimum 60° orientation. Thus, the predicted optimum geometry and its associated energy are not dependent on the spin-polarization approximation made, since spin-polarization effects are not relevant at this geometry.

7.3 The Nitrogen-Substituted Analogue (N-Phy$_2$)

When the central carbon atom of phenalenyl is replaced by a nitrogen atom, the chemistry changes dramatically. The SOMO orbital of C-Phy is now doubly occupied, owing to the extra electron present in nitrogen relative to carbon. This means
that both the bonding and anti-bonding orbitals formed by the highest-occupied molecular orbitals’ (HOMO) overlap are completely filled. This effectively breaks the 2-electron/multi-center bond found in C-Phy$_2$. However, this does not preclude the emergence of interesting physics. An inspection of the rotational scan of N-Phy$_2$ given in Figure 7.8 shows that there is now a minimum at a relative rotation angle of 30° and an associated rotational barrier at 60°. This is an entirely unexpected feature for a system that, a priori, one would think binds by π-stacking and van der Waals interactions alone. If this were true, a much flatter rotation curve showing little preference for any particular angle would be expected.

The source of the rotational barrier in N-Phy$_2$ is as unexpected as the barrier itself. Often, a simple molecular orbital picture is enough to explain a bonding effect, and it is reasonable to ask if that is true here. Since it is generally the highest-energy molecular orbitals that form bonding interactions, attention can often be restricted to these high-lying states. The Hartree-Fock energies of the highest occupied and second highest occupied molecular orbitals of N-Phy$_2$ are shown in Figure 7.9 as a function of rotation angle. Also shown are the orbitals themselves at 0°, 30°, and 60°. Both of these orbitals are doubly occupied in the ground-state electronic configuration. The lower-energy orbital is clearly a dimer bonding orbital and the higher-energy one is its associated anti-bonding orbital. Since both orbitals are occupied, the net effect is essentially non-bonding. There is an interesting effect where the two orbitals, because of the molecular symmetry, become nearly degenerate at 30°.

This simple molecular orbital picture does not readily show the reason for the barrier in Figure 7.8. To understand the source of the barrier one must break the energy into its component pieces. The Hamiltonian in Equation 2.4 can be broken into several physically meaningful pieces, yielding the energy expression of Equation 2.12 plus the classical nucleus-nucleus interaction term. There is the kinetic energy,
Figure 7.9: Hartree-Fock energies for the highest and second-highest occupied molecular orbitals in N-Phy₂. The insets show the orbitals themselves with blue and red representing the sign of the orbital.

given in terms of the Kohn-Sham orbitals $|\psi_i\rangle$ as

$$E_{\text{kin}} = -\frac{1}{2} \sum_i \langle \psi_i | \nabla^2 | \psi_i \rangle , \quad (7.3)$$

the electron-nucleus interaction given by

$$E_{\text{N–e}} = -\sum_J \int \frac{Z_J n(\vec{r})}{|\vec{r} - \vec{R}_J|} d^3 \vec{r} , \quad (7.4)$$

the nucleus-nucleus interaction given by

$$E_{\text{N–N}} = \sum_{I<J} \frac{Z_I Z_J}{|\vec{R}_I - \vec{R}_J|} , \quad (7.5)$$

where $I$ and $J$ run over all classical nuclei, the electron-electron interaction given by

$$E_{\text{e–e}} = \int \frac{n(\vec{r}_1)n(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d^3 \vec{r}_1 d^3 \vec{r}_2 , \quad (7.6)$$

and the exchange-correlation interaction given by one of the approximations discussed
Figure 7.10: Energy partitioning as a function of rotation angle in the N-Phy$_2$ system at a separation of 3.3 Å. Here, the energy is broken up into a kinetic piece, an electrostatics piece, and an exchange-correlation piece. The kinetic piece dominates the total energy profile.

A plot of the energy broken up into a kinetic piece, an electrostatic plus exchange piece (defined as the sum of the electron-nucleus, nucleus-nucleus, and electron-electron interaction energies), and an MP2 correlation piece is given in Figure 7.10, which readily shows that it is the kinetic energy that is responsible for the barrier evident at 60° in Figure 7.8. The electrostatic/exchange piece favors a local minimum at 60° but the cost in kinetic energy is high for that electron configuration, resulting in a local maximum in the total energy at 60° and a local minimum at 30° where the kinetic energy is relaxed. It is interesting that correlation plays little role in the nature of the N-Phy$_2$ rotation curve.

### 7.4 The Boron-Substituted Analogue (B-Phy$_2$)

When the central carbon of the phenalenyl molecule is substituted with a boron atom, the ability to form the 2-electron/multi-center bond vanishes. Boron has one fewer electron than carbon so the electron that was sitting in the SOMO of C-Phy

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is removed. As in the case of N-Phy$_2$, this removes the capability of forming a 2-electron/multi-center bond. The rotation curve for B-Phy$_2$ is shown in Figure 7.11. Here, the results of MP2 calculations and vdW-DF qualitatively disagree. The vdW-DF predicts an energy barrier to rotation near 60°, whereas MP2 predicts a relatively flat rotation curve at that angle. At first glance, it would seem that there is a discrepancy between the vdW-DF and MP2 correlation, the former giving a rotation barrier that the latter does not. However, deeper investigation shows that the spurious energy barrier is actually a consequence of the exchange used alongside the vdW-DF.

