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Magnetic Fields and Density Functional Theory

Author

Salsbury, Freddie, Jr., Ph.D. Thesis

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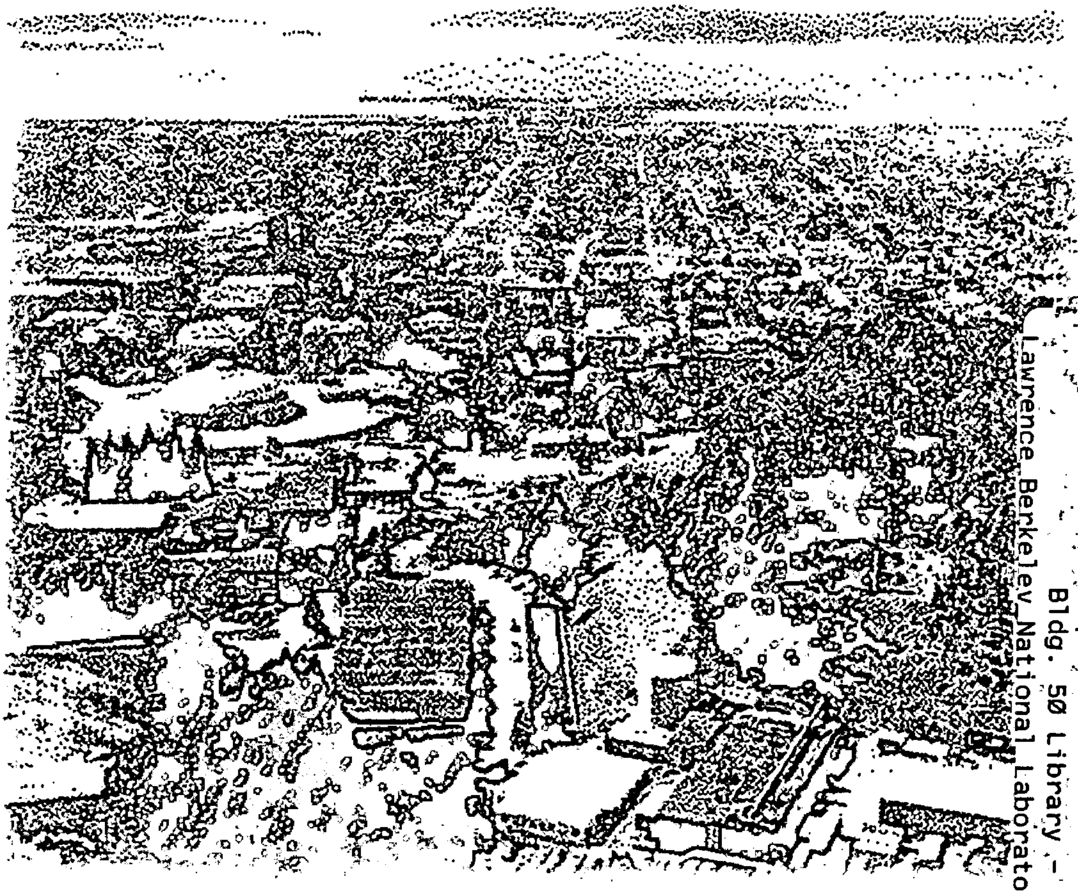

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Magnetic Fields and Density Functional Theory

Freddie Salsbury, Jr.
Ph.D. Thesis

Department of Chemistry
University of California, Berkeley

and

Materials Sciences Division
Ernest Orlando Lawrence Berkeley National Laboratory
University of California
Berkeley, CA 94720

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Abstract

Magnetic Fields and Density Functional Theory

by

Freddie Salsbury, Jr.

Doctor of Philosophy in Chemistry

University of California at Berkeley

Professor Alexander Pines
and Professor Robert A. Harris

A major focus of this dissertation is the development of functionals for the magnetic susceptibility and the chemical shielding within the context of magnetic field density functional theory (BDFT). These functionals depend on the electron density in the absence of the field, which is unlike any other treatment of these responses.

There have been several advances made within this theory. The first of which is the development of local density functionals for chemical shieldings and magnetic susceptibilities. These are the first such functionals ever proposed. These parameters have been studied by constructing functionals for the current density and then using the Biot-Savart equations to obtain the responses. In order to examine the advantages

and disadvantages of the local functionals, they were tested numerically on some small molecules.

In order to mitigate some of the difficulties encountered with local functionals, nonlocal functionals of the electron density were also developed. The consideration of nonlocal functionals led to the examination of the exchange energy in the presence of a constant magnetic field. In order to avoid divergences, every other treatment of the exchange has required the screening of the exchange by correlation. The first exchange functional in which this divergence was avoided because of the bound state nature of the electronic system was constructed. Additionally, a conjecture was made for the form of the full exchange-correlation energy functional. In both instances, the functionals depend on the ground state electron density in the absence of any magnetic field.

The J, or indirect spin-spin coupling, was also examined. Estimates were made of some intermolecular xenon J couplings, which are motivating some experimental work. This estimate was done using BDFT, but the approach was different from that used for the chemical shielding and the susceptibility as it was a direct energy treatment, that is, the Biot-Savart integrals were not used.

An investigation was also made into the recently discovered magnetic field-dependent quadrupole splitting. The physical origin and magnitudes of both the linear and

quadratic dependencies on the magnetic field were explained.

Professor Alexander Pines
and Professor Robert A. Harris
Thesis Committee Chairs

Magnetic Fields and Density Functional Theory

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Freddie Salsbury, Jr.

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Introduction

Magnetic Fields and Density Functional Theory

This thesis presents theoretical developments in the study of Nuclear Magnetic Resonance parameters including the magnetic susceptibility. The first three chapters contain introductory material on magnetic interactions, electronic structure and density functional theory. The next part of the thesis present developments in magnetic field density functional theory, which builds upon the introductory chapters. The purpose of this work has been to develop a framework for the computation of NMR parameters from ground state electron densities. This work has, hopefully, constructed a foundation upon which others can now build so as to perform computational investigations of NMR parameters within the context of this theory. This theory should provide a new paradigm for the interpretation of magnetic responses to weak, i.e., NMR strength, magnetic fields. This theory should be especially applicable to large systems, such as biomolecules, as it is not only a density functional theory, but also one in which excited state corrections are not needed for the computation of NMR parameters.

The last part of this thesis focuses on the estimation of parameters that were previously thought to be unobservable: intermolecular J couplings and field-induced quadrupole shifts. The former still have yet to be investigated experimentally, however, this work shows that they are in principle observable due to the increase in sensitivity obtained by using optically pumped xenon. One could imagine exploiting these couplings in the NMR of biomolecules with which xenon forms van der Waals complexes. The field-induced quadrupole shifts were measured experimentally first, and then their existence was explained as detailed in this work. This effect is interesting as it shows that in some, albeit rare, instances the perturbation of the electron density due to the magnetic field, cannot be neglected.

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I have many people to thank for their assistance and support over the past few years. First of all, I must thank Professor Robert Harris with whom my research was conducted. He taught me how to do theoretical research by first giving me a problem and working with me on it. After I worked on that problem, most of which is not even in this thesis, we figured out stuff to work on together. Sometimes I would come up with something and other times he would. I also felt like a collaborator rather than as a student while working with Bob. He gave me the intellectual freedom to attack many different problems: many of which did not work, the ones that did are reported in this thesis.

I also must thank the my other major intellectual mentor over the past 4 years: Professor Alexander Pines. I thank him for accepting me into his group and letting me pursue my research interests within his group. He has created an incredible research environment with many talented and energetic scientists with whom it has been a pleasure to interact with. The enthusiasm and energy of Alex and his group are always inspiring.

Dione Carmichael has been invaluable for keeping the group running on a day-to-day basis and for providing a constant source of fascinating conversation and advice.

I have known far too many pinenuts to acknowledge them on an individual basis and so I can only acknowledge a few. Dr. Thomas Meersmann presented me with the problem of the field-induced quadrupolar splitting that is explained in Chapter

9. I also have had the opportunity to talk to him about possible experiments that he will perform someday. Dr. Marco Tomaselli with whom I never had the pleasure of working with on any experiments, but with whom I have had many enlightening scientific conversations. Many other members of the group, too many to name, have contributed in a positive way to the atmosphere of the group.

I also must thank many members of the department; students, postdocs, and professors, for providing social distractions and intellectual conversations. Many of these occurred at the chem keg on Fridays that has been an important social weekly event for me. All the keg czars over the past few years deserve a thumbs up for keeping the beer coming. Thanks to the entire chem keg crowd, especially Chris Maierle who also has the joy of working with Bob, Sarah de Forest, Ryan Trump and Andre Miller, but many others as well for keeping me out of lab on Friday nights at least. I also must thank Seth Bush who overlaps as a pinenut, former keg czar and a generally fun and good friend for lots of good times and conversations. I'm sure there are others to be thanked, and I apologize for any omissions.

Chapter 1

Introduction to Magnetic Fields

In order to understand how magnetic fields and density functional theory are linked in Nuclear Magnetic Resonance (NMR), a review of how magnetic fields enter into quantum mechanics is needed. As quantum phenomena are typically obtained from classical phenomena through the correspondence principle, a review of some elements of classical mechanics is warranted. [1]

1.1 The Basics

A charged particle of mass m and charge e in a magnetic field, $\tilde{B}(\tilde{r},t)$ has the following Hamiltonian. [2] [3]

$$H = \frac{1}{2m}[\tilde{p} - \frac{e}{c}\tilde{A}(\tilde{r},t)]^2 \tag{1.1}$$

In the Hamiltonian, $\tilde{p}$ is the particle momentum and $\tilde{A}(\tilde{r})$ is the vector potential given by

$$\tilde{B}(\tilde{r},t) = \nabla \times \tilde{A}(\tilde{r},t). \tag{1.2}$$

Thus, the introduction of a magnetic field changes the effective momentum felt by the charged particle as a free particle in the absence of a field would have a different Hamiltonian.

$$H = \frac{1}{2m}[\tilde{p}]^2 \tag{1.3}$$

The search for a Hamiltonian starts with an observed force law. To obtain the Hamiltonian from Equation 1.1, the starting point is the Lorentz force law.

$$m\tilde{a} = e[\tilde{E}(\tilde{r},t) + \frac{1}{c}\tilde{v} \times \tilde{B}(\tilde{r},t)]. \tag{1.4}$$

This is the experimentally observed force law for a particle in an electromagnetic field specified by $\tilde{E}(\tilde{r},t)$ and $\tilde{B}(\tilde{r},t)$. The magnetic field acts in a direction perpendicular to the particle's velocity causing particles to move in a helix. This distinguishes the effect of a magnetic field from the effect of an electric field. To obtain the Hamiltonian from the force law, a consistent Lagrangian must be found and the Hamiltonian obtained from the Lagrangian. [4]

To obtain a Lagrangian, one assumes that the state of a mechanical system at a particular time can be specified by some function of its position and its velocity. It is assumed that higher derivatives of position are not needed. This function that specifies the state of a mechanical system in classical mechanics is the Lagrangian. For simplicity, consider a single particle. Now to obtain the equations of motion for the particle between $\tilde{r}(t^{''})$ and $\tilde{r}(t^{'})$, one invokes the principle of least action that is sometimes called Hamilton's principle. The action, S, is defined as the time integral of the Lagrangian:

$$S = \int_{t'}^{t''} L(\tilde{r}, \tilde{v}, t) dt. \tag{1.5}$$

The principle of least action requires that the system follow the trajectory that minimizes the action. So a variation of the action is performed:

$$\delta S = \delta \int_{t'}^{t''} L(\tilde{r}, \tilde{v}, t) dt = 0. \tag{1.6}$$

This minimizes the action because if there exists a function $\tilde{r}(t)$ which minimizes S, then changing $\tilde{r}(t)$ slightly to $\tilde{r}(t) + \delta\tilde{r}(t)$, produces a change in S given by

$$\delta S = \int_{t'}^{t''} L(\tilde{r} + \delta\tilde{r}, \tilde{v} + \delta\tilde{v}, t) dt - \int_{t'}^{t''} L(\tilde{r}, \tilde{v}, t) dt; \tag{1.7}$$

expanding this out in a power series gives leading terms that are linear and the condition that there is a minimum implies that the linear terms vanish. Thus, the variation suffices to minimize the action. Upon performing the variation, the following is obtained:

$$\delta S = \int_{t'}^{t''} -\frac{d}{dt}(\frac{\partial L}{\partial \tilde{v}}) + \frac{\partial L}{\partial \tilde{r}} \delta \tilde{r} dt = 0 \tag{1.8}$$

which with the variation vanishing at the endpoints yields,

$$\frac{d}{dt}(\frac{\partial L}{\partial \tilde{v}}) - \frac{\partial L}{\partial \tilde{r}} = 0. \tag{1.9}$$

This results in Lagrange's equation. With multiple degrees of freedom the variations must be performed independently for each degree of freedom.

The following Lagrangian gives the correct force law for a particle in an electromagnetic field,

$$L(\tilde{r}, \tilde{v}, t) = \frac{1}{2} m v^2 - e\Phi(\tilde{r}, t) + \frac{e}{c} \tilde{v} \bullet \tilde{A}(\tilde{r}, t). \tag{1.10}$$

$\Phi(\tilde{r}, t)$ and $\tilde{A}(\tilde{r}, t)$ are the parameters which determine the electromagnetic field as given by

$$\tilde{B}(\tilde{r}, t) = \nabla \times \tilde{A}(\tilde{r}, t). \tag{1.11}$$

$$\tilde{E}(\tilde{r},t) = -\nabla\Phi(\tilde{r},t) - \frac{1}{c}\frac{\partial}{\partial t}\tilde{A}(\tilde{r},t). \tag{1.12}$$

$\tilde{A}(\tilde{r},t)$ is the vector potential and $\Phi(\tilde{r},t)$ is the scalar potential. For time independent fields, they produce the magnetic and electric fields, respectively. To show that this Lagrangian gives the correct force law, Lagrange's equation is used to establish consistency. In particular, allowing

$$\frac{\partial L}{\partial v_i} = mv_i + \frac{e}{c}A_i(\tilde{r},t) \tag{1.13}$$

$$\frac{\partial L}{\partial r_i} = -e\frac{\Phi(\tilde{r},t)}{\partial x_i} + \frac{e}{c}\sum_{j=1}^{3} v_j \frac{\partial A_j(\tilde{r},t)}{\partial x_i} \tag{1.14}$$

then with some algebra, and using Equations 1.10 and 1.11, the correct force law is obtained.