Figure 7.12 shows the B-Phy$_2$ rotation curve calculated within the NWchem pack-
age for three different exchange functionals. The calculations were performed with the Dunning cc-pVDZ basis set using the densest available integration grid. Shown in the figure are the results for exact exchange, which uses Hartree Fock theory to calculate the exchange term exactly, a local Slater-type exchange, and the semi-local PBE exchange. Each of these are discussed in more detail in Section 2.3.4. As can be seen in the figure, exact exchange gives a flat rotation curve near 60°, just as the MP2 result does. This is not surprising since Hartree-Fock theory is the starting point for the MP2 calculations. Slater exchange gives a very different curve, exhibiting the rotational barrier seen in the vdW-DF curve in Figure 7.11. No correlation is paired with these functionals so the entire effect is coming from exchange alone. The spurious barrier given by Slater exchange is not removed when a gradient correction is added to the exchange term.

The most obvious culprit for this spurious rotational barrier is the self-interaction that is inherent in the Hartree term. When the electron-electron interaction is written in terms of the total charge density as

$$E_{e-e} = \int \frac{n(\vec{r}_1)n(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d^3\vec{r}_1 d^3\vec{r}_2 ,$$

(7.7)

each electron necessarily interacts with itself. This is because the density is made up of all the electrons, so when the full density is used to determine the electron-electron interaction there will be terms arising from an electron in an orbital interacting with the same electron in the same orbital. This self-interaction problem can be circumvented in wave function approaches where the electron-electron interaction is written in terms of interacting orbitals rather than interacting densities, as

$$E_{e-e} = \sum_{i<j} \int \frac{\psi_i^*(\vec{r}_1)\psi_j^*(\vec{r}_2)\psi_i(\vec{r}_1)\psi_j(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d^3\vec{r}_1 d^3\vec{r}_2 .$$

(7.8)

By skipping the terms where $i = j$ the self-interaction is missed. This is not
possible in pure DFT where the energy is written entirely as a functional of the total electron density. Part of the job of the exchange functional is to remove this self interaction, but it is not always done adequately.

To investigate whether the spurious rotational barrier is caused by the self-interaction, a calculation was performed in NWChem using the self-interaction correction of Perdew and Zunger. In this approach, the orbitals are determined (they are required anyway for the kinetic energy term in the Hamiltonian) and the orbital-orbital self-interaction—calculated from the $i = j$ terms in Equation 7.8—for each orbital is subtracted from the total energy. When this calculation was performed, however, the barrier evident in Figures 7.11 and 7.12 actually got worse, indicating that self-interaction is likely not the cause of the spurious barrier.

It is interesting to ask why there is no barrier in the B-Phy$_2$ case (when exchange is properly handled) but there is in the N-Phy$_2$ case. A look at the energy partitioning for the B-Phy$_2$ case, shown in Figure 7.13, is particularly telling. Here, the kinetic energy barrier so pronounced in N-Phy$_2$ is much more subtle. What little barrier there is emanating from the kinetic piece is largely compensated by the electrostatics/exchange piece. It is interesting to note that here, unlike in the case of N-Phy$_2$, the correlation piece actually favors a local maximum at 60°, although the magnitude of the correlation contribution is quite small.

**7.5 Conclusions**

The vdW-DF performed well in the extremely delicate case of C-Phy$_2$, even in the face of the approximation made to enable spin-polarized calculations. The computed results agree well with experiment and with quantum-chemistry results. The nitrogen-substituted N-Phy$_2$ system showed an unexpected total-energy barrier to rotation. Further investigation yielded the kinetic energy as the determining factor in that
Figure 7.13: Energy partitioning as a function of rotation in the B-Phy$_2$ system at a separation of 3.3 Å. Again, the energy is broken into a kinetic piece, an electrostatics piece, and an exchange-correlation piece.

barrier. It is still not clear why kinetic energy so strongly disfavors the 60° rotation of N-Phy$_2$. A more careful study of the molecular orbitals may provide a way toward understanding this puzzle. The boron-substituted B-Phy$_2$ dimer also showed a total energy barrier at 60° that was removed when exact exchange was used. This barrier is already present at the local exchange level and remains if a gradient-corrected functional is used. The origins of this barrier are unclear, but it does not appear as though self-interaction is to blame.
Part III

Machine Learning with Network Functions
Chapter 8

Network Functions—Theory

The concept of network functions arose from a desire to use machine learning techniques to find quantitative relationships between a set of observations and a corresponding set of independent variables. The situation arises often in physics where a set of independent variables are altered, the dependent variable is measured, and one wishes to find the mathematical relationship between these entities. The major driving force behind the development of network functions was to use machine learning to solve the exchange-correlation problem within DFT. That is, to use network functions to find the relationship between the density and the (accurately calculated) exchange-correlation energy. They could also be used to search for a functional giving the kinetic energy from the density. This would ignite the field of orbital-free DFT, where the quantum-mechanical solution to the electronic-structure problem doesn’t even require solving the Schrödinger equation. There are many other important uses for network functions, but these served as the driving force behind the development of network functions.

Network functions are, as the name implies, functions that are represented as networks. They take a set of inputs, perform a specific, ordered set of fundamental operations on those inputs and yield an output value. In this respect they are equiv-
alent to functions. Internally, network functions have a set of parameters that can be changed via some appropriate training algorithm that depends on the particular problem being solved. In this way, a single network function can represent many different functions, just by varying the parameters. Changing the parameters has the effect of changing the ordered set of fundamental operations performed on the input set, thereby changing the function. A particularly useful property of network functions, is that they can be trained to become the mapping between the inputs and the outputs for a set of training data. Thus, a network function can infer the mathematical relationship buried in the data.

It should be pointed out that, although network functions share some properties with neural networks, the underlying philosophy of the two is quite distinct. The goal with neural networks is to find a mapping, any mapping that takes you from input to output. This is done with a static set of internal functions that take weighted inputs (the weights being the training parameters) and perform a predetermined operation on them. It is not what operations are performed that is being trained into the network but only how much each input should be weighted before being passed as input to the operation. Network functions, by contrast, use nodes that are designed to allow an ever-changing internal function to be explored. The inputs are not weighted (unless the target function requires it) but the fundamental operations performed on them by each node are continuously varied via a carefully chosen parameter set. If the training converges, the network represents a function that is an exact replica of the target function. Thus, whereas neural networks generally give poor results when a point far from the region of training data is queried, network functions can sometimes find the exact mapping for all parameter space.
8.1 A Note About Notation

The math behind network functions is not terribly complicated, but the notation needed to describe it can become quite cumbersome. This section serves as a reference for the notation that will be used throughout this chapter and the next.

- Let $\vec{x}^{(i)}$ denote the input(s) to node $i$
- Let $\vec{x}$ denote the input to the network
- Let $\tau^{(i)}$ denote the output of node $i$
- Let $\tau$ denote the output of the network
- Let $y$ denote the known, target value of a network output (used during training)
- Let $E$ denote the total error in the network

Subscripts indicate one of a series, as in $\vec{x}^{(i)} = (x_1^{(i)}, x_2^{(i)}, \cdots, x_j^{(i)}, \cdots, x_N^{(i)})$.

8.2 Anatomy of a Network Function

At its most basic, a network function consists of a set of nodes, each performing a specific task. These nodes are arranged in layers and the network is created by connecting the layers. Each node takes a set of inputs, performs a calculation with it and passes the result to the next layer. The network topology is a convenient way to computationally invoke function composition. When the output of node $i$ is passed as input to node $i+1$, the function that the network, up through node $i$, represents is being composed with the function that is represented by node $i+1$. This function composition of tunable internal functions is what makes network functions so powerful.
8.2.1 Nodes

Each node in a network function takes a set of input values $\vec{x}^{(i)}$ and performs a simple computation on them to produce a single output value. Node $i$’s output, $\tau^{(i)}$, is calculated as

$$\tau^{(i)} = \sum_j [C_{1,j}^{(i)} e^{x_j^{(i)}} + C_{2,j}^{(i)} \ln(x_j^{(i)}) + C_{3,j}^{(i)} x_j^{(i)} + C_{4}^{(i)}], \quad (8.1)$$

where each $C_{k,j}^{(i)}$ is a trainable, complex coefficient corresponding to the $j^{th}$ input value of node $i$, and the sum runs over each of the values in the input set, $\vec{x}^{(i)}$. This form was chosen because it is a simple formula that allows many fundamental operations to be performed on the input, as will be discussed in Section 8.3.

8.2.2 Layers

Within the network, nodes are collected into layers. The concept of layers is not central to network functions and it is not necessary. The concept is a convenient way to limit the input possibilities of a particular node. The number of nodes in a layer is arbitrary but, once chosen, is fixed within a given calculation. This is also
not a necessary restriction but it simplifies the bookkeeping considerably and all the networks considered herein will have a constant number of total nodes in a constant set of layers. Each layer is connected to its immediate neighbors by connecting the output of each node in layer $i$ to the input of every node in the layer $i+1$, as depicted in Figure 8.1.

8.3 What Network Functions Can Do

From the definition of a node function given in Equation 8.1, it is not readily apparent what types of calculations nodes, or networks for that matter, are capable of carrying out. This section begins with examples of the fundamental operations that can be carried out by a node, either alone or in a pair. Some examples of functions that can be exactly represented by small networks will be given, and these will be used to show that network functions are a universal approximator in the sense that, if the target function has an expansion that is uniformly convergent, a network function can approximate the function to arbitrary precision.

8.3.1 Some Fundamental Operations Among Nodes

One of the most important aspects of network functions is the concept of a fundamental operation. These are operations performed on an input data set to obtain an output. Multiplying two inputs together would be an example of a fundamental operation performed on data. This section gives some other examples of fundamental mathematical operations that can be performed by either a single node, or two nodes linked in series. In the following, let $a$, $b$, and $c$ be complex constants and let the first node have two inputs, that is let $\mathbf{x}^{(1)} = (x_1, x_2)$.

\[ ax_1 + bx_2 + c \]
The function given in Equation 8.1 has, contained within it, the power to multiply inputs by a complex scalar and add a complex constant. Thus, each node can form an arbitrary linear combination of its inputs.

\( ae^{x_1} \)

One of the functions that is directly performed by a node is to exponentiate an input with a complex coefficient. Thus, the exponentiation operation can be carried out by a single node.

\( a \ln_b(x_1) \)

The natural logarithm is a built-in function of each node. Logarithms with other bases can be formed by multiplication with a factor that is the natural logarithm of the desired base, \( b \).

\( a x_1^b \)

Raising an input to a complex power takes two nodes. The first performs the calculation

\[
\tau^{(1)} = b \ln(x) \tag{8.2}
\]

and the second follows with

\[
\tau^{(2)} = a e^{\tau^{(1)}} = a e^{b \ln(x)} = a x^b . \tag{8.3}
\]

\( a x_1^b x_2^c \)

Products of inputs can be formed from two sequentially-connected nodes. The algorithm is similar to that for \( a x^b \). The first node computes

\[
\tau^{(1)} = b \ln(x_1) + c \ln(x_2) \tag{8.4}
\]
and the second follows with

\[ \tau^{(2)} = a e^{\tau^{(1)}} = a e^{b \ln(x_1) + c \ln(x_2)} = ax_1^b x_2^c. \]

In fact, two nodes in series can form the product of an arbitrary number of inputs, each to an arbitrary complex power.

### 8.3.2 A Function Representer

If the target function is one that can be written as a finite composition of the available fundamental operations, it can be represented exactly by a network function of appropriate size. This means that a network can be trained to become the target function exactly, and for all values of input parameters. Note the striking difference here between network functions and neural networks, the latter of which only approximate the target function in some region of parameter space near the training data.