Quantum mechanic, however, is formulated with a Hamiltonian. [1] Hence, there be must a change from Lagrangian to Hamiltonian mechanics. The Hamiltonian is just a Legendre transform of the Lagrangian:

$$H = \tilde{p} \bullet \tilde{v} - L. \tag{1.15}$$

The momentum $\tilde{p}$, is the canonical momentum that is given in Equation 1.13. This is the canonical momentum, because if $\tilde{A}$ and Φ are independent of some degree of freedom, y, then $\frac{\partial L}{\partial y} = 0$. Hence, y is a conserved quantity. Upon substitution of the correct Lagrangian into the Hamiltonian, the following is obtained,

$$H = \frac{mv^2}{2} + e\Phi(\tilde{r}, t) = \frac{1}{2m}[\tilde{p} - \frac{e}{c}\tilde{A}(\tilde{r}, t)]^2 + e\Phi(\tilde{r}, t) \tag{1.16}$$

The latter is the usual Hamiltonian that is used in quantum mechanics with appropriate operator substitutions. Thus, the quantum Hamiltonian for a particle in a magnetic field with no electric field is simply

$$H = \frac{1}{2m}[i\nabla - \frac{e}{c}\tilde{A}(\tilde{r})]^2 \tag{1.17}$$

with $\hbar = 1$.

As the vector potential is in the Hamiltonian, it should be examined more carefully. The physical observable is the magnetic field, which is the curl of the vector potential. Hence, the vector potential is defined uniquely only up to the gradient of a scalar, $\nabla S(\tilde{r})$, i.e.,

$$\tilde{B}(r) = \nabla \times \tilde{A}(\tilde{r}) = \nabla \times (\tilde{A}(\tilde{r}) + \nabla S(\tilde{r})). \tag{1.18}$$

Such a transformation is referred to as a gauge transformation, or a change in gauge. This transformation does not change the field in any manner. The field is the physical quantity and so a gauge transformation cannot affect any observable result. This invariance under a change of gauge is referred to as gauge invariance and any exact theory is gauge invariant. Gauge dependencies should be avoided as they lead to unphysical dependencies on the vector potential. The nonuniqueness of the vector potential does lead to an extra phase factor in the wavefunction. In particular, given the Hamiltonian of Equation 1.17, and a wavefunction Ψ, then the gauge transformation from Equation 1.18 leads to a phase change, $\Psi \rightarrow \Psi e^{(\frac{ieS(\tilde{r})}{c})}$.

Although gauge invariant theories should be developed, in practice a gauge must be chosen and then error checked for by verifying gauge invariance, or its lack. A common gauge to use is the Coulomb gauge.

$$\nabla \bullet \tilde{A}(\tilde{r}) = 0. \tag{1.19}$$

This is convenient as now the momentum and the vector potential commute. [5] The two fields of interest in this work will be the uniform field and the dipole field with the dipole at the origin. Hence, the gauges used will be respectively, [6]

$$\tilde{A}(\tilde{r}) = \frac{1}{2}\tilde{B} \times \tilde{r} \tag{1.20}$$

$$\tilde{A}(\tilde{r}) = \frac{\tilde{\mu} \times \tilde{r}}{r^3}. \tag{1.21}$$

The use of the vector potential in quantum mechanics does have physical consequences. The most famous such effect is the Aharonov-Bohm effect; a purely quantum mechanical effect due to the vector potential. [7] Two variants of this problem exist: a bound state version and an interference problem. The latter is more famous, but the former is simpler. Hence, the former shall be sketched out here.

Suppose there is a hollow cylindrical shell with a trapped particle inside the shell, and a uniform magnetic field enclosed by the shell. This field does not penetrate into the shell. Hence, the particle never feels the field. The particle is truly trapped by the shell. Hence, its wavefunction vanishes at the inner and outer walls and at the top and bottom of the cylinder. Classically, there is no force on the particle as there is no field inside the cylindrical shell. However, quantum mechanics predicts a shift in the particle's energy. The shift arises because the field vanishes inside the shell, but the vector potential does not vanish. Application of Stokes theorem indicates that to obtain a field B in the z direction inside the volume enclosed by the shell, the following vector potential may be used

$$A(r) = \frac{Br_a^2}{2r}\theta. \tag{1.22}$$

Solving the Schrödinger equation with this vector potential causes an observable change in the particle's energy despite the field only being present in a region with the particle cannot access. The Aharonov-Bohm effect is a dramatic example of the nonlocal nature of magnetic interactions in quantum mechanics.

1.2 Spin Hamiltonian

The Hamiltonian derived above for a charged particle in a magnetic field looks quite different from the Hamiltonians usually seen in NMR. This is because the Hamiltonians of NMR are written as nuclear spin Hamiltonians and the electron interactions are subsumed into the NMR parameters.

The nuclear spin Hamiltonian for a pair of nuclear spins is, [8]

$$H_{\mu}^{spin} = -\tilde{\mu}_1 \bullet \tilde{B} - \tilde{\mu}_2 \bullet \tilde{B} + \tilde{\mu}_1 \bullet \tilde{\tilde{\sigma}}_1 \bullet \tilde{B} + \tilde{\mu}_2 \bullet \tilde{\tilde{\sigma}}_2 \bullet \tilde{B} + \tilde{\mu}_1 \bullet \tilde{\tilde{J}}_{12} \bullet \tilde{\mu}_2 + \tilde{\mu}_1 \bullet \tilde{\tilde{D}}_{12} \bullet \tilde{\mu}_2 \tag{1.23}$$

Notice that the magnetic susceptibility is not present, as it does not involve the nuclear spin. Instead the magnetic susceptibility is of the form $\tilde{B} \bullet \tilde{\tilde{\chi}} \bullet \tilde{B}$. As such the magnetic susceptibility a purely electronic property, and is independent of the nuclear spin. This nuclear spin Hamiltonian is an effective Hamiltonian as it contains only the two nuclei explicitly. This Hamiltonian has been written in its simplest form. It can be written in slightly different forms as well, which you may find in other works. [9]

The first two terms are the Zeeman interactions. These correspond to the classical interactions between a nuclear dipole μ_i and an applied field. The subscripts indicate the two different nuclei. Hence, these are single spin operators that depend upon just the interaction of external field and a single spin. The electrons are not involved. Hence, this interaction shall not be considered in detail. The third and the fourth terms are the chemical shielding terms. The chemical shielding tensors are denoted by $\tilde{\bar{\sigma}}_i$. These terms contain in them the coupling between the electrons and each nuclear spin separately with the applied field. These operators are still single spin operators. The difference between these and the Zeeman terms is the electronic coupling, hence these operators probe the electrons. The next to last term is the J coupling, also known as the indirect spin-spin coupling. This is the coupling between the two nuclei, which is manifest through the electrons. Unlike the first four operators, this is a two spin operator. The last term is the dipolar coupling, or the direct spin-spin coupling. The dipolar coupling does not involve electronic interactions. It is the direct nuclei-nuclei interaction. As such it is mentioned here only for completeness. These terms will be examined in more detail later. First, the connections between the spin Hamiltonian and the full Hamiltonian should be made clear.

Perturbation theory is the method of choice as the interaction of the magnetic fields with the electrons is much weaker than the electron-electron interaction. [6] A molecular system may be considered as consisting of 2 weakly coupled subsystems. The wavefunction for the full molecular system is Ψ. The first system consists of the electrons that feel a fixed scalar nuclear potential, the second contains the nuclei that feel a uniform external applied field and the dipolar coupling. For simplicity, it is easiest to consider only the chemical shielding at first as the remaining interactions are analogous. The effective spin Hamiltonian is,

$$H_\mu^{spin} = -\tilde{\mu} \bullet \tilde{B} + (< \psi|H_{\mu e}|\psi >)_e. \tag{1.24}$$

The expectation value is taken over the electronic coordinates as indicated by the subscript e. $H_{\mu e}$ is the coupling between the nucleus and the electrons. Hence, the effective Hamiltonian depends explicitly only upon the nuclear spin coordinates, so it is referred to as the spin Hamiltonian. To illustrate what the second, perturbative interaction is, start with the full Hamiltonian for the two coupled systems,

$$H = -\tilde{\mu} \bullet \tilde{B} + \sum_k \frac{1}{2}(\tilde{p}_k + \frac{\tilde{A}(\tilde{r}_k)}{c})^2 + V(\tilde{r}) \tag{1.25}$$

where atomic units have been used, the sum runs over the k electrons, and the $\tilde{r}$ in $V(\tilde{r})$ refers to all the k electronic coordinate vectors. As this Hamiltonian will cause the chemical shielding, the total vector potential is the superposition of two vector potentials: the potentials due to the nuclear dipole and the uniform external field. Hence,

$$\tilde{A}(\tilde{r}_k) = \tilde{A}^B(\tilde{r}_k) + \tilde{A}^\mu(\tilde{r}_k) = \frac{\tilde{B} \times \tilde{r}_k}{2} + \frac{\tilde{\mu} \times \tilde{r}_{k\mu}}{r_{k\mu}^3}. \tag{1.26}$$

Of course, the first term is not uniquely defined as a uniform external field has an arbitrary origin. So any physical property should be invariant under the transform

$\tilde{r}_k \rightarrow (\tilde{r}_k - \tilde{S})$. The second term has a natural origin at the nucleus that creates it.

With this in mind, the Hamiltonian can be rewritten as follows:

$$\begin{aligned} H &= -\tilde{\mu} \bullet \tilde{B} + \sum_k \frac{1}{2}(\tilde{p}_k + \frac{\tilde{A}_k^B}{c})^2 + V(\tilde{r}) \\ &+ \sum_k \frac{1}{c}(\tilde{p}_k + \frac{\tilde{A}_k^B}{c}) \bullet \tilde{A}_k^\mu + ... \end{aligned} \tag{1.27}$$

Advantage has been taken of the divergencelessness of the gauge choice, and hence, the commutation properties. This has been done for simplicity only. The term quadratic in the vector potential due to the nuclear spin has been dropped as not contributing to the shielding. The term quadratic in the vector potential due to the external field also does not contribute to the shielding, and will be dropped later. If the nuclear vector potential is explicitly placed into the equations then the last term becomes,

$$\sum_k \frac{1}{c}((\tilde{p}_k + \frac{\tilde{A}_k^B}{c}) \bullet \frac{\tilde{\mu} \times \tilde{r}_{k\mu}}{r_{k\mu}^3}, \tag{1.28}$$

which is reminiscent of the classical Biot-Savart law that will be discussed later in more detail.

Taking the expectation value of the full Hamiltonian with respect to the electronic coordinates will generate the spin Hamiltonian. This is

$$H = -\tilde{\mu} \bullet \tilde{B} + E_e + (< \psi | H_{\mu e} | \psi >)_e \tag{1.29}$$

in which E_e is the electronic energy and is constant, independent of the spins and hence, can be dropped. After doing so, the spin Hamiltonian of Equation 1.24 is generated. The last term is the portion of the spin Hamiltonian due to the electrons coupling with the nucleus. This is the coupling that leads to the chemical shielding. Explicitly, the latter term can be written as,

$$< \psi|H_{\mu e}|\psi >_e = < \psi|\tilde{\mu} \bullet \sum_k \frac{1}{c}(\frac{\tilde{r}_{k\mu} \times (\tilde{p}_k + \frac{\tilde{A}_k^B}{c})}{r_{k\mu}^3})|\psi >_e . \tag{1.30}$$

Notice that between the bra and the ket are operators with two different dependencies on the applied field. The momentum has no explicit dependence on the field, whereas the vector dependence is first order. If the exact electronic wavefunctions determined in the presence of field were used, these different dependencies would not matter. However, typically the zeroth order electronic wavefunction, i.e. the wavefunction without the field, is used as the starting point. To treat the two portions of the Hamiltonian on equal footing, perturbation theory must be performed, at least in this treatment,

$$\psi_e(\tilde{B}) = \psi_e^0 + \Sigma_j B_j \psi_{ej}^1. \tag{1.31}$$

This allows one to write the portion of the coupled Hamiltonian in a perhaps more familiar fashion as,

$$< \psi | H_{\mu e} | \psi >_e = \tilde{\mu} \bullet \tilde{\tilde{\sigma}} \bullet \tilde{B}, \tag{1.32}$$

σ is the chemical shielding tensor and contains all the electronic information in the problem as neither the J coupling nor the magnetic susceptibility have been considered.

The integral over electronic coordinates can be divided into two parts

$$\tilde{\tilde{\sigma}}_D \bullet \tilde{B} = < \psi^0 | \sum_k \frac{1}{c^2} (\frac{(\tilde{r}_{k\mu} \times \tilde{A}_k^B)}{r_{k\mu}^3}) | \psi^0 >_e \tag{1.33}$$

$$\tilde{\tilde{\sigma}}_P \bullet \tilde{B} = \sum B_j < \psi^0 | \sum_k \frac{1}{c^2} (\frac{\tilde{r}_{k\mu} \times \tilde{p}_k}{r_{k\mu}^3}) | \psi_j^1 >_e + c.c. \tag{1.34}$$

The first part is the diamagnetic shielding and the second the paramagnetic shielding. The latter is the more difficult term to understand as it requires knowledge of the excited states to calculate the perturbed wavefunction to first order. In particular, excited states which must be known are those that are connected to the ground state by magnetic dipole transitions. This separation into diamagnetic and paramagnetic is a standard separation. However, such a separation is not gauge invariant. The sum is a physical quantity and hence, is invariant under gauge transforms; it is the individual quantities that are not invariant. One should be careful not to ascribe undue physical significance to these quantities, with one exception. In the present gauge, the Coulomb gauge, closed shell atomic systems are purely diamagnetic, and so in this gauge paramagnetic components result from the breaking of atomic symmetry. This statement is not necessarily true in other gauges, though the overall numeric result is independent of gauge. Additionally, one must realize that while the precise separation into paramagnetic and diamagnetic depends upon the gauge, one cannot always find a gauge in which the shielding is purely diamagnetic. The only instances where one can do so are for systems that are spherically symmetric, or which have only one or two electrons. In all other instances, the shielding, and the other responses, will have both paramagnetic and diamagnetic portions.

The shielding interactions may be more familiarly represented as a change in the magnetic field felt by the nucleus due to electron currents. The connection between this representation and the above explanation can be made through the classic Biot-Savart law.