By way of example, suppose the target function is \( \sin(x) \). This can be written

\[ \sin(x) = \frac{e^{ix} - e^{-ix}}{2i}, \]

where \( i = \sqrt{-1} \) is the usual imaginary number. A network of only 3 nodes can
Figure 8.3: The minimal network required to obtain a Gaussian function in two parameters $x$ and $y$.

perform this function exactly for all $x$. This network is depicted in Figure 8.2. This network is not unique and other networks could perform the same function, but with an increase in the number of nodes and parameters. It is important to note that the smallest network that represents the function should be used, to avoid over-fitting the data.

As a second example suppose the data are generated from a Gaussian distribution in two variables, $x$ and $y$. That is, suppose the target function is

$$f(x, y) = e^{-(x^2+y^2)}.$$  \hspace{1cm} (8.7)

The minimal network required to obtain this function is shown in Figure 8.3. Again, only a few nodes are required to represent the function exactly for all possible inputs $x$ and $y$.

8.3.3 A Universal Approximator

The previous subsection gave two examples of functions that can be represented exactly in a finite (small) number of nodes. What happens if the target function is pathological, or can’t be represented in a finite number of fundamental operations? This may occur with extremely noisy data or for discontinuous or piece-wise defined functions. The examples given in the previous subsection were both of functions that are often used as basis functions (when integrated over the proper domain) for
expanding some other function. Since a finite network can form each basis function, and each node is capable of forming a linear combination of its inputs, network functions are a universal approximator in the sense that, \textit{given that the target function has an expansion in terms of a representable basis, a network function exists which can represent the target function to arbitrary accuracy, even if the target function itself is not representable.}

Expanding in a standard set of basis functions like plane-waves or Gaussians is actually a worst-case scenario. One can imagine expanding the target function in a finite set of basis functions and then “relaxing” each basis function until the result requires the fewest terms to represent the target function to a given accuracy. At worst this would be equivalent to expanding in a standard basis, and at best could be much better.

\section*{8.4 Training the Network}

The most critical step in network construction, if the network is to represent a particular target function, is training. There are many algorithms that can be used to train the network. The first step in all of them is defining an error function. This was defined as

\begin{equation}
E = \sum_j (\tau_j - y_j)(\tau_j - y_j)^*,
\end{equation}

where the index \( j \) runs over all example input/output sets, \( \tau_j \) is the network output corresponding to input set \( \vec{x}_j \), \( y_j \) is the known, target value of the function, and the star represents complex conjugation. This definition guarantees that the error is always a non-negative, real number. In fact, the global minimum of this function is an error of zero, which occurs when the network function exactly matches all training data.
Training the network involves changing the parameters, \( C_k^{(i)} \), for each input to node \( i \) such that the network’s output looks more like the target outputs. This means the derivative of the error with respect to each network parameter must be calculated. By the chain rule, the derivative of the error with respect to a parameter \( C_k^{(i)} \) can be written

\[
\frac{\partial E}{\partial C_k^{(i)}} = \sum_j (\tau_j - y_j) \frac{\partial (\tau_j - y_j)^*}{\partial C_k^{(i)}} + (\tau_j - y_j)^* \frac{\partial (\tau_j - y_j)}{\partial C_k^{(i)}}
\]

\[
= \sum_j (\tau_j - y_j) \frac{\partial \tau_j^*}{\partial C_k^{(i)}} + (\tau_j - y_j)^* \frac{\partial \tau_j}{\partial C_k^{(i)}}
\]

\[
= \sum_j (\tau_j - y_j) \frac{\partial \tau_j^*}{\partial \tau_j^{(i)}} \frac{\partial \tau_j^{(i)}}{\partial C_k^{(i)}} + (\tau_j - y_j)^* \frac{\partial \tau_j}{\partial \tau_j^{(i)}} \frac{\partial \tau_j^{(i)}}{\partial C_k^{(i)}}. \tag{8.9}
\]

The term \( \frac{\partial \tau_j^{(i)}}{\partial C_k^{(i)}} \) is just the derivative of the output of a node with respect to one of its parameters. These are tabulated in Table 8.1. The terms \( \frac{\partial \tau_j^*}{\partial \tau_j^{(i)}} \) and \( \frac{\partial \tau_j}{\partial \tau_j^{(i)}} \) give the change in the output of the network with respect to the output of node \( i \). If node \( i \) is in the final layer, this is just 1 since the output of the last node is the output of the network. If node \( i \) is not the final node, its output, \( \tau^{(i)} \), is the input to another node and the chain rule requires knowledge of how the output of the network changes with respect to the input of the other node. Thus, derivative of a node’s output with respect to its inputs are also needed. This is easily calculated from Equation 8.1 as

\[
\frac{\partial \tau^{(i)}}{\partial x_j^{(i)}} = C^{(i)}_{1,j} x_j + \frac{C^{(i)}_{2,j}}{x_j} + C^{(i)}_{3,j} \tag{8.10}
\]

Since the output of a node in layer \( i \) becomes input to all the nodes in layer \( i + 1 \), to get the full derivative needed by the chain rule the derivative in Equation 8.10 must be calculated and summed for all nodes in layer \( i + 1 \).

Armed with these derivatives, the network can now be trained by any of several methods. The simplest approach is a steepest descent algorithm, in which the param-
Table 8.1: The derivatives of the training error, $E$. Both the derivative of $E$ with respect to each network parameter ($\frac{\partial E}{\partial C_k}$) and the derivative of $E$ with respect to the inputs of each node ($\frac{\partial E}{\partial \vec{x}(i)}$) are required to train the network.