In classical electricity and magnetism, the Biot-Savart law reproduces the observed induced B field generated by a current. [2] An infinitesimal wire of length dl which carries current I produces an infinitesimal field element at a position x which is,

$$d\tilde{B} = I\frac{(d\tilde{l} \times \tilde{x})}{cx^3}. \tag{1.35}$$

Now for a general current density $\tilde{J}(\tilde{r}')$, the expression can be generalized to

$$\tilde{B}(\tilde{r}) = \int \tilde{J}(\tilde{r}') \times \frac{(\tilde{r} - \tilde{r}')}{(\tilde{r} - \tilde{r}')^3} d\tilde{r}'. \tag{1.36}$$

Of course, this begs the question as to what the current density is especially in a molecular system. Classically, the current is the rate of particle flow through a surface, and so quantum mechanically this would be expressed as

$$\frac{d\int|\psi|^2dV}{dt} = -\int \tilde{j} \bullet d\tilde{f} \tag{1.37}$$

$$= -\int \nabla \bullet \tilde{j} dV. \tag{1.38}$$

$\tilde{j}$ is the current density and Gauss's theorem has been used to convert the surface integral into a volume integral. This comes from the equation of continuity which follows from charge conservation, i.e. [3],

$$\frac{d|\psi|^2}{dt} + \nabla \bullet \tilde{j} = 0. \tag{1.39}$$

Now carrying the derivative through one obtains the following, after using the time-dependent Schrödinger equation $i\frac{\partial\psi}{\partial t} = H\psi$,

$$\frac{d\int|\psi|^2dV}{dt} = i\int(\psi H^*\psi^* - \psi^* H\psi)dV. \tag{1.40}$$

If we start with the system in the absence of a magnetic field, then the Hamiltonian is just $\frac{-\nabla^2}{2m} + V$ and so we have that

$$
\begin{aligned}
& i\int(\psi H^*\psi^* - \psi^* H\psi)dV \\
= & -\int \nabla \bullet (\frac{i}{2}(\psi\nabla\psi^* - \psi^*\nabla\psi))dV \qquad (1.41) \\
= & -\int \nabla \times \tilde{j}dV. \qquad (1.42)
\end{aligned}
$$

Thus the current density, $\tilde{j}$, is defined with the momentum and vanishes for purely real wavefunctions, e.g., closed shell systems in their ground states without a field.

The more interesting case is when there is a magnetic field present. The simplest way to see how the current density varies in this instance is to note that the current density can be written as

$$\tilde{j} = -\frac{1}{2}(\psi\tilde{p}\psi^* - \psi^*\tilde{p}\psi). \qquad (1.43)$$

Then make the usual substitution, $\tilde{p} \longrightarrow \tilde{p} + \frac{\tilde{A}}{c}$ as discussed before Qquation 1.15. The following expression for the current density is obtained,

$$\tilde{j} = \frac{i}{2}(\psi\nabla\psi^* - \psi^*\nabla\psi) - \frac{\tilde{A}}{c}\psi^*\psi. \qquad (1.44)$$

The first portion is the paramagnetic current density and the second is the diamagnetic current density. As usual, the division between paramagnetic and diamagnetic is not gauge invariant, but the current density as a whole is gauge invariant. This is because the current density is a physical observable. A more rigorous approach would be consider the change of the Hamiltonian due to the change of the vector potential that interested readers can find elsewhere [5]. Notice that with this definition of the current density, the expression for the chemical shielding can be rewritten as,

$$\tilde{\mu} \bullet \tilde{\tilde{\sigma}} \bullet \tilde{B} = \tilde{\mu} \bullet \int \frac{1}{c} \frac{\tilde{r} \times \tilde{J}}{r^3} Dr. \tag{1.45}$$

In this treatment, the applied field and the nuclear moment have been treated differently. In particular, the current density has been considered as being induced by the applied field. So the current density can be considered as the response by the electrons to the perturbing uniform field. This unequal treatment is merely convenient. One could equally well reverse the present treatment and consider the current density induced by the nuclear magnetic moment and take the dot product with the applied field. This is referred to as the inverse Biot-Savart law and in an exact theory is equivalent to the Biot-Savart law.

This use of the Biot-Savart law for the calculation of magnetic responses is referred to as a susceptibility treatment of magnetic responses. The alternative treatment is an energy approach in which the magnetic responses are treated as energy derivatives. For example, from examining Equations 1.33-1.45 one has that ,

$$\tilde{\tilde{\sigma}} = \frac{\partial^2 E}{\partial \tilde{B} \partial \tilde{\mu}}. \tag{1.46}$$

E is the electronic energy, and derivatives are taken in the limit of both fields becoming zero. In an exact theory, both approaches are equivalent. It is only with approximation that they may become different. Writing the shielding as an energy derivative has the advantage of making it clear that the shielding is a tensorial property, as the fields are each a vector. Additionally, this form demonstrates that one cannot make statements about the symmetry of the shielding without considering the symmetry of the electron distribution.

All the magnetic responses, or more properly, the lowest order magnetic responses, not just the chemical shielding, are second order with respect to the fields. This is because a magnetic field is odd under time reversal, unlike an electric field, which is even. The energy is even under time reversal as the Schrödinger equation for closed shell systems is even under time reversal. This requires magnetic fields to couple in even orders to closed shell systems. [7] Time reversal along with the extraordinary weak effect of magnetic fields upon most systems explains why one need only consider 3 magnetic fields for NMR parameters: the fields from two dipoles and one applied uniform field. In particular, the electronic energy of a closed shell molecular system with i number of nuclei in a NMR magnet can be written as:

$$E = E^0 + \tilde{B} \bullet \frac{\partial^2 E}{\partial \tilde{B} \partial \tilde{B}} \bullet \tilde{B} + \sum_i \tilde{B} \bullet \frac{\partial^2 E}{\partial \tilde{B} \partial \tilde{\mu}_i} \bullet \tilde{\mu}_i + \sum_{i>j} \tilde{\mu}_i \bullet \frac{\partial^2 E}{\partial \tilde{\mu}_i \partial \tilde{\mu}_j} \bullet \tilde{\mu}_j. \qquad (1.47)$$

The different terms are respectively: the zero field electronic energy, the energy due to the magnetic susceptibility, χ, the energy due to the chemical shieldings of the nuclei, σ_i, and the energy due to the indirect spin-spin couplings between the pairs of nuclei, J_{ij}. In principle, the expansion could be carried out to higher orders. One could expand the magnetic interactions to fourth order, and obtain terms coupling up to four nuclear spins. Presently, such effects are far too small to be observed in NMR. One could also include mixed electric-magnetic properties such as a magnetic-field induced quadrupole moment. This has only been observed recently and will be discussed later in Chapter 9. Notice that at this level, there is no separation into diamagnetism and paramagnetism. It is only when the energy is divided into these two terms that the shielding, and the other responses, become separated. This is not a surprise as paramagnetism and diamagnetism are not in themselves uniquely defined. Notice as well, that in the Biot-Savart law there is no such separation unless one makes one in the current density. Hence, if expressions are obtained for the energy or the current density respectively which avoid this separation, then one avoids the whole issue of gauge invariance at this level in the responses.

1.3 Nuclear Magnetic Resonance Parameters

Now that the connection between the spin Hamiltonian and the full Hamiltonian has been made for the chemical shielding, a more thorough discussion of the parameters of NMR is justified. [8] [9].

The chemical shielding is the best known of the different parameters and is the one, which is most important to this work. In general, the chemical shielding is a second rank tensor with 9 independent components. This is obvious as the shielding is defined as

$$\tilde{\tilde{\sigma}} = \frac{\partial^2 E}{\partial \tilde{B} \partial \tilde{\mu}}. \tag{1.48}$$

Each field has three components - x, y and z in Cartesian coordinates - so the whole tensor has 9 components and no specific symmetry in general. Any second rank tensor can be broken up into three pieces with definite symmetries: a scalar with one independent component, a symmetric traceless tensor with 5 independent components, and an antisymmetric tensor with 3 independent components, i.e.,

$$\tilde{\tilde{\sigma}} = \frac{\sigma}{3} \begin{matrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{matrix} + \begin{matrix} a_{11} & a_{12} & a_{13} \\ a_{12} & a_{22} & a_{23} \\ a_{13} & a_{23} & a_{33} \end{matrix} + \begin{matrix} 0 & b_{12} & b_{13} \\ -b_{12} & 0 & b_{23} \\ -b_{13} & -b_{23} & 0 \end{matrix} . \tag{1.49}$$

The antisymmetric component, however, is not directly observable in NMR experiments - though it may be observed in relaxation measurements [8]. Hence, there are 6 independent elements. A simple argument with spin 1/2 particles can explain this effect. The splitting of the energy levels of a spin 1/2 particle in a magnetic field is given by the magnitude of the field. Hence, the Larmor frequency becomes proportional to only the symmetric components as,

$$\omega \propto B_0[\epsilon^t(1-\sigma^t)(1-\sigma)\epsilon]^{1/2} \tag{1.50}$$

$$\propto B_0[\epsilon^t(1-\sigma^t-\sigma+\sigma^t\sigma)\epsilon]^{1/2}, \tag{1.51}$$

where ϵ is the unit vector along the external field, and the t indicates the transpose. As the shielding tensor is small the last term may be disregarded which results in,

$$\omega \propto B_0[\epsilon^t(1-(\sigma^t+\sigma))\epsilon]^{1/2} \tag{1.52}$$

$$\propto B_0[\epsilon^t(1-\sigma^{symmetric})\epsilon]^{1/2}. \tag{1.53}$$

The symmetry of the particular system may reduce the number of independent elements even further, if the system has a highly symmetric electron distribution, in which the symmetry of the electron distribution follows the nuclear symmetry. For example, a linear molecule has only 3 independent axes. These consist of an axis on the line through the bond and two axes perpendicular to the bond. The two perpendicular axes are equivalent due to symmetry. Hence, the shielding tensor has only three components and the two perpendicular components are identical. So there are only two independent components. Additionally, symmetry constraints on the paramagnetic contribution can cause it to vanish for particular symmetries, i.e. spherical symmetry or in the direction parallel to the bond axis in a linear molecule. When the electronic distribution has the highest possible symmetry , i.e. spherical, the shielding tensor is at its most symmetric. As a result, only the isotropic component survives. Motion that is faster than the NMR timescale can also average out the shielding tensor. For example, in liquids or gases one typically only observes the isotropic component as the rest are averaged away by rapid tumbling. This is because the rapid motion cause reoriention of the molecules with respect to the field, and so any anisotropy is cancelled away.

Typically, one takes the asymmetric tensor resulting from a calculation, symmetrizes it and then diagonalizes it. The eigenvalues are referred to as the principal values $\sigma_{11}, \sigma_{22}, \sigma_{33}$ and the eigenvectors as the principal axes, hence, the term Principal Axis System (PAS) for the axis system spanned by the set of eigenvectors. By convention, the principal values are ordered such that

$$\sigma_{33} > \sigma_{22} > \sigma_{11}. \tag{1.54}$$

However, experimentally these are not the chemical shielding tensor elements as the chemical shielding is not the actual observed quantity in NMR. Rather, the chemical shift is measured and defined in ppm,

$$\delta = 10^6 \frac{(\nu_s - \nu_{ref})}{\nu_{ref}} \tag{1.55}$$

s is the system of interest, ref is a reference, and ν_i is the frequency observed which is given as

$$\nu = \frac{\gamma B_0(1-\sigma)}{2\pi}. \tag{1.56}$$

Now in most instances, σ is much less than unity and so to a good approximation the σ which is contained in the definition of ν_{ref} in the denominator of Equation 1.55 can be neglected. However, it may be important to consider this for systems with large shieldings. One should always keep in mind the relative nature of shifts.

One typically characterizes spectra by linear combinations of the principal values. These combinations are more reliably obtained from experimental spectra on samples with a range of orientations, i.e., powders that give powder patterns. In particular, these parameters are the anisotropy

$$\delta\sigma = \sigma_{33} - \frac{(\sigma_{22}+\sigma_{11})}{2}, \tag{1.57}$$

the asymmetry, η, and the isotropic shift , σ,

$$\eta = \frac{(\sigma_{22}-\sigma_{11})}{(\sigma_{33}-\sigma_{iso})} \tag{1.58}$$

$$\sigma_{iso} = \frac{\sigma_{11}+\sigma_{22}+\sigma_{33}}{3}. \tag{1.59}$$

These particular linear combinations are useful because in an axially symmetric system the asymmetry vanishes and the anisotropy becomes

$$\delta\sigma = \sigma_{\parallel} - \sigma_{\perp}. \tag{1.60}$$

Axially or nearly axially symmetric systems are commonly encountered in experimental situations.

Another important physical effect to consider when comparing theoretical and experimental shieldings is the effect of rovibrational averaging. [9] Te majority of experiments are carried out at room temperature. However, theoretical shifts are usually calculated at a fixed geometry. So to compare exactly a theoretical shift and an experimental shift one should average the theoretical results over a chemical shielding surface. A chemical shielding surface is a surface showing the shielding for different nuclear geometries much like a potential energy surface, but with the shieldings instead of the energies plotted. In principle, one must do this for both the zero-point and thermal vibrations. Now this can rarely be done at present due to the computational cost of most theoretical treatments, which provides further motivation for the development of new theoretical techniques.

The magnetic susceptibility is not really a NMR parameter as it is independent of the nuclei and depends only on the electrons. However, as the Biot-Savart integrals demonstrate it is related to the chemical shielding and hence should be examined.

Unlike the chemical shielding, the susceptibility truly is a symmetric tensor,

$$\tilde{\tilde{\chi}} = \frac{\partial^2 E}{\partial \tilde{B} \partial \tilde{B}}. \tag{1.61}$$

As such it has 6 independent components and can be decomposed into isotropic and symmetric components. The symmetry arguments, which lead to various components vanishing, are identical to the ones used for the chemical shielding as experimentally one observes symmetric tensors for both.

The J coupling is the third magnetic response to be considered here. It is the most difficult to understand theoretically, and is the source of much confusion. It is becoming of increased importance experimentally, especially in the study of biological molecules.

The J coupling can also be written as an energy derivative just as the shielding and the susceptibility. This makes it apparent that it is in general a second rank tensor with no particular symmetry. The J coupling needs to be examined more carefully as the J coupling does not arise from a single interaction: rather, there are 3 different interactions that give rise to the J coupling. These interactions have different properties and so need to be examined individually.

The J coupling arises from the same interactions between the nucleus and the electron that cause the hyperfine and fine structure. [6] [9] In particular, there are the dipolar, orbital and Fermi contact interactions. The orbital interaction is between the orbital motion of the electrons and the magnetic moment of the nucleus. The dipolar interaction is between the magnetic moment of the electrons and the magnetic moment of the nucleus. The Fermi contact interaction results from the electrons penetrating into the nucleus. These three interactions provide different mechanisms for couplings between a nucleus and the electrons. As the electrons are coupled in a molecular system between different nuclei, these interactions provide an indirect coupling between the nuclei.