<table>
<thead>
<tr>
<th></th>
<th>$\frac{\partial E}{\partial \text{Re}(C_k)}$</th>
<th>$\frac{\partial E}{\partial \text{Im}(C_k)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_1$</td>
<td>$e^x$</td>
<td>$ie^x$</td>
</tr>
<tr>
<td>$C_2$</td>
<td>$\ln(x)$</td>
<td>$i \ln(x)$</td>
</tr>
<tr>
<td>$C_3$</td>
<td>$x$</td>
<td>$ix$</td>
</tr>
<tr>
<td>$C_4$</td>
<td>$1$</td>
<td>$i$</td>
</tr>
</tbody>
</table>

Parameters at each step are adjusted in the direction that initially maximizes the decrease in error. In this case, a rule to update parameter $C_k^{(i)}$ at step $t + 1$, given its value at step $t$, would be

$$C_k(t + 1) = C_k(t) - \alpha \nabla E,$$  \hspace{1cm} (8.11)

where $\alpha$ is a step length that is determined by requiring that the step places the network at a local minimum along the direction $\nabla E$.

A more efficient route to optimization can be found by using a conjugate gradient algorithm, in which the search direction is chosen to be conjugate to directions already searched. This helps avoid “undoing” progress that has already been made. A parameter update rule in this case would be

$$C_k(t + 1) = C_k(t) - \alpha \vec{g},$$  \hspace{1cm} (8.12)

where $\vec{g}$ is given by the usual conjugate gradient algorithm.

There are certainly other choices for training, but whichever parameter update rule is chosen, the training continues until, ideally, the error becomes zero, indicating that the network has found a function that models the data. If the network is of insufficient size to model the data or they emanate from a non-analytical function, the training can be stopped when the total error gets to a sufficiently small value.
When the training is stopped, the network represents a function that is either exactly capable of producing the output (in the case that the total error reaches zero), or a good approximation to such a function (in the case the error remains non-zero). It should be stressed that the function represented is an analytical function in closed form, not a numerical function that must be evaluated through the network.

8.4.1 Remarks on Training

Training the network is difficult and time-consuming. The quality of the training and the time it takes to reach an answer depend critically on the starting configuration of the network. Since a universal means to obtain a good initial configuration is not known, the configuration must be guessed. This is done by randomly initializing all parameters in the network within some reasonable bounds. There are many drawbacks to this approach. First, it is sometimes the case that the randomization of network parameters leads to a function that runs into numerical overload. That is, sometimes the initialization leads to a function which exceeds the capability of a double precision variable to contain the value. This results in the output of the network being a numerical infinity. In other cases, the network starts far from the optimum solution and, due to fairly simplistic training algorithms used, may meander aimlessly or get trapped in a local minimum. These problems could be avoided by a more judicious choice of starting parameters and a more sophisticated training algorithm. Investigations into improved algorithms is ongoing work.

The best approach, given the limitations of the algorithms employed here, seems to be to monitor the training and restart if the error decreases too slowly or if the network gets stuck in a local minimum. A restart is obviously required if a numerical infinity is reached, though in testing this generally only happens at the initial stage, when random initialization leads to numerical overflow. Since it is paramount to good performance and usability of network functions, better initialization and training
procedures are obvious ground for future work.

8.4.2 The Complex Natural Logarithm

The complex natural logarithm poses a particular problem for training a network. The complex log is a multivalued function meaning that a particular complex input \( x \) can produce an infinite number of possible outputs. This is because, for a complex number \( a + ib \),

\[
e^{a+i(b+2\pi n)} = e^{a}e^{ib}e^{2\pi n} = e^{a+bi},
\]

with \( n \) an integer. That is, a shift in the imaginary part of \( x \) by an integer multiple of \( 2\pi \) does not change the value of \( e^{x} \). The natural logarithm is defined such that

\[
c = e^{x} \Rightarrow \ln(c) = x.
\] (8.14)

But, since \( e^{a+ib} = e^{a+i(b+2\pi n)} \) we have

\[
c = e^{a+i(b+2\pi n)} \Rightarrow \ln(c) = a + i(b + 2\pi n).
\] (8.15)

That is, for a number \( x = a + ib \) there are an infinite number of values \( \ln(a + ib) \) each differing by a multiple of \( 2\pi \) in the imaginary part. The usual approach to solve this problem is to take the range of the imaginary part of \( \ln(x) \) to lie in the region \( -\pi \leq \Im(\ln(x)) \leq \pi \). Such an approach poses a problem for training because it means the function \( \ln(x) \) may be discontinuous. If the imaginary part of the \( \ln \) function is near \( \pi \), for example, it is possible that a slight adjustment of parameters will make it suddenly jump to being near \( -\pi \). As such, derivatives cannot be calculated at the point of discontinuity and errors may suddenly jump or the training can get stuck. This is a problem that has not been resolved as yet in the network function training but it is the subject of ongoing work. Nevertheless, even with this occasional
discontinuity networks can and have been trained successfully. The degree of difficulty that a particular discontinuous ln poses for a network depends on its location in the network. It is possible for a discontinuous jump in the ln function to cause the error to increase or decrease by a large or small amount, depending on the precise form of the function at that point.