Consider the orbital interaction between a nucleus and an electron,

$$H^o = \frac{1}{2c}\frac{\tilde{\mu}_n \times \tilde{r}}{r^3} \bullet \tilde{p}. \tag{1.62}$$

In which the electron's momentum couples to the field produced by the nucleus. This direct coupling between a nucleus and an electron causes an indirect coupling between pairs of nuclei which using perturbation theory gives a paramagnetic component that is,

$$\tilde{j}^{orb} = \frac{1}{4c^2}\sum_n \frac{< 0|(\sum_k r_{1k}^{-3}\tilde{r}_{1k} \times \nabla_k)|n >< n|(\sum_j r_{2j}^{-3}\tilde{r}_{2j} \times \nabla_j)|0 >}{E_n - E_0}. \tag{1.63}$$

The letters j and k index the electrons and 1 and 2 refer to the nuclei. This is the paramagnetic contribution. There is also a diamagnetic component. These components arise in precisely the same manner in perturbation theory as they do in the chemical shielding.

This contribution has no particular symmetry and is a full second rank tensor as the two dipolar fields may be different and are vectors. For most compounds containing light atoms this component is rather small, but for heavier nuclei this component can be considerable. [9]

The dipolar component arises from a Hamiltonian of the form, again for a single nucleus and a single electron,

$$H^D = \frac{1}{c}\frac{(\tilde{\mu}_n \times \tilde{r}) \bullet (\tilde{\mu}_e \times \tilde{r})}{r^3}. \tag{1.64}$$

$\tilde{\mu}_n$ is the nuclear moment and $\tilde{\mu}_e$ is the electron moment. This leads to an indirect nuclear coupling of the form,

$$\begin{aligned} J^{dip} &= \frac{1}{4c^2}\sum_n \frac{< 0|(\sum_k 3r_{1k}^{-3}(\tilde{S}_k \bullet \tilde{r}_{1k})r_{1k} - r_{1k}^{-3}S_k)|n >}{E_n - E_0} \\ &\quad \times < n|(\sum_j 3r_{2j}^{-3}(\tilde{S}_j \bullet \tilde{r}_{2j})r_{2j} - r_{2j}^{-3}S_j)|0 > . \end{aligned} \tag{1.65}$$

S_k is the spin of the electron and $\tilde{\mu}_e = frac{-}\tilde{S}_k 2c$ in atomic units. This contribution also has no particular symmetry and is a full second rank tensor as the two-dipolar fields may be different and are vectors. For most compounds containing light atoms this component is rather small, but for heavier nuclei this component can be considerable. The dipolar component is usually even smaller than the orbital portion and so is often ignored. [9]

The third interaction that creates the J coupling is the Fermi contact interaction.

This is the largest interaction for light atoms and often is the only one considered by experimentalists.

The Fermi contact interaction arises classically from an electron penetrating into the inside of a spherical magnetic dipole. Quantum mechanically, this is approximated as

$$H^F = \frac{1}{c}\delta(\tilde{r})\tilde{\mu}_e \bullet \tilde{\mu}_n. \tag{1.66}$$

The use of a delta function is an approximation, however, for chemical purposes the approximation typically suffices as deviations from the delta function appear on length scales on the order of hundredths of angstroms. [10] The contact interaction has a very different character than the other interactions that contribute to the J coupling. The delta function renders the interaction isotropic as loosely speaking it depends only on the amount of electron density that connect the two nuclei by penetrating to the nuclei in question.

The coupling which arises from the contact interaction,

$$J^{fc} = \frac{1}{4c^2}\sum_n \frac{< 0|(\sum_k \delta(\tilde{r}_{1k})\tilde{S}_k)|n >< n|(\sum_j \delta(\tilde{r}_{2j})\tilde{S}_j)|0 >}{E_n - E_0}. \tag{1.67}$$

This interaction is the dominant interactionfor light atoms.

Hence, the anisotropic component of the J coupling is often neglected, and the J coupling is often considered as a purely scalar interaction, even when the anisotropy is not averaged away. There have recently been some interesting experiments, especially with InP, which exploit the large anisotropic components that can arise in atoms of heavier elements. [11]

J couplings are often referred to as through-bond interactions. This is because the coupling depends upon the electron distribution, and for the Fermi contact term in particular on the correlation between electrons penetrating to each nucleus, and so they will be large in those circumstances when the nuclei "share" electrons, i.e., when a chemical bond exists. Later in this work, a particular example of small J couplings between atoms that are not directly bonded is explicated.

There are only 2 important NMR parameters remaining: the dipolar coupling and the quadrupolar coupling. The former is a purely nuclear interaction, and so despite being extremely important in solid-state NMR, will not be discussed further.

The quadrupolar coupling is not a magnetic property. Rather it is an electrical interaction. Nuclei with spins greater than 1/2, have an asymmetric nuclear charge distribution. Thus besides having a magnetic dipole, they can have an electric quadrupole. This quadrupole will interact with electric field gradients at the nucleus created by the electron density. So to have an observable quadrupole moment, two conditions must be fulfilled: the nucleus must have a spin greater than 1/2, and there must exist an electric field gradient. The latter condition, for example, means that no atom or molecule in a site with cubic or higher symmetry would have a nonzero quadrupole coupling, regardless of spin.

The vanishing of the quadrupole for any free atom in a magnetic field assumes that the magnetic field does not distort the electron distribution. While this is almost true, i.e., is valid to a very large degree of accuracy, observation of field-dependent quadrupole splittings of atoms in the gas phase allows one to measure the weak distortion of the electron distribution by the applied magnetic field. This has been observed recently in experiments and a more detailed theoretical description will be given later in this work in Chapter 9. However, this does serve to illustrate a point. When a property vanishes at a given order in perturbation theory, a higher order property may be observable despite being significantly weaker. For example, the field-dependent quadrupole splittings of Xe atoms are about hertz as opposed to megahertz. [12]

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Chapter 2

Electronic Structure Theory: An Introduction

To understand the parameters of NMR, an understanding of the electron distribution and its interaction with nuclei is needed. Two questions arise immediately: how is the electronic distribution, or the electronic structure, determined, and what approximations are used to calculate the NMR parameters? This thesis does not concern itself explicitly with the former, but some understanding of that topic is required. The latter question is at the heart of this work, and so some discussion of other modern methods is needed. This chapter is meant to be a brief overview and an interested reader is encouraged to look elsewhere for more details. [1]

The goal of electronic structure theory is to determine molecular structure and molecular properties from first principles. This would require solving at least the

Schrödinger equation, if not some relativistic analogue such as the Dirac equation or even the Breit equation. The first simplification is to consider the Schrödinger equation and to consider relativistic effects to be unimportant that suffices for most, but not all chemistry. Schrödinger's equation cannot be solved exactly for many-electron systems. As a result, a plethora of methods has been developed geared towards solving different aspects of the whole problem. Two immediate simplifications are made. First, the Schrödinger equation of interest will be the time-independent equation as the stationary state electronic structure is the relevant piece. Second, the Born-Oppenheimer separation will be made, whereby electronic and nuclear coordinates are separated. The latter has already been assumed in the previous derivations. Unless otherwise indicated, the systems are assumed to be closed shell systems in which the electrons are spin paired. This thesis will mostly consider density functional theory (DFT) which, however, will be introduced later.

The simplest starting point is Hartee-Fock theory. This conceptually can be considered as molecular orbital theory with a Hamiltonian. The essential elements are the same: the atoms are assigned one-electron orbitals that mix together to form molecular one-electron orbitals. The Hamiltonian determines the mixing of orbitals; this is an addition Hartee-Fock makes on molecular orbital theory. [2]

The first simplification made in Hartee-Fock is the decomposition of the full many-electron Hamiltonian into a set of one-electron Hamiltonians. This decomposition is common to all one-electron theories. For simplicity, start with the hydrogen molecule, i.e., two electrons and two nuclei, as the generalization for arbitrary number of nuclei and electrons just requires indexing,

$$H_{elec} = -\frac{\nabla_1^2}{2} - \frac{\nabla_2^2}{2} - \frac{1}{r_{1a}} - \frac{1}{r_{2a}} - \frac{1}{r_{1b}} - \frac{1}{r_{2b}} + \frac{1}{r_{12}}. \tag{2.1}$$

The numbers index electrons and the letters the hydrogen nuclei with nuclear charge, Z =1. Atomic units have been used, and the Born-Oppenheimer separation has been made, hence, the absence of the nuclear kinetic energy. The nuclei-nuclei repulsion is also absent as it is a constant. This replusions, however, must be added to the energy after solving the electronic problem to obtain the total energy. The Hamiltonian can also be written in a more transparent form,

$$H = h(1) + h(2) + \frac{1}{r_{12}}. \tag{2.2}$$

Where the electronic Hamiltonian, whose label has been dropped, is written as the sum of one-electron terms plus an interaction term. The later term is the one to be approximated. In Hartree theory, one considers an electron moving in the mean field of all the other electrons, or the other one in this example. Hartee-Fock adds the incorporation of exchange, i.e. the energetic consequence of the antisymmetrization required by the Pauli principle, to Hartree theory. We must consider the hydrogen molecule in its triplet state for the exchange interaction. More precisely, the Hartee-

Fock Hamiltonian is,

$$H = \sum_i f(i) \tag{2.3}$$

where f(i) is the Fock operator for the ith electron which has the mean field and the single-electron term, i.e.,

$$f(i) = h(i) + \nu^{HF}(i). \tag{2.4}$$

Of course, this just places all the physics into $\nu^{HF}(i)$, which must now be defined in order for the approximation to have meaning. So let,

$$\nu^{HF}(1) = \sum_b \int d\tilde{r}_2 \psi_b^*(2) \frac{1}{r_{12}} (1 - P_{12}) \psi_b(2). \tag{2.5}$$

This defines the Hartee-Fock potential where $\psi_b(2)$ indicates the bth orbital with the second electron and the sum runs over all occupied orbitals. The integral over $1/r_{12}$ is just the classic Coulomb repulsion between two electrons, and the use of electron 2 is arbitrary as its coordinates are integrated over and the electrons are identical particles. The integral over $1/r_{12}(P_{12})$ is the nonclassical portion. It is the exchange interaction as the permutation operator, P_{12}, interchanges electrons one and two. So the separation of the Hartree-Fock potential into two components defines the Coulomb potential

$$J_j = \int d\tilde{r}_2 \psi_b^*(2) \frac{1}{r_{12}} \psi_b(2), \tag{2.6}$$

and the exchange potential

$$K_j = \int d\tilde{r}_2 \psi_b^*(2) \frac{1}{r_{12}} P_{12} \psi_b(2). \tag{2.7}$$

There is an additional approximation that must be done to implement Hartee-Fock theory, or most other electronic structure methods, which is the use of a finite basis set. A wavefunction can be expanded out exactly by using the elements of any complete set of functions. Complete sets of functions, however, are infinite, so any real calculation must use a finite set of functions. The set of functions used to expand out the one-electron orbitals is called the basis set. The basis set affects the zero field energy or electron distribution merely by making them less accurate, though with large basis sets or through clever manipulations, high accuracy can be reached. The use of a finite set of basis functions has a special consequence when used to calculate magnetic properties within Hartree-Fock theory . This is the introduction of a gauge-dependence. In particular, a finite basis set renders the magnetic interaction dependent upon the choice of origin for the applied field. This is unphysical and hence, problematic. A brute force method of minimizing this problem is to use a very large basis set. Another more physical method that sometimes works, is to disregard gauge issues and pick the origin so that physically relevant regions, i.e. regions of high electron density, are well sampled by the basis functions. Gauge-independence, however, can be reintroduced even with a finite basis at an additional, though not considerable, computational cost. [3] [4]

The solution to the origin problem, as it is called, involves explicitly incorporating the vector potential into the orbitals in an exponential factor. There are several different methods for doing so, of which the two most common are the gauge-including atomic orbital method (GIAO) and the individual gauge for localized orbitals (IGLO) method. As might be deduced from their names, the methods differ in where the exponential prefactor is incorporated. In GIAO, the factor is included with each atomic orbital whereas in IGLO the exponential multiples the molecular orbitals. Explicitly, an atomic basis function in the absence of a vector potential is related to the function used in the GIAO method as

$$|\phi_n >= exp(\frac{-i}{c}\tilde{A}_B(\tilde{R}_n) \bullet \tilde{r})|\psi_n > \tag{2.8}$$

where $|\psi_n >$ is the original atomic orbital, $\tilde{R}_n$ is the location of the same atomic orbital, and

$$\tilde{A}_B(\tilde{R}_n) = \frac{\tilde{B} \times (\tilde{R}_n - \tilde{G})}{2}. \tag{2.9}$$

$\tilde{G}$ is an arbitrary vector which may be picked to be zero because the matrix elements

$$< \phi_m|\tilde{p} + \frac{\tilde{A}_B}{c}|\phi_n > \tag{2.10}$$

become independent of it as can be shown with some algebra.