8.5 Using Network Functions to Find Functionals

In density functional theory, a functional is generally written in the form

\[ F[n(\vec{r})] = \int f(n(\vec{r})) d\Omega , \]

that is, as an integral of some function of the density over a volume. This may be a single spatial integral in the case of a local functional, or higher integrals in the case of non-local functionals. In order to train a network function to find a functional, it makes sense to perform the integration explicitly, using the network to find \( f(n(\vec{r})) \) only. This can be accomplished by using virtual replicas of a network and summing their outputs to simulate the integral. For example, suppose we write a functional as

\[ F[n(\vec{r})] = \int n(\vec{r}_1)\phi(\vec{r}_1, \vec{r}_2)n(\vec{r}_2)d^3\vec{r}_1d^3\vec{r}_2 . \]

Then, what is really needed is for the network to find the kernel function \( \phi(\vec{r}_1, \vec{r}_2) \). The fact that an integration is required is already known and should not be left to the network to learn. The way to proceed is to make a virtual copy of the network for each pair of points, \( \vec{r}_1 \) and \( \vec{r}_2 \). If we assume that the form of the kernel function is independent of \( \vec{r}_1 \) and \( \vec{r}_2 \), then we can pass as input to each copy of the network the particular values \( n(\vec{r}_1) \) and \( n(\vec{r}_2) \). If the density is represented on a grid with \( N \) points, there will be \( \frac{N^2-N}{2} \) copies of the network, each with identical parameters.
The output of each copy of the network is then summed to obtain the integral and the value $F[n(\vec{r})]$. The error in the network is the difference between this summed set of outputs and the known value for $F[n(\vec{r})]$. Since each network copy has weight 1 when contributing to the sum, the derivative of the total error with respect to the output of each copy is just 1, so no extra derivatives are necessary by the chain rule.

For example, suppose the density is represented on a grid of $10 \times 10 \times 10$ points. We imagine making 499,500 virtual copies of the network with identical parameters. Since all copies have the same parameters, only one copy actually needs to be stored. Training the network proceeds by passing each pair of points to a particular copy and summing the outputs to produce the total network output. This summed value, $\tau_{\text{sum}}$ is used in the error function (Equation 8.8) as usual. The derivatives of network error with respect to parameters for each virtual copy of the network are also summed and the results are used to update the network parameters. In this way, the integral of a function over a volume can be trained to a known value.

### 8.6 Future Improvements

There are two main areas where network functions need more work to make them a robust tool for finding mathematical relationships. The first has already been discussed in Section 8.4.2. The complex logarithm is a multi-valued function leading most programming languages to return the imaginary part of a complex ln calculation that lies between $-\pi$ and $\pi$. This poses problems for the training algorithm because it means that a tiny change in the parameters of a node can cause a discontinuity in the output. This problem needs to be circumvented before network functions can be used reliably.

Another avenue for improvement lies with the initialization of the network. At present, a network is initialized with all its parameters set to a random value in some
small region about zero. This is likely not an ideal starting point. Since optimization algorithms depend critically on the starting location, it is likely that choosing a better starting guess will dramatically improve training performance. A thorough study needs to be undertaken to find a generally good way to pick a starting configuration for the network.

As a further point, it is not yet clear what happens when noisy data is fed to the network. It is likely that for small values of noise, the function found by the network will be unchanged in form but with slightly altered parameters. For example, a square root might be found to be $x^{0.499852}$ rather than $x^{0.5}$. This type of change can be easily spotted by a human and corrected for. For larger values of noise, the network may not be able to represent the function well with a form similar to the true form. In this case, the universal approximator capacity of the network will likely take over and the result will be an approximation to the function good to some predefined tolerance over a particular range. A thorough study of the effects of noise should be undertaken to test these hypotheses.
Chapter 9

Using Network Functions

The last chapter laid out the theoretical foundations of network functions and, ideally, this chapter would showcase their capabilities. However, time constraints and technical difficulties have made the actual use of network functions difficult. Work is continuing on the development of the code with the hope that it will perform as expected in the near future. With that being said, this chapter will give two simple examples of the use of network functions. In the first of these, the network was able to learn the target function exactly. The second case is a bit more difficult and at first only an approximation was found, although the network was eventually able to learn the function exactly. The remainder of the chapter deals with future plans for network functions, once all the training problems have been worked out. In particular, it discusses use of network functions in finding a kinetic-energy density functional and an exchange-correlation density functional.

9.1 Test Cases

Training a network is a difficult procedure with many intricacies. For that reason, the results presented in this subsection do not represent “typical” results in the sense that some tricks were used to aid training. The most substantial of these was use
of the exact minimal network needed to obtain the desired result. In any general problem, the minimal required network size will not be known in advance, so training must proceed by starting with a small network and working toward larger ones as the smaller ones are deemed insufficient. Restarting training runs that were making little progress was another training technique used. This example is intended as a proof of principles that the network is capable of actually learning a target function, not a proof that this will be easy.

9.1.1 Coulomb’s Law

In Gaussian units Coulomb’s Law for two point charges, each of charge $q$ can be written $E = \frac{q^2}{r}$, where $E$ is the interaction energy and $r$ is the distance between the two charges. This was the first and perhaps simplest test case given to the network. Inputs to the network will be the charge $q$ and the separation distance $r$. To obtain the correct function, only two nodes are required. The first must take the negative natural logarithm of $r$ and add to it twice the natural logarithm of $q$. The second node must then exponentiate this sum to obtain the final result. Such a network is shown in Figure 9.1. A larger network would also be capable of yielding the correct function, but training would likely be more difficult due to the larger number of training parameters that would be present and the risk of over-fitting would be increased.

The training profile of the network is given in the inset in Figure 9.2. In this particular case, about 800 steps were required to train the network to a total error
Figure 9.2: The network function trained for Coulomb’s Law. The blue region marks the range of the training data, solid dots are calculated directly from Coulomb’s Law and the red curve is the output of the network function. The inset shows the log of the error as a function of iteration during the training of the network. Training was halted when the error became less than $1 \times 10^{-16}$.

The resulting network function is plotted in the figure. The blue region comprises the range of training data given to the network. That is, the training data were selected at random from that range. The solid dots are calculated from Coulomb’s Law and the red curve shows the value of the network function. As can be seen in the figure, the network function exactly matches Coulomb’s Law over a large range of $r$. In fact, since it has found the actual function $\frac{q^2}{r}$ it will perfectly match Coulomb’s Law over the entire input range. This is a fundamental difference between network functions and neural networks. A neural network will produce wildly incorrect values if evaluated far from the region of input training data. A network function, if properly trained, will produce correct results for any value of the input parameters, regardless of where training data lie, provided that the training data is reasonably representative of the function.
9.1.2 The Fermi Distribution Function

For fermions, the expected distribution among energy states of energy $\varepsilon$ for a particular value of the temperature, $T$, is given by

$$f(\varepsilon, \mu, T) = \frac{1}{1 + e^{\frac{\varepsilon - \mu}{k_B T}}},$$

(9.1)

where $\mu$ is the chemical potential and $k_B$ is Boltzmann’s constant. This function is called the Fermi distribution function.

The Fermi distribution function can be represented exactly by the network shown in Figure 9.3. However, it is useful to ask what happens, in the more typical case, if the network fails to learn the function exactly. In this case, the network can still approximate the function well in the region of the training data, but, like all similar but different functions, the approximation will eventually break down in some region.

By way of example we take $\mu = 0$ and $k_B T = 1$, then we can write Equation 9.1 as a function of the energy only, and the network required to represent it needs only three sequentially placed nodes. If a network is then trained to a local minimum which is not the one corresponding to the network having learned the target function, the network will approximate the target function in the region of the training data but will fail for points outside of this region. Figure 9.4 shows the results of training a network with three sequentially placed nodes to a local minimum in the error. The network was trained on 200 data points coming from the range $-5 \leq \varepsilon \leq 5$. As is evident in the figure, the network represents the function well in the region of the
Figure 9.4: Network output for a network with three sequentially-placed nodes trained to represent the Fermi distribution function given \( \mu = 0 \) and \( k_B T = 1 \), with training data taken from the interval \(-5 \leq \varepsilon \leq 5\). This network was not trained to the global minimum but to a local minimum that only allows it to approximate the Fermi function in the region of the training data. The network is an excellent approximation to the target function for negative values of \( \varepsilon \). This remains true to about \(-100\), at which point the network output begins to deviate from the true Fermi distribution function. The network fails completely for values of \( \varepsilon \gtrsim 5 \). The inset shows the log of the error in the network as a function of training iteration.

Training data. It remains an excellent approximation of the target function out to \( \varepsilon \gtrsim -100 \), at which point it begins to slowly deviate. The deviation is remarkably slow, reaching only a 25% underestimation of the target function by \( \varepsilon \approx -1000 \). However, the network fails completely for large \( \varepsilon \). That the minimum found is not the global minimum is evident from this failure and from the residual error in the network, which is shown in the inset of Figure 9.4. Had the network learned the true target function, the total error would be near numerical zero. This example highlights the extreme care that must be taken when training network functions if the network is to represent the target function well outside of the region of training. It also serves
Figure 9.5: Result of a network function being trained to the true global minimum for data obtained via the Fermi function. The blue shaded region shows the range of training data given to the network. In this case, the network was able to learn the function exactly for all values of the input parameter. Here, the network is not an approximation to the Fermi function but, rather, it is the Fermi function. The inset shows the error in the network as a function of training iteration.

to highlight the great power of network functions. The network was able to learn to approximate the function that generated the data set it was given. However, the existence of a network that exactly represents the target function is what sets network functions apart from neural networks and makes them so powerful, as is the relative ease with which a network can learn to approximate the target function within some range. The difficulty in training a network to the correct function for all values of the input parameters is the standard global optimization problem, which is well known in many fields. Here, at least, we are afforded the luxury of knowing whether or not we have found the global or a local minimum, as the global minimum has an error of exactly zero.

It is useful to compare the approximation of the Fermi function shown in Figure 9.4 with the true Fermi function learned by a network. The network output of a
network trained to the global minimum is shown in Figure 9.5. In contrast to the previous case, this network has obtained the true Fermi function. Not only is it a good approximation in the region of the training data, but it is numerically correct over the entire domain. Fifty training points were randomly chosen in the region denoted by the blue shading in the figure, but the network was trained to the global minimum with numerically zero error. Again, this example serves to highlight the utility of network functions, which can be used to represent a function over its entire domain, in contrast to neural networks that will only approximate the function over some sub-domain.

9.2 Future Uses in DFT

9.2.1 Kinetic Energy Functional

There is no known density functional that can give the non-interacting kinetic energy accurately. The kinetic energy of a state $|\psi\rangle$ is written as

$$T = -\frac{1}{2} \langle \psi | \nabla^2 | \psi \rangle ,$$

(9.2)

rather than as a functional of the density. With most density functionals, the kinetic energy term is the only place where eigenstates show up in density functional theory. The sole exception to this are meta-GGA functionals, which use the kinetic-energy density as an ingredient in the exchange-correlation functional. If a density functional could be found for the kinetic energy, it would no longer be necessary to solve the Schrödinger equation to obtain the Kohn-Sham orbitals. This would represent a huge simplification on the electronic structure problem. Instead of diagonalizing large matrices to find eigenstates, the problem would reduce down to using the total-energy functional and its functional derivative to minimize the energy with respect to the
density. The minimizing density would be the ground-state density, found without ever solving the Schrödinger equation.

The kinetic energy functional is a universal functional, meaning that it does not depend on the system under study. Once it is found, it will apply to all systems of interest. This means it may be possible to find the functional in a simplified system, then apply it to more difficult systems. One way to approach this using network functions, is to solve for the density and kinetic energy in a simple system, preferably one that can be worked out analytically, then train the network to find the link between the density and kinetic energy. This does not guarantee the correct functional since, although the kinetic energy functional is universal, all aspects of it may not be evident in every system. If the link were found between density and kinetic energy in one system, this does not guarantee that that particular system exhibits all the possible dependence of the kinetic energy on the density. As an analogy, one would likely not know about van der Waals interactions if NaCl were the only system ever studied.