So once a basis set has been introduced, each one-electron orbital must be expanded in terms of the basis,

$$\psi_i = \sum_{\mu=1}^{K} C_{\mu i}\phi_\mu \tag{2.11}$$

This expansion reduces the problem to solving for the set of expansion coefficients $C_{\mu i}$. Eliminating spin, and using the Fock operator from Equation (2.4), results in an equation for the one-electron molecular orbitals,

$$f(\tilde{r})\psi_i(\tilde{r}) = \epsilon_i\psi_i(\tilde{r}). \tag{2.12}$$

An equation for the expansion coefficients can now be obtained from the molecular orbital equation. In practice, the basis functions used are usually atomic centered. Hence, the expansion of molecular orbitals in basis functions is equivalent to the expansion of molecular orbitals as linear combinations of atomic orbitals as done in molecular orbital theory. The difference is the use of the Fock equation to obtain the coefficients. Explicitly by direct substitution, multiplication by $\phi_\mu^*(1)$ on the left and integration,

$$\sum_{\nu} C_{\nu i} \int d\tilde{r}_1 \phi_{\mu}^{*}(1) f(1) \phi_{\mu}(1) = \epsilon_i \sum_{\nu} C_{\nu i} \int d\tilde{r}_1 \phi_{\mu}^{*}(1) \phi_{\mu}(1). \tag{2.13}$$

The above can be rewritten as a matrix equation,

$$\tilde{\tilde{F}}\tilde{\tilde{C}} = \tilde{\tilde{S}}\tilde{\tilde{C}}\tilde{\tilde{\epsilon}} \tag{2.14}$$

in which $\tilde{\tilde{F}}$ is the Fock matrix, $\tilde{\tilde{C}}$ is the matrix of coefficients, $\tilde{\tilde{S}}$ the overlap matrix defined as

$$S_{\mu\nu} = \int d\tilde{r}_1 \psi_{\mu}^{*}(1) \psi_{\mu}(1). \tag{2.15}$$

$\tilde{\tilde{\epsilon}}$ is the diagonal matrix of the orbital energies. The solution of the Hartree-Fock problem is now just a matrix equation. This matrix form still has three complications. The first is that the equation is nonlinear. This is an essential feature that is in the Hartree-Fock equation from the beginning and cannot be removed. Hence, iterations are required to solve the Hartree-Fock equations, regardless of their form. A guess for the initial expansion must be made, and the equations iterated until the final coefficients match the initial coefficients within some error margin. Second, the matrix equation is not in the usual form of an eigenvalue problem, i.e.,

$$\tilde{\tilde{F}}'\tilde{\tilde{C}}' = \tilde{\tilde{C}}'\tilde{\tilde{\epsilon}}. \tag{2.16}$$

Though a matrix equation of this form may be obtained merely by orthogonalization of the S matrix, i.e., finding $\tilde{\tilde{X}}$ such that

$$\tilde{\tilde{X}}^{\dagger}\tilde{\tilde{S}}\tilde{\tilde{X}} = \tilde{\tilde{1}}. \tag{2.17}$$

Let,

$$\tilde{\tilde{C}}' = \tilde{\tilde{X}}^{-1}\tilde{\tilde{C}} \tag{2.18}$$

$$\tilde{\tilde{F}}' = \tilde{\tilde{X}}^{\dagger}\tilde{\tilde{F}}\tilde{\tilde{X}} \tag{2.19}$$

so that,

$$\tilde{\tilde{F}}\tilde{\tilde{C}} = \tilde{\tilde{F}}\tilde{\tilde{X}}\tilde{\tilde{C}}' \tag{2.20}$$

$$\tilde{\tilde{S}}\tilde{\tilde{C}}\tilde{\tilde{\epsilon}} = \tilde{\tilde{S}}\tilde{\tilde{X}}\tilde{\tilde{C}}'\tilde{\tilde{\epsilon}} \tag{2.21}$$

and now

$$\tilde{\tilde{X}}^{\dagger}\tilde{\tilde{F}}\tilde{\tilde{X}}\tilde{\tilde{C}}' = \tilde{\tilde{X}}^{\dagger}\tilde{\tilde{S}}\tilde{\tilde{X}}\tilde{\tilde{C}}'\tilde{\tilde{\epsilon}} \tag{2.22}$$

$$= \tilde{\tilde{F}}'\tilde{\tilde{C}}' = \tilde{\tilde{C}}'\tilde{\tilde{\epsilon}}. \tag{2.23}$$

So one issue now remains to be dealt with, the explicit form of the Fock matrix elements. First, define the electron density, $\rho(\tilde{r})$, and the density matrix, $P_{\mu\nu}$,

$$\begin{aligned}\rho(\tilde{r}) &= 2\sum_{a}^{N/2}|\psi_a(\tilde{r})|^2 \\ &= \sum_{\mu\nu}[2\sum_{a}^{N/2}C_{\mu a}C^*_{\nu a}]\phi_\mu(\tilde{r})\phi^*_\nu(\tilde{r}) \\ &= \sum_{\mu\nu}P_{\mu\nu}\phi_\mu(\tilde{r})\phi^*_\nu(\tilde{r})\end{aligned} \tag{2.24}$$

$$P_{\mu\nu} = 2\sum_{a}^{N/2}C_{\mu a}C^*_{\nu a}. \tag{2.25}$$

The definition of the density matrix is useful as the Fock equation can now be rewritten as,

$$f(\tilde{r}_1) = h(\tilde{r}_1) + \frac{1}{2}\sum_{\alpha\beta}P_{\alpha\beta}[\int d\tilde{r}_2\phi^*_\beta(\tilde{r}_2)(2 - P_{12}r_{12}^{-1})\phi_\alpha(\tilde{r}_2)] \tag{2.26}$$

this form is interesting because it shows that the Fock operator can be separated into two pieces. The first piece does not depend upon the density matrix and when matrix elements are taken, only one integration is required. The second part depends upon the density matrix, and requires integration over two sets of electron coordinates. Hence, the integrals are referred to as two electron integrals. The latter integrals are the only ones that change during interation, as can be seen from the explicit form of $h(\tilde{r}_1)$.

In order to describe the solution of the Hartree-Fock equations, all that remains to be done is to put the pieces together. In particular, the following steps need to be done. First, a basis set must be chosen and a nuclear geometry specified. Second, a guess must be made at the density matrix, from which both one and two electron portions of the overlap and Fock integrals are obtained. Then the overlap matrix is diagonalized and the transformation matrix found. Using the guess density matrix, the Fock matrix is obtained and then transformed using the transformation matrix. This Fock matrix must be diagonalized to obtain the eigenvalues and the expansion coefficients. These expansion coefficients must then be transformed using $\tilde{\tilde{C}} = \tilde{\tilde{X}}\tilde{\tilde{C}}'$ and a new density matrix calculated from the expansion coefficients. If the new density matrix agrees with the initial density matrix to within some error margin, then the process is done. More likely the process must be started over using more the new density matrix rather than the original guess at the density matrix.

Note that because of the two electron integrals, the energy in Hartree-Fock is not the sum of the energy eigenvalues, rather the energy is,

$$\begin{aligned} E^{HF} &= \sum_a E_a - \sum_{ij} (\frac{1}{2} \int d\tilde{r}_1 d\tilde{r}_2 (\phi_i^*(\tilde{r}_1)\phi_j^*(\tilde{r}_2) r_{12}^{-1} \phi_i(\tilde{r}_1)\phi_j(\tilde{r}_2) \\ &- \phi_i^*(\tilde{r}_1)\phi_j^*(\tilde{r}_2) r_{12}^{-1} \phi_j(\tilde{r}_1)\phi_i(\tilde{r}_2))). \end{aligned}$$

A simpler notation is often used,

$$\int d\tilde{r}_1 d\tilde{r}_2 (\phi_i^*(\tilde{r}_1)\phi_j^*(\tilde{r}_2) r_{12}^{-1} \phi_l(\tilde{r}_1)\phi_k(\tilde{r}_2) - \phi_i^*(\tilde{r}_1)\phi_j^*(\tilde{r}_2) r_{12}^{-1} \phi_k(\tilde{r}_1)\phi_l(\tilde{r}_2)) = < ij||lk > \tag{2.28}$$

and in this notation,

$$E^{HF} = \sum_a E_a - \sum_{ij} \frac{1}{2} < ij||ij > . \tag{2.29}$$

To obtain properties rather than the ground state field independent energy, as described above, one needs to modify the Hamiltonian and to take derivatives. Explicitly, at the Hartree-Fock level the chemical shielding for nucleus i is,

$$\sigma^i_{\alpha\beta} = \sum_{\mu\nu} D^{HF}_{\mu\nu} \frac{\partial^2 h_{\nu\mu}}{\partial B_\alpha \partial \mu_\beta} + \sum_{\mu\nu} \frac{\partial D^{HF}_{\mu\nu}}{\partial B_\alpha} \frac{\partial h_{\nu\mu}}{\partial \mu_\beta} \tag{2.30}$$

$D^{HF}_{\mu\nu}$ is the Hartree-Fock density matrix,. $h_{\mu\nu}$ the one electron Hamiltonian matrix elements in the atomic orbital representation in which the atomic orbitals are labeled by μ, ν. Notice that because basis functions that depend upon the applied field are often used,

$$\frac{\partial <\mu|h|\nu>}{\partial B_\alpha} =< \frac{\partial \chi_\mu}{\partial B_\alpha}|h\nu> + <\mu|\frac{\partial h}{\partial B_\alpha}|\nu> + <\mu|h|\frac{\partial \chi_\nu}{\partial B_\alpha}> . \tag{2.31}$$

This expression is really more general than indicated. If one obtains, a density matrix from another theory, i.e., Moller-Plesset theory, then one obtains the properties from that density matrix.

While properties derived from Hartree-Fock theory are often reasonable, they can be improved upon, by using other theories. This improvement comes about because Hartee-Fock theory is not exact. The details of electron correlation are ignored. This causes a difference in energy between the exact energy and the Hartree-Fock energy, this energy difference is defined as the correlation energy,

$$E^{corr} = E^{exact} - E^{HF}. \tag{2.32}$$

Most research in electronic structure theory is centered on going beyond Hartree-Fock by removing some of the approximations made in a computationally useful manner.

The wavefunction-based methods of improving upon Hartree-Fock are not the focus of this work, and as such they will only be dealt with qualitatively in a broad overview. Incorporation of correlation could be done using perturbation theory for many systems, in the form of Moller-Plesset perturbation theory (MP theory). Or, it could be done exactly, at least in principle, without perturbation theory, using the method of configuration interaction (CI). As the idea of an exact theory is promising, it should be examined closely.

Configuration Interaction methods are based on improving Hartree-Fock theory by considering the exact wavefunction as a linear combination of N-electron wavefunctions. Given a set of m one-electron orbitals, the wavefunction is given as a linear combination of all wavefunction made by placing electrons in N orbitals. So even with small basis sets, the number of terms in the expansion is very large. One of the wavefunctions in the expansion is the Hartree-Fock ground state. All the other wavefunctions can be considered as excitations from the ground state. Explicitly,

$$|\psi >_{exact}= a_0|\psi >_{HF} + \sum_{ij} a_{ij}|\psi_j^i > + \sum_{ijkl} a_{ijkl}|\psi_{jk}^{il} > + \sum_{ijklmn} a_{ijklmn}|\psi_{jkm}^{iln} > + \ldots \tag{2.33}$$

where the lowered indices label the orbitals in the Hartee-Fock ground state from which electrons have been removed, and the raised indices label the orbitals to which the electrons have been excited. The series extend up to all N electron excitations. The a's indicate the degree of mixing and so for most systems a_0 will be the largest a. It can be show that this expansion is exact within a basis set, i.e., at the infinite basis set limit the answer is the exact solution of the original Hamiltonian.

The problem when using the full series, which is full configuration interaction (FCI), is the number of terms. Consider benzene in a minimal basis. A minimal basis is one where a single function is used for each occupied atomic orbital along with one function for each unoccupied orbital of the same n and l as the occupied orbitals. So benzene would have one function per hydrogen, plus 5 for carbon for a total of 36 spatial functions that generate 72 spin functions as each orbital function can be associated with a spin up or spin down electron. So there would be $\genfrac{}{}{0pt}{}{72}{42} \approx 1.64 * 10^{20}$ different expansions terms! This is far too many terms for any feasible calculation. So full CI must remain a dream. Rather partial CI methods can be done, where only some excitations are included. For example, there is CISD, configuration interaction singles and doubles, where only terms that involve removing one or two electrons from the Hartee-Fock ground state are considered. So for the example of a minimal basis benzene, there are 42 orbitals from which to remove an electron and 30 originally unoccupied orbitals to place one into so there are 1260 single excitations, and there are 374535 double excitations, for a total of 375795 excitations, almost 15 order of magnitudes fewer than with FCI! Though in both cases the number of terms can be reduced as wavefunctions with different spin symmetries, e.g. singlets and triplets, will not mix, but the number of excitations is still considerable. The result is that this method is very expensive computationally and has a very unfavorable scaling with molecular size, so it is not practical for large molecules, at least in its present form. A more practical, though with a higher scaling that Hartree-Fock, method of mixing in contributions from Hartree-Fock excitations is to use perturbation theory, i.e. Moller-Plesset (MP) theory. This theory consists of using ordinary perturbation theory, i.e.

Raleigh-Schrödinger theory, with a particular partitioning of the Hamiltonian,

$$H = H_{HF} + V \tag{2.34}$$

$$V = \frac{1}{2}\sum \frac{1}{r_{ij}} - \sum_{i} \nu^{HF}(i). \tag{2.35}$$

So the starting point is the Hartree-Fock Hamiltonian and the perturbation is the different between the exact Coulomb potential and the Hartree-Fock potential.

Elementary perturbation theory gives the zeroth, first and second order ground state energies as the following:

$$\begin{aligned}
E^0 &= \sum_a E_a & (2.36)\\
E^1 &= <\psi_0|V|\psi_0> = <\psi_0|(\sum \frac{1}{r_{ij}} - \sum_i \nu^{HF}(i))|\psi_0> & (2.37)\\
&= \frac{1}{2}\sum_{ab} <ab||ab> - \sum_a <a|\nu^{HF}|a> & (2.38)\\
&= -\frac{1}{2}\sum_{ab} <ab||ab> & (2.39)\\
E^2 &= \sum{}'_n \frac{|<0|V|n>^2}{E_0^0 - E_n^0}, & (2.40)
\end{aligned}$$

As usual the summation for the second order energy is over all states except the ground state and all are zeroth order states. The Hartree-Fock ground state energy is the sum of $E^0 + E^1$ and so Hartree-Fock theory is correct to first order in correlation.

Going to second order in correlation results in Moller-Plesset second order perturbation theory (MP(2)). So which states contribute to the second order energy? It turns out that only states that are double excitations from the Hartree-Fock ground state contribute. A doubly excited wavefunction is a wavefunction obtained by removing two electrons from orbitals which are filled in the Hartree-Fock ground state and placing them into orbitals that are empty in the Hartree-Fock ground state, i.e., promoting two electrons from occupied orbitals into virtual orbitals. The Coulomb operator is a two electron operator, hence the appearance of only one and two electron integrals, and so it can only give nonzero matrix elements between wavefunctions that differ by only double excitations. The single excitations can be ruled out as well because the Hartree-Fock ground state is correct to first order already. That single excitations do not couple directly to the Hartree-Fock ground state can be proven rigorously as Brillouin's theorem. So the second order energy can be written as,

$$\begin{aligned} E^2 &= \frac{1}{4}\sum_{abcd} \frac{| < \psi_0 | \sum_{i>j} r_{ij}^{-1} | \psi_{ab}^{cd} > |}{\epsilon_a + \epsilon_b - \epsilon_c - \epsilon_d} && (2.41) \\ &= \frac{1}{4}\sum_{abcd} \frac{| < ab || cd > |^2}{\epsilon_a + \epsilon_b - \epsilon_c - \epsilon_d} && (2.42) \end{aligned}$$

in which a and b index the orbitals from which the electrons have been excited and r and s index the orbitals to which the electrons are promoted into. The ϵ's are the orbital energies from the solution to the Hartree-Fock equations.

One could, of course, continue of beyond second order. The computational scaling, however, becomes increasingly higher. There also are some other wavefunction-based theories that can improve on Hartree-Fock, again with at the expense of additional computer time, thereby restricting their use to smaller systems. These methods are less commonly used for magnetic responses and so will not be surveyed here. An interested reader may find them elsewhere. The increase in computational cost is what makes using wavefunction based theories beyond Hartree-Fock difficult. It would be very useful to have a theory that has a similar computational complexity to Hartree-Fock, which is also capable of correcting the deficiencies of Hartee-Fock. Such a method is Density Functional Theory, the subject of the next chapter.

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Chapter 3

Introduction to Density Functional Theory

The existence of a theory which at worst is as simple as Hartree-Fock theory, but which can in principle be exact, would be rather advantageous as it would increase the scope of electronic structure theory. Such a theory does exist: Density Functional Theory. This thesis is an explicit realization of a variant of density functional theory, magnetic field density functional theory. As such, an introduction to the basis of density functional theory is necessary for understanding this work. [1]

An N-particle system in 3 dimensions is represented by a wavefunction, $\psi(\tilde{r}_1, \tilde{r}_2, ..., \tilde{r}_N, s)$, which is a function of 3N spatial variables plus the 3N spin variables, s. For most of this work, closed shell electronic systems shall be considered with $S_{tot} = 0$. Hence, the spin label will now be dropped when considering the electrons. Of course, the nuclear spin will be explictly considered. The probability distribution for a state, irrespective of spin, is,

$$\psi(\tilde{r}_1, \tilde{r}_2, ..., \tilde{r}_N)\psi^*(\tilde{r}_1, \tilde{r}_2, ..., \tilde{r}_N). \tag{3.1}$$

This is interpreted as the probability of having particle one at position r_1, particle two at position r_2, up to particle N being at position r_N. If this probability distribution is integrated over all but one set of coordinates, then the result is the probability of there being a particle at a particular position irrespective of the position of any other particle. The identity of the particle is also lost, however, for a set of identical particles, such as electrons in a molecule, there is no identity to lose. By integrating the N-electron wavefunction over all the coordinates save for the coordinates of one electron, the probability distribution for all the electrons is obtained. This is the electron density.

$$\rho(\tilde{r}_1) = \int \psi(\tilde{r}_1, \tilde{r}_2, ..., \tilde{r}_N)\psi^*(\tilde{r}_1, \tilde{r}_2, ..., \tilde{r}_N) d\tilde{r}_2 ... d\tilde{r}_N \tag{3.2}$$

Unlike the N-particle wavefunction, the electron density is a physical observable. In particular, it is measured in x-ray diffraction experiments. These two aspects of the electron density: its physical existence and functional dependence on only three coordinates, render theories invoking it more amenable to intuitive thought and simplification. Hence, it would be advantageous to transform electronic structure theory, or some aspects of it, into a theory based upon electron densities not many-particle wavefunctions. Formally, this is done in part by the theorems of Hohenberg and Kohn. [2]

The first theorem is an existence statement. The external potential, $\nu(\tilde{r})$, is determined to within an additive constant, by the electron density, and vice versa. Hence, the electron density determines both the numbers of electrons in a system and the scalar potential felt by these electrons. Thus, the electron density determines all the ground state properties of a system. As the electron density is itself a function of the position vector, $\tilde{r}$, properties that are determined by the electron density are referred to as functionals of the electron density. A functional is merely a function of some quantity that is a function of other variables, i.e., a function of a function. This theorem demonstrates the existence of a density functional theory, but does not present a prescription for determining anything from the density. As presented here, the Hohenberg-Kohn theorem is restricted to ground states in the absence of a magnetic field. There are generalizations that lift all of these restrictions. This work, however, will restrict itself to ground states.

In DFT, there is no general prescription for the construction of functionals. This is a significant problem in density functional theory: the lack of a hierarchy of methods such as those present in wave function theory. This means more care must be devoted in the use of density functional theory and more creativity and work devoted to functional construction. Problems that are intractable in wavefunction based theories, however, can be computed and understood using density functional theory. [3]

The proof of the first Hohenberg-Kohn theorem is rather simple and relies on the variational principle. Generalizations are possible [4], but this is the simplest version. Start by considering the electron density for the nondegenerate ground state of some N-electron system. Suppose there exist two different potentials, $\nu(\tilde{r})$, and $\nu'(\tilde{r})$ that each have the same ground state electron density, $\rho(\tilde{r})$. If these two potentials differ by more than a constant then they must have different Hamiltonians, H, and H', which generate the same electron density, but with different wavefunctions ψ, and ψ'. Now to prove the theorem one simply uses the wavefunction from Hamiltonian H as a trial wavefunction for Hamiltonian H', and vice versa and arrive at a contradiction. In particular,

$$\begin{aligned} E_0 &< <\psi'|H|\psi'>=<\psi'|H'|\psi'>+<\psi'|(H-H')|\psi'> && (3.3)\\ &= E_0'+\int d\tilde{r}\rho(\tilde{r})[\nu(\tilde{r})-\nu'(\tilde{r})] && (3.4)\\ E_0' &< <\psi|H'|\psi>=<\psi|H|\psi>+<\psi|(H'-H)|\psi> && (3.5)\\ &= E_0-\int d\tilde{r}\rho(\tilde{r})[\nu(\tilde{r})-\nu'(\tilde{r})]. && (3.6)\end{aligned}$$

Add these together and a contradiction is reached,

$$E_0+E_0'<E_0+E_0'. \tag{3.7}$$

Hence, the original supposition was wrong. Thus, there can only be one external potential that generates a particular electron density as its ground state.

The second Hohenberg-Kohn theorem provides density functional theory with a formal variational principle. For an approximate density, $\rho'(\tilde{r})$, which integrates to the number of electrons such that, $\rho'(\tilde{r}) \geq 0$, then,

$$E_0 \leq E[\rho'(\tilde{r})] \tag{3.8}$$

E_0 is the exact energy and $E[\rho'(\tilde{r})]$ is energy obtained from using the approximate density.

In wavefunction based theories, the energy can be broken down into several different components, e.g. kinetic, exchange, correlation and electron-nuclear. [5] This useful separation can also be done in density functional theory.

The first separation that can be done is separating out the external potential, i.e.,

$$E[\rho(\tilde{r})] = \int \rho(\tilde{r})\nu(\tilde{r})d\tilde{r} + F[\rho(\tilde{r})]. \tag{3.9}$$

$F[\rho(\tilde{r})]$ is everything else. This unknown functional is also composed of several pieces.

$$F[\rho(\tilde{r})] = T[\rho(\tilde{r})] + E_{xc}[\rho(\tilde{r})] + J[\rho(\tilde{r})] \tag{3.10}$$

$T[\rho(\tilde{r})]$ is the kinetic energy, which in density functional theory must be approximated.

$J[\rho(\tilde{r})]$ is the classical electron-electron interaction, e.g.,

$$J[\rho(\tilde{r})] = \frac{1}{2}\int d\tilde{r}d\tilde{r}'\frac{\rho(\tilde{r})\rho(\tilde{r}')}{|\tilde{r}-\tilde{r}'|}. \tag{3.11}$$

This is already known from classical electrostatics as a functional of the density. [6] Notice, this is a nonlocal functional as the value of the classical term at a particular point in $\tilde{r}$ depends upon an integral over all space due to the $d\tilde{r}'$ integral.

$$\frac{\delta J}{\delta\rho(\tilde{r})} = \int d\tilde{r}'\frac{\rho(\tilde{r}')}{|\tilde{r}-\tilde{r}'|} \tag{3.12}$$

Other nonlocal functionals will appear later in this work. Most functionals in density functional theory are local. The locality is due to the manner in which they are constructed, and not necessarily due to any fundamental physics. The last piece $E_{xc}[\rho(\tilde{r})]$ is the quantum mechanical exchange and correlation which also must be approximated. As a further ansatz, the exchange and correlation are often considered individually, e.g.,

$$E_{xc}[\rho(\tilde{r})] = E_x[\rho(\tilde{r})] + E_c[\rho(\tilde{r})]. \tag{3.13}$$

The main problem in density functional theory is the actual construction of approximations to the functionals. The first set of approximations was actually constructed long before the theorems of density functional theory were proven. This model is the Thomas-Fermi model that was developed in the early years of the 20th century. [7], [8], [9] The electrons are treated statistically in a simplified model also referred to as the electron gas model. Despite being a rather approximate model, the Thomas-Fermi theory still forms the basis for most functional construction. There are at least three different methods of deriving the Thomas-Fermi functionals, the original electron gas method, plus more modern scaling and propagator methods.

The scaling method is the simplest of the three. [1] By scaling, one simply means multiplication of the coordinate vectors by a parameter λ. The wavefunction, ψ, scales as,

$$\psi_\lambda = \lambda^{3N/2}\psi(\lambda\tilde{r}_1, \lambda\tilde{r}_2, .., \lambda\tilde{r}_N). \tag{3.14}$$

$\lambda^{3N/2}$ preserves the normalization. The kinetic energy scaling can also be derived remembering that the expectation values are integrals that must be scaled as well,

$$\begin{aligned} T[\psi] &= <\psi|\sum_i -\frac{\nabla_i^2}{2}|\psi> && (3.15)\\ T[\psi_\lambda] &= <\psi_\lambda|\sum_i -\frac{\nabla_i^2}{2}|\psi_\lambda> && (3.16)\\ &= \lambda^2 <\psi|\sum_i -\frac{\nabla_i^2}{2}|\psi>. && (3.17)\end{aligned}$$

This is an exact scaling of the kinetic energy, and so even though it is derived from wavefunctions, it should be applicable to density functionals as well. The simplest such functional that satisfies this scaling property is,

$$T[\rho(\tilde{r})] = \int d\tilde{r}\rho^{5/3}(\tilde{r}). \tag{3.18}$$

A factor of λ^5 is obtained from the $\rho^{5/3}(\tilde{r})$ upon scaling and a factor of λ^{-3} from the integral. Scaling does not allow one to obtain constants, and so scaling can only be used to obtain a form. Constants must be obtained from other methods, or by fitting to experimental data.

The original electron gas method does allow one to obtain not only the scale, that is, the power of the density, but also the constants. Consider a zero temperature electron gas. [10] Space is divided into many different cubic cells with sides of length a, and the particles are considered as being in a three dimensional infinite well, i.e., a particle in a 3D box, then the energy levels are

$$E(n_x, n_y, n_z) = \frac{h}{8ma^2}(n_x^2 + n_y^2 + n_z). \tag{3.19}$$

For large quantum numbers, the distribution of energy levels becomes nearly continuous and so the number of energy levels smaller than a given energy, $\sigma(\epsilon)$, can be approximated by one octant of a sphere. Only one octant is required as the n$_i$'s must be positive.

$$\begin{aligned}\sigma(\epsilon) &= \frac{1}{8}\frac{(4*\pi*(n_x^2+n_y^2+n_z)^{1/2})^3}{3} && (3.20)\\ &= \frac{\pi}{6}(\frac{8ma^2\epsilon}{h^2})^{3/2} && (3.21)\end{aligned}$$

The density of states, $g(\epsilon)$, is quite easily determined as,

$$g(\epsilon) = \frac{\pi}{4}(\frac{8ma^2}{n^2})^{3/2}\epsilon^{1/2}. \tag{3.22}$$

To determine the total energy of the electrons and the number of electrons per cell all that is left is to evaluate the appropriate integrals,

$$E = 2\int \epsilon f(\epsilon)g(\epsilon)d\epsilon N = 2\int f(\epsilon)g(\epsilon)d\epsilon \tag{3.23}$$

The 2 is from the double occupancy due to spin, and $f(\epsilon)$ is the distribution function. For a zero temperature electron gas, the distribution function is just the zero temperature limit of the Fermi-Dirac distribution, which is just a Heaviside function, centered on the Fermi energy. Hence, the energy becomes,

$$\begin{aligned}E &= 2\int_0^{\epsilon_f} d\epsilon\frac{\pi}{4}(\frac{8ma^2}{h^2})^{3/2}\epsilon^{3/2} && (3.24)\\ &= \frac{8\pi}{5}(\frac{2m}{h^2})^{3/2}a^3\epsilon_f^{5/2}. && (3.25)\end{aligned}$$

The energy is obtained as a function of the Fermi energy. One can also obtain the number of electrons per cube as a function of the Fermi energy. Then an inversion is possible to obtain the energy as a functional of the electron density. This method, that is, obtaining the density and the energy both as functionals of the same quantity and then inverting, is a common method of constructing functionals. The number of electrons per cell is,

$$\begin{aligned} N &= 2\int_0^{\epsilon_f} d\epsilon \frac{\pi}{4}(\frac{8ma^2}{h^2})^3 \epsilon^{1/2} && (3.26) \\ &= \frac{8\pi}{3}(\frac{2m}{h^2})^{3/2} a^3 \epsilon_f^{3/2}. && (3.27) \end{aligned}$$

Now upon performing the inversion,

$$E = \frac{3h^2}{10m}(\frac{3}{8\pi})^{2/3} a^3 (\frac{N}{a^3})^{5/3} \qquad (3.28)$$

then substituting in the density $\frac{N}{a^3}$ and transforming to an integral, the following is obtained;

$$E = \frac{3h^2}{10m}(3\pi^2)^{2/3} \int \rho^{5/3}(\tilde{r}) d\tilde{r}. \qquad (3.29)$$

This has the same form as the result obtained by scaling arguments, as it should, but the constant has also been obtained. This is a kinetic energy functional as the electrons have been treated as particles in a three-dimensional box. Hence, the exchange and correlation energies have been completely neglected thus far.

Correlation is typically treated by numerically evaluating the correlation energy for a uniform electron gas and then fitting the results to an analytic form. [11] Exchange can be added to Thomas-Fermi theory via the method of Dirac. The result is Thomas-Fermi-Dirac theory. [12] Dirac theory is derived in a slightly different manner then the one elucidated above.