There are very few problems that can be solved exactly in quantum mechanics, but one of the simplest is the infinite square well. For an infinite square well of length $L$ with the origin placed at one side of the well, the normalized eigenstates are given by

$$|\psi_n\rangle = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right),$$  \hspace{1cm} (9.3)

with corresponding charge-density

$$n(x) = \sum_n |\psi_n|^2 = \frac{2}{L} \sum_n \sin^2\left(\frac{n\pi x}{L}\right),$$ \hspace{1cm} (9.4)
and kinetic energy

\[ T = -\frac{1}{2} \sum_n \langle \psi_n | \nabla^2 | \psi_n \rangle = \frac{1}{2} \sum_n \left( \frac{n\pi}{L} \right)^2. \]  

(9.5)

These values could be fed into a network function to derive a kinetic-energy density functional.

Another way to generate training data for a kinetic-energy functional would be using Hartree-Fock theory. There are many codes that can perform Hartree-Fock calculations. Any of them could be used to generate a HF density. The kinetic energy can be computed from the orbitals as

\[ T = -\frac{1}{2} \sum_j \langle \phi_j | \nabla^2 | \phi_j \rangle. \]  

(9.6)

Many codes will output the orbitals on a grid of arbitrary density, so this quantity could be computed numerically to good accuracy. The resulting density and kinetic energy could then be used as training data for the network. The fact that correlation is ignored in Hartree-Fock theory does not pose a problem for the kinetic-energy functional. Using Hartree-Fock calculations to generate training data would allow the network to be trained on realistic data from molecular or condensed-phase systems.

Ideally, the functional found from the infinite square well and the one found from applying Hartree-Fock theory to simple molecules would be identical. If differences are evident, however, they likely represent interesting physics.

### 9.2.2 Exchange-Correlation Functional

The exchange-correlation functional discussed in Section 2.3.4 represents the single most important approximation in modern density functional theory. Current functionals, especially the vdW-DF, perform well in a variety of situations. There is
ample room for improvement, however, and finding a truly accurate and transferable exchange-correlation functional remains the holy grail of DFT development.

As with the kinetic-energy functional discussed in the preceding section, a density and its corresponding energy are required to train a network function to find a functional. Quantum-chemistry codes using high-level theory (e.g. coupled cluster) can be used to generate a density and its corresponding exchange-correlation energy. These data could then be fed to the network to learn the connection between them.
Chapter 10

Conclusions and Outlook

Part I

Part I laid out the theoretical background for the computational quantum mechanics used in this work, including wave function methods and density functional theory. The main focus of the discussion was inclusion of van der Waals interactions within DFT. The vdW-DF was described, including a way to improve the scaling through clever use of the convolution theorem. A program to implement this was developed in-house, eventually becoming part of the standard Quantum-Espresso release.

Part II

For many decades, density functional theory along with its associated exchange-correlation approximations have formed the backbone of computational chemical physics. However, their inability, until relatively recently, to properly account for van der Waals interactions has been a major drawback to their use. These days, van der Waals interactions can be included with DFT-D in a semi-classical way or by using the non-local vdW-DF (there are other ways not discussed in this work). Either way, it is becoming clear that van der Waals interactions play a larger role in
the physics of many systems than was previously thought.

Some systems that, by all appearances, have little to do with van der Waals interactions, including the Mg(BH₄)₂ system investigated in Chapter 6, require proper inclusion of van der Waals interactions to accurately compare to experiment. van der Waals interactions were able to settle the longstanding disagreement between theorists about the correct ground-state phase of Mg(BH₄)₂—despite its having been experimentally determined several years ago. van der Waals interactions proved critical for describing water’s properties in small clusters and bulk ice Iₜ. A host of properties were improved over LDA and GGA relative to experiment and careful quantum-chemistry calculations, when van der Waals interactions were included via the vdW-DF. This improvement extended, through a significant approximation, to the melting temperature of ice, which had previously been calculated at 400 K. van der Waals effects became necessary even for binding in the phenalenyl system and its closed-shell analogues. Here, Hartree-Fock and the revised PBE generalized gradient approximation exhibit no binding. All the analogues showed interesting physics despite their relative simplicity.

These were just a few systems where van der Waals interactions have been found to be of critical importance to compare with experiment or high-level quantum-chemistry calculations. It is likely that other systems, thought previously to have no need for van der Waals interactions, may at least be affected by them if not changed dramatically. The future is promising for DFT since there now exist a number of ways—some not discussed in this work—to include van der Waals interactions within it. These interactions will undoubtedly prove important in many systems of interest to all fields.
Part III

The final portion of this work described a new way of thinking about functions on a computer; as a collection of nodes, which can be composed to form wonderfully complex functions. These networks of nodes can be trained via well-known training algorithms to learn a target function. This means, when given experimental data, they can learn the function that generated them. It also means that, when given the electron charge-density on a grid, it is possible to learn the functional that converts this to an energy. The training is difficult, however, and needs to be undertaken in an intelligent manner.

It seems clear that network functions posses great potential for use in function approximation and discovery processes. The fact that a finite, and generally even small, network can exactly learn some target function gives them great power. But there are many difficulties that come with that power. It is hoped that the near future will see time invested in the programs that implement network functions, both to remove existing bugs and expand their intelligence. It is through practical application, rather than theoretical existence, that network functions become powerful. This application has started, as was discussed in this work, but it has far to go before it is routine.
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Part IV

curriculum vitae
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Publications


**Presentations**

➤ The Nature of Binding in the Phenalenyl Dimer and its Derivatives
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Posters

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Grants

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➤ Programming Experience in High-Level Codes
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   – Multi-Scale Modeling
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   – Statistical Mechanics of Complex Systems
   – Novel Algorithms

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➤ Chemical Physics

➤ Physics of Weakly-Bound Systems