Note that the exchange energy, $K[\rho]$, can be expressed via the density matrix, [1],

$$K[\rho] = \frac{1}{4}\int \frac{1}{r_{12}}|\rho(\tilde{r}_1, \tilde{r}_2)|^2 d\tilde{r}_1 d\tilde{r}_2, \tag{3.30}$$

So the density matrix for a closed shell N-particle system,

$$\rho(\tilde{r}_1, \tilde{r}_2) = 2\sum_{i}^{N/2} \psi_i(\tilde{r}_1)\psi_i^*(\tilde{r}_2) \tag{3.31}$$

should be the starting point in which case the Hartree-Fock energy can be expressed as

$$\begin{aligned} E_{HF}[\rho] &= \int [\frac{-1}{2}\nabla_1^2 \rho(\tilde{r}_1, \tilde{r}_2)]_{r_{\tilde{1}}=r_{\tilde{2}}} d\tilde{r}_1 + \int \rho(\tilde{r})\nu(\tilde{r})d\tilde{r} + J[\rho] \\ &- \frac{1}{4}\int \frac{1}{r_{12}}\rho(\tilde{r}_1, \tilde{r}_2)\rho(\tilde{r}_2, \tilde{r}_1)d\tilde{r}_1 d\tilde{r}_2. \end{aligned}$$

The first term is the kinetic energy, the second term is the electron-nuclear potential energy, the third the classical Coulomb interaction and the last the exchange interaction. Correlation has been completely neglected. Two of these terms are automatically in the form of density functionals, the other two – the kinetic and exchange energies – are functionals of the density matrix and they need to be expressed in terms of the electron density. Within the Thomas-Fermi-Dirac model, one starts with the electron gas model as before. The orbitals appropriate for this system when there are large numbers of particles and periodic boundary conditions can be employed, are plane waves

$$\psi(k_x, k_y, k_z) = \frac{1}{V^{1/2}} e^{i\tilde{k}\bullet\tilde{r}}. \tag{3.33}$$

The k's are the quantum numbers for the particle in a box, i.e.,

$$k_j = \frac{2\pi n_j}{V^{1/3}}. \tag{3.34}$$

The density matrix can now be obtained quite easily as

$$\rho(\tilde{r}_1, \tilde{r}_2) = \frac{2}{V} \sum_{occupied\tilde{k}} e^{i\tilde{k}\bullet(\tilde{r}_1 - \tilde{r}_2)}. \tag{3.35}$$

Of course, this begs the question as to what the occupied k's are, however, this question only need to be answered indirectly. First, make the sum into an integral in k space,

$$\rho(\tilde{r}_1, \tilde{r}_2) = \frac{1}{4\pi^3} \int e^{i\tilde{k}\bullet(\tilde{r}_1 - \tilde{r}_2)} d\tilde{k} \tag{3.36}$$

$$= \frac{1}{4\pi^3} \int_0^{k_f} k^2 dk \int e^{i\tilde{k}\bullet\tilde{r}_{12}} sin\theta d\theta d\phi \tag{3.37}$$

and then take the diagonal elements, which give the electron density,

$$\rho(\tilde{r}) = \frac{k_f^3}{3\pi^2} \tag{3.38}$$

$$k_f(\tilde{r}) = [3\pi^2 \rho(\tilde{r})]^{1/3}. \tag{3.39}$$

Again, the electron density has been obtained as a functional of one quantity, the Fermi momentum in this instance, and the quantity of interest, i.e., the density matrix that will generate the energies, has been obtained as a functional of the Fermi momentum as well. Hence, an inversion can be done at the end to transform between functionals of the Fermi momentum and the electron density. The integrations to obtain the density matrix must now be performed with a particular choice of coordinates. For a uniform electron gas, the most sensible choice is,

$$\tilde{r} = \frac{\tilde{r}_1 + \tilde{r}_2}{2} \tag{3.40}$$

$$\tilde{s} = \tilde{r}_1 - \tilde{r}_2 \tag{3.41}$$

thus,

$$\rho(\tilde{r}_1, \tilde{r}_2) = \frac{1}{4\pi^3}\int_0^{k_F} k^2 dk \int_0^{\pi} \sin\theta e^{kr_{12}\cos\theta} d\theta \int_0^{2\pi} d\phi \quad (3.42)$$

$$= 3\rho(\tilde{r})[\frac{x - xcosx}{x^3}] \quad (3.43)$$

$$x = k_F(\tilde{r})s. \quad (3.44)$$

The scalar dependence on s has occurred because of the choice to have $\tilde{s}$ lie on the k_z axis. In order to obtain the Thomas-Fermi energy, the gradients must be transformed into the $\tilde{r}$ and $\tilde{s}$ coordinate system, and then the following result is obtained

$$T[\rho] = T[\rho]_{TF} - \frac{1}{8}\int \nabla_{\tilde{r}}^2 \rho(\tilde{r}). \quad (3.45)$$

The second term vanishes for any well behaved and bounded electron density. The exchange energy can be obtained every more easily by substitution and integration with the result,

$$K[\rho] = \frac{3}{4}(\frac{3}{\pi})^{1/3}\int \rho^{4/3}(\tilde{r})d\tilde{r}. \quad (3.46)$$

The entire Thomas-Fermi-Dirac functional can be used to obtain energies. It's very simple, but is not particularly accurate. Hence, it sees little use in its entirety. The Dirac functional is often used with a more exact treatment of the kinetic energy, namely, Kohn-Sham Density functional theory in the local density approximation

(LDA). [13] Or in chemical applications, the Dirac functional is used as a starting point for more sophisticated functionals [3].

Another method of deriving the Thomas-Fermi-Dirac functionals is to use the single-electron propagator. [14] [15] This method has the advantage of being generalizable. Obtaining gradient corrections to the kinetic and exchange energies is one way in which the Thomas-Fermi-Dirac method can be extended. Another extension, in the context of magnetic responses, is illustrated in Chapter 4 of this thesis.

Both the density matrix and the propagator can be written in an orbital representation,

$$\rho(\tilde{r},\tilde{r}') = 2\sum_{i=1}^{i=N/2} \phi_i(\tilde{r})\phi_i^*(\tilde{r}') \tag{3.47}$$

$$= 2\sum_{i=1}^{i=\infty} \phi_i(\tilde{r})\phi_i^*(\tilde{r}')\theta(\epsilon_F - \epsilon_i) \tag{3.48}$$

$$< \tilde{r}t|e^{-iHt}|r'0 >= \sum_{j=1}^{j=\infty} |e^{-iE_jt}\phi_j(\tilde{r})\phi_j^*(\tilde{r}') \tag{3.49}$$

Now a clever trick is to use an integral representation of the Heaviside function, $\theta(\epsilon_F - \epsilon_i)$

$$\theta(\epsilon_F - \epsilon_i) = \lim_{\gamma\to 0}\frac{1}{2\pi i}\int_{-\infty-i\gamma}^{\infty-i\gamma}\frac{dt}{t}e^{it(\epsilon_F-\epsilon_i)} \tag{3.50}$$

so that

$$\begin{aligned} \rho(\tilde{r},\tilde{r}') &= 2\sum_{i=1}^{i=\infty}\phi_i(\tilde{r})\phi_i^*(\tilde{r}')\lim_{\gamma\to 0}\frac{1}{2\pi i}\int_{-\infty-i\gamma}^{\infty-i\gamma}\frac{dt}{t}e^{it(\epsilon_F-\epsilon_i)} & (3.51)\\ &= \frac{2}{2\pi i}\int_{-\infty-i\gamma}^{\infty-i\gamma}\frac{dt}{t}e^{it\epsilon_F} < \tilde{r}t|e^{-iHt}|r'0 > . & (3.52)\end{aligned}$$

A representation of the density matrix in terms of the propagator is obtained. As the kinetic and exchange energies can be written in terms of the density matrix, an analytic approximation to the propagator generates approximations to the energy functionals.

Explicitly, the lowest level of approximation that can be done is to go just beyond the free particle propagator. [16]

$$< \tilde{r}t|e^{-iHt}|r'0 >= (\frac{1}{2i\pi t})^{3/2}e^{(-i\frac{(\tilde{r}-\tilde{r}')^2}{2t}-tiW(\tilde{r}',\tilde{r}))} \qquad (3.53)$$

in which

$$W(\tilde{r}',\tilde{r}) = \int_0^1 V(\tilde{r}+(\tilde{r}'-\tilde{r})\epsilon)d\epsilon. \qquad (3.54)$$

Integration generates a density matrix

$$\rho(\tilde{r},\tilde{r}') = 2(\frac{k^2}{2\pi|r'-r|^2})^{3/2}J_{3/2}(k|r'-r|)\theta(k^2) \qquad (3.55)$$

where

$$k^2 = 2(\epsilon_F - W(\tilde{r}', \tilde{r})). \tag{3.56}$$

$J_{3/2}$ is a Bessel function of order 3/2. From this density matrix, the kinetic energy functional can be obtained using Equation (3.32) , and the density by taking the limit $\tilde{r}' \longrightarrow \tilde{r}$,

$$\begin{aligned} T_s[\rho(\tilde{r})] = \int d\tilde{r} - [\frac{k}{2\pi|\tilde{r} - \tilde{r}'|})^{3/2}\theta(k^2)[(\frac{k^2}{|\tilde{r}' - \tilde{r}|})^2 J_{7/2}(k|\tilde{r} - \tilde{r}'|) \\ - \frac{3k}{|\tilde{r} - \tilde{r}'|} J_{5/2}(k|\tilde{r} - \tilde{r}'|) + 2(\tilde{r} - \tilde{r}') \bullet \nabla_r W(\tilde{r}, \tilde{r}') J_{3/2}(k|\tilde{r} - \tilde{r}') \\ - \frac{|\tilde{r} - \tilde{r}'|}{k} \nabla_r^2 W(\tilde{r}, \tilde{r}') J_{1/2}(k|\tilde{r} - \tilde{r}'|) + (\frac{|\tilde{r} - \tilde{r}'|}{k})^2 |\nabla_r W(\tilde{r}, \tilde{r}')|^2 J_{-1/2}(k|\tilde{r} - \tilde{r}'|)] \end{aligned} \tag{3.57}$$

Inversion to remove the Fermi momentum results in the Thomas-Fermi relation plus corrections. The propagator method has the advantage of being the most readily generalizable. An improved approximation to the propagator will result in improved functionals. In chapter four this will be done explicitly .

The more exact treatment of the kinetic energy that allowed density functional theory to find practical implementation is the Kohn-Sham density functional theory [13]. The usefulness of this theory relies on the realization that most of the energy in a bound system is kinetic and virtually all the kinetic energy can be obtained by considering a noninteracting system with the same electron density.

In particular, consider the following equations, which are true exactly for N noninteracting electrons,

$$T[\rho] = \sum_{i}^{N} < \psi_i| -\frac{1}{2}\nabla^2|\psi_i > \tag{3.58}$$

$$\rho(\tilde{r}) = \sum_{i}^{N}\sum_{s} |\psi_i(\tilde{r},s)|^2 \tag{3.59}$$

where s is the spin variable, and the exact result for N interacting electrons is,

$$T = \sum_{i}^{N} n_i < \psi_i| -\frac{1}{2}\nabla^2|\psi_i > \tag{3.60}$$

$$\rho(\tilde{r}) = \sum_{i}^{N} n_i \sum_{s} |\psi_i(\tilde{r},s)|^2, \tag{3.61}$$

For an interacting system, this sum runs over an infinite number of orbitals with occupation numbers, $0 \leq n_i \leq 1$.

To take advantage of these exact identities, a noninteracting reference system is invoked so there are no electron-electron potential terms. Instead, the electrons move in an effective potential, the Kohn-Sham potential $\nu_{ks}(\tilde{r})$, which constraints the noninteracting electron density to match the true density. This potential must obviously include both the electron-electron and electron-nuclear potentials.

Specifically, one solves the Kohn-Sham equations for the Kohn-Sham orbitals, ϕ_i,

$$[-\frac{1}{2}\nabla^2 + \nu_{eff}(\tilde{r})]\phi_i = \epsilon_i\phi_i, \tag{3.62}$$

where

$$\rho(\tilde{r}) = \sum_{i}^{N} \sum_{s} |\phi_i(\tilde{r}, s)|^2, \tag{3.63}$$

and it can be shown that,

$$\begin{aligned} \nu_{eff}(\tilde{r}) &= \nu_{ks}(\tilde{r}) = \nu(\tilde{r}) + \frac{\delta J[\rho]}{\delta\rho(\tilde{r})} + \frac{\delta E_{xc}[\rho]}{\delta\rho(\tilde{r})} & (3.64) \\ &= \nu(\tilde{r}) + \int \frac{\rho(\tilde{r}')}{|\tilde{r} - \tilde{r}'|} d\tilde{r}' + \nu_{xc}(\tilde{r}). & (3.65) \end{aligned}$$

The density must of course be solved self-consistently just as in Hartree-Fock theory and there are N one-electron orbitals, ϕ_i. The form of the KS equations are very similar to that of Hartree-Fock theory; the difference lies in the $\nu_{eff}(\tilde{r})$ that must be approximated, unlike the potential in HF theory. The Kohn-Sham potential can in principle be exact, which is not the case in Hartree-Fock theory. Orbital energies are also obtained in Kohn-Sham theory,

$$\epsilon_i = < \phi_i| - \frac{1}{2}\nabla^2 + \nu_{eff}|\phi_i > . \tag{3.66}$$

Kohn-Sham density functional theory simplifies the problem of finding functionals by handling the noninteracting kinetic energy exactly. The Kohn-Sham energy is not just the sum of the Kohn-Sham orbital energies,

$$E = \sum_i \epsilon_i - \frac{1}{2}\int \frac{\rho(\tilde{r})\rho(\tilde{r}')d\tilde{r}d\tilde{r}'}{|\tilde{r}-\tilde{r}'|} + E_{xc}[\rho] - \int \nu_{xc}\rho(\tilde{r})d\tilde{r} \qquad (3.67)$$

Functionals must now be discovered for the exchange-correlation and for any difference between the kinetic energy on an interacting and noninteracting system. The difference between the kinetic energies of interacting and noninteracting systems is incorporated into $E_{xc}[\rho(\tilde{r})]$ through the adiabatic connection formula. [16] To obtain this, first expand out the $E_{xc}[\rho(\tilde{r})]$,

$$E_{xc}[\rho(\tilde{r}) = (V_{ee}[\rho(\tilde{r})] - J[\rho(\tilde{r})]) + (T[\rho(\tilde{r})] - T_s[\rho(\tilde{r})]). \qquad (3.68)$$

For future simplicity, the full electron-electron interaction is denoted as $V_{ee}[\rho(\tilde{r})]$, the Kohn-Sham kinetic energy as $T_s[\rho(\tilde{r})]$, and the true kinetic energy as $T[\rho(\tilde{r})]$.

First, revert to wavefunction formalism and consider a system with a scaled electron-electron interaction, λV_{ee}. If $\lambda = 1$, then the system is the real fully interacting system, if $\lambda = 0$, then the system is completely noninteracting, and $0 < \lambda < 1$ corresponds to systems with a reduced Coulomb interaction between the electrons. If the wavefunctions for each Hamiltonian along the path from $\lambda = 0$ to $\lambda = 1$ are constrained to give the same electron density, i.e., that for $\lambda = 1$, then one has a smooth connection between the Kohn-Sham noninteracting system at $\lambda = 0$ and the true interacting system at $\lambda = 1$. This idea forms the basis for the adiabatic connection.

In particular, consider,

$$F_\lambda[\rho(\tilde{r})] = <\phi_\lambda|(T+\lambda V_{ee})|\phi_\lambda> \tag{3.69}$$

$$F_1[\rho(\tilde{r})] = T[\rho(\tilde{r})] + V_{ee}[\rho(\tilde{r})] \tag{3.70}$$

$$F_0[\rho(\tilde{r})] = T_s[\rho(\tilde{r})] \tag{3.71}$$

$$E_{xc}[\rho(\tilde{r})] = \int_0^1 \frac{\partial F_\lambda[\rho(\tilde{r})]}{\partial\lambda} d\lambda - J[\rho(\tilde{r})] \tag{3.72}$$

So if $\frac{\partial F_\lambda[\rho(\tilde{r})]}{\partial\lambda}$ is known, and if approximations are made to this quantity over the whole range of λ, then the full energy can be obtained.

$$E_\lambda = F_\lambda[\rho(\tilde{r})] + \int \rho(\tilde{r})\nu(\tilde{r})d\tilde{r} \tag{3.73}$$

$$= <\psi_\lambda|F_\lambda + \sum_i^N \nu(\tilde{r}_i)|\psi_\lambda> \tag{3.74}$$

$$= <\psi_\lambda|(T+\lambda V_{ee}) + \sum_i^N \nu(\tilde{r}_i)|\psi_\lambda> \tag{3.75}$$

Due to the Hellmann-Feynman theorem,

$$\frac{\partial E_\lambda}{\partial\lambda} = <\psi_\lambda|\frac{H_\lambda}{\partial\lambda}|\psi_\lambda> \tag{3.76}$$

$$= <\psi_\lambda|\frac{\partial F_\lambda}{\partial\lambda} + \sum_i^N \frac{\partial\nu(\tilde{r}_i)}{\partial\lambda}|\psi_\lambda> \tag{3.77}$$

$$= <\psi_\lambda|V_{ee} + \sum_i^N \frac{\partial\nu(\tilde{r}_i)}{\partial\lambda}|\psi_\lambda> \tag{3.78}$$

$$\rightarrow \frac{\partial F_\lambda}{\partial\lambda} =<\psi_\lambda|V_{ee}|\psi_\lambda> . \tag{3.79}$$

Hence, an explicit form of the difference between the noninteracting and interacting kinetic energies is not needed, but the price paid is the need to approximate the electron-electron interaction over a range of interaction strengths.

Kohn-Sham theory can be generalized beyond the outline presented above. One such generalization is to incorporate spin so as allow for open shell systems. [17] Another generalization is Current Density Functional Theory (CDFT). [18] [19]The latter generalization is more relevant for this work. The Kohn-Sham theorems as presented above are valid whenever there is a scalar potential. Magnetic fields require the incorporation of a vector potential. Thus a generalization is required. This generalization was performed as a theorem by Rajagopal and Calloway. [18] They showed that one could obtain Hohenberg-Kohn theorems for a system in an arbitrary magnetic field. The energy functionals in this theory, however, are no longer functionals of just the electron density, but rather of the electron and current densities. This makes functional construction more complicated as there are now two independent variables. As a result, it was not until several years later that the first functionals were constructed to take advantage of the theorems of Rajagopol and Calloway. This was the construction of Current Density Functional Theory by Vignale and Rasolt. [19] While being a very nice theory due to its generality, unfortunately, its complexity has rendered it useless for molecular properties. In particular, there have been several valiant attempts by people from N.C. Handy's group to calculate magnetic susceptibilities and chemical shieldings for small molecules, but all the attempts have been computationally demanding, and not accurate. [20] Hence, a different theory is required for practical computation and especially for improved understanding of molecular magnetic responses. The actual formulation of CDFT done by Vignale and Rasolt involved formulating the functionals as functionals of the scalar $\rho(\tilde{r})$, and the vector $\tilde{\nu}(\tilde{r})$ where,

$$\tilde{\nu}(\tilde{r}) = \nabla \times [\frac{\tilde{j}_p(\tilde{r})}{\rho(\tilde{r})}]. \tag{3.80}$$

$j_p(\tilde{r})$ is the paramagnetic current density. Although the paramagnetic current density is not by itself gauge invariant, $\tilde{\nu}(\tilde{r})$ is invariant. Thus, they were able to formulate their theory in terms of gauge invariant quantities.

Start by considering a general formulation of CDFT. The energy of a system in an external magnetic field is thus,

$$E[\rho(\tilde{r}), \tilde{j}_p(\tilde{r})] = E_0[\rho(\tilde{r}), \tilde{j}_p(\tilde{r})] + \int \rho(\tilde{r})\frac{A^2}{2}d\tilde{r} + \int \tilde{j}_p(\tilde{r}) \bullet \tilde{A}(\tilde{r})d\tilde{r} \tag{3.81}$$

where,

$$E_0[\rho(\tilde{r}), \tilde{j}_p(\tilde{r})] = T_s[\rho(\tilde{r}), \tilde{j}_p(\tilde{r})] + \int \rho(\tilde{r})\nu(\tilde{r})d\tilde{r} + J[\rho(\tilde{r})] + E_{xc}[\rho(\tilde{r}), \tilde{j}_p(\tilde{r})]. \tag{3.82}$$

Notice the dependence upon the paramagnetic current density of both the kinetic and exchange-correlation energies. $T_s[\rho(\tilde{r}), \tilde{j}_p(\tilde{r})]$ can be defined in the normal Kohn-

Sham manner except the vector potential must be included as well, i.e.,

$$[\frac{1}{2}(-i\nabla + \tilde{A}_{eff}(\tilde{r}))^2 + V_{eff}(\tilde{r})]\phi_i(\tilde{r}) = \epsilon_i\phi_i(\tilde{r}) \tag{3.83}$$

$$\rho(\tilde{r}) = \sum_{i=1}^{N} \phi_i^2 \tag{3.84}$$

$$\tilde{j}_p(\tilde{r}) = -\frac{i}{2}\sum_{j}^{N}[\phi_j^*(\tilde{r})\nabla\phi_j(\tilde{r}) - \nabla\phi_j^*(\tilde{r})\phi_j(\tilde{r})]. \tag{3.85}$$

The effective vector and scalar potentials need to be obtained by finding the energies and then taking functional derivatives with respect to the paramagnetic current density and the electron density respectively.

$$\begin{aligned} E[\rho(\tilde{r}), \tilde{j}_p(\tilde{r})] &= \sum_{i}^{N}\frac{1}{2}\int \phi_j^*(\tilde{r})(-i\nabla + \tilde{A}(\tilde{r}))^2\phi_j(\tilde{r})d\tilde{r} + J[\rho(\tilde{r})] \\ &+ \int \rho(\tilde{r})\nu(\tilde{r}) + E_{xc}[\rho(\tilde{r}), \tilde{j}_p(\tilde{r})] \\ &= \sum_{i}^{N}\frac{1}{2}\int \phi_j^*(\tilde{r})(-i\nabla + \tilde{A}_{eff}(\tilde{r}))^2\phi_j(\tilde{r})d\tilde{r} \\ &+ \frac{1}{2}\int((\tilde{A}(\tilde{r}))^2 - (\tilde{A}_{eff}(\tilde{r}))^2\rho(\tilde{r})d\tilde{r} \\ &+ \int \tilde{j}_p(\tilde{r}) \bullet (\tilde{A}(\tilde{r}) - \tilde{A}_{eff}(\tilde{r}))d\tilde{r} + J[\rho(\tilde{r})] \\ &+ \int \rho(\tilde{r})\tilde{\nu}(\tilde{r})d\tilde{r} + E_{xc}[\rho(\tilde{r}), \tilde{j}_p(\tilde{r})] \end{aligned} \tag{3.86}$$

After taking functional derivatives ,

$$
\begin{aligned}
V_{eff} &= \nu(\tilde{r}) + \frac{1}{2}[(\tilde{A}(\tilde{r}))^2 - (\tilde{A}_{eff}(\tilde{r}))^2] + \frac{\partial J[\rho(\tilde{r})]}{\partial \rho(\tilde{r})} + \frac{\partial E_{xc}[\rho(\tilde{r}), \tilde{j}_p(\tilde{r})]}{\rho(\tilde{r})} && (3.87) \\
&= \nu(\tilde{r}) + \frac{1}{2}[(\tilde{A}(\tilde{r}))^2 - (\tilde{A}_{eff}(\tilde{r}))^2] + \frac{\partial J[\rho(\tilde{r})]}{\partial \rho(\tilde{r})} + V_{xc}(\tilde{r}) && (3.88) \\
\tilde{A}_{eff}(\tilde{r}) &= \tilde{A}(\tilde{r}) + \frac{\partial E_{xc}[\rho(\tilde{)}, \tilde{j}_p[\tilde{r}]}{\partial \tilde{j}_p[\tilde{r}]} = \tilde{A}(\tilde{r}) + \tilde{A}_{xc}(\tilde{r}).
\end{aligned}
$$

Notice how complex the situation has become. There is an effective vector potential as well as an effective scalar potential. Additionally, the effective scalar potential depends on both the real and effective vector potentials.

The equation for the Kohn-Sham orbital also becomes quite complicated.

$$
\begin{aligned}
(&- \frac{1}{2}\nabla^2 + \nu(\tilde{r}) + \frac{\partial J[\rho(\tilde{r})]}{\partial \rho(\tilde{r})} + \frac{\partial E_{xc}[\rho(\tilde{r}), \tilde{j}_p(\tilde{r})]}{\rho(\tilde{r})} + \frac{1}{2}(\tilde{A}(\tilde{r}))^2 - \frac{i}{2}(\tilde{A}(\tilde{r}) \bullet \nabla + \nabla \bullet \tilde{A}(\tilde{r})) \\
&- \frac{i}{2}(\tilde{A}_{xc}(\tilde{r}) \bullet \nabla + \nabla \bullet \tilde{A}_{xc}(\tilde{r})))\phi_i(\tilde{r}) = \epsilon_i \phi_i(\tilde{r}) && (3.90)
\end{aligned}
$$

Now using the gauge invariant vector $\tilde{n}u(\tilde{r}) = \nabla \times [\frac{\tilde{j}_p(\tilde{r})}{\rho(\tilde{r})}]$ one obtains slightly different expressions for the exchange-correlation vector and scalar potentials,

$$
\begin{aligned}
V_{xc}(\tilde{r}) &= \frac{\partial E_{xc}[\rho(\tilde{r}), \tilde{n}u(\tilde{r})]}{\rho(\tilde{r})} - \frac{\tilde{j}_p(\tilde{r}) \bullet \tilde{A}_{xc}(\tilde{r})}{\rho(\tilde{r})} && (3.91) \\
\tilde{A}_{xc}(\tilde{r}) &= \frac{1}{\rho(\tilde{r})} \nabla \times \frac{\partial E_{xc}[\rho(\tilde{r}), \nu(\tilde{r})]}{\partial \tilde{\nu}} && (3.92)
\end{aligned}
$$

so these gauge invariant exchange-correlation potentials can be used instead. While using $\tilde{\nu}(\tilde{r})$ has the advantage of rendering the theory gauge invariant, it makes an already complex theory even more complicated. It's no surprise that despite tremendous effort, CDFT has not proven useful for molecular magnetic responses.

Another theory that has proven more useful in practical calculations, is the coupled DFT approach of Malkin, Malkina and Salahub. [21] This method is /approximationa perturbation theory approach in which matrix elements are taken with respect to the Kohn-Sham orbitals. This is mildly suspicious as the Kohn-Sham orbitals are intended solely for the determination of the kinetic energy of noninteracting systems. In order to obtain reasonable results an empirical fix is required. The results obtained for many systems are surprisingly good, and better than Hartree-Fock results.

In particular, in order to perform perturbation theory, one needs matrix elements for the paramagnetic portion of the chemical shielding,

$$\frac{< \psi_a | (h_k^1)_\alpha | \psi_k >}{\epsilon_k^0 - \epsilon_a^0} \tag{3.93}$$

where

$$(h_k^1)_\alpha = -\frac{1}{2c}((\tilde{r} - \tilde{R}_k) \times \nabla)_\alpha \tag{3.94}$$

is the perturbation. Most of the details are irrelevant for this work. All that is necessary, is to notice that the Kohn-Sham orbital energies are used in the denominator. An interested reader can examine the details of the perturbation treatment for himself in reference 21.

Using these equations did not lead to good results until an empirical correction was made in the denominator

$$\epsilon_k^0 - \epsilon_a^0 \rightarrow \epsilon_k^0 - \epsilon_a^0 + \alpha. \tag{3.95}$$

The "level shift" α, was made because Kohn-Sham theory tends to describe unoccupied orbitals badly. Other than that there is no justification for this shift and it should be considered as an ad hoc adjustment of the theory to match experimental data. Notice there is also a complete neglect of any explicit dependence of the exchange-correlation functional upon the magnetic field. Though given the weakness of NMR fields, this neglect is likely not to be significant.

The desire to have an alternative to both CDFT and Salahub's treatment for magnetic responses in weak magnetic fields lead Harris and Grayce to demonstrate the existence of yet another type of density functional theory, the Magnetic Field Density Functional Theory. [22] This theory is the main topic of this thesis.

There are a few main features of this theory: rigorous dependence on only the electron density and the magnetic field, lose of universality with respect to the vector potential, no separation into paramagnetism and diamagnetism, and the second order property theorem. The latter is the most important piece of the theory. The second order property theorem says that in a weak magnetic field the second order responses are functionals of the electron density in the absence of the magnetic field. This is an incredibly profound statement! According to this, NMR is really probing the ground state electronic structure of the systems. All the methods that require excited state corrections are doing something unnecessary that clouds understanding of the responses and make computations more demanding.

To demonstrate the existence of this theory, first note that for a fixed gauge then in the absence of an accidental degeneracy, the ground state wavefunction is a unique functional of the magnetic field and the scalar potential. Thus, for a fixed magnetic field, there is a one-to-one correspondence between the electron density and the scalar potential. This is where universality is lost as one cannot arbitrarily vary the field with a fixed functional, i.e., the functional and field must vary together otherwise there is a many to one mapping from density to scalar potential. The magnetic field may be considered as a parameter as in this work as there is only one field of interest: the two-dipole field and limits thereof. The field may instead be considered as the variable that replaces the current density. The lack of universality is an advantage here because for a large class of problems, the weak field magnetic responses, there is now a density functional theory of one variable alone.

Kohn-Sham equations exist in this theory as in most other variants of density functional theory. There are, however, two possible sets of Kohn-Sham equations. The first is the more typical,

$$[\frac{1}{2}(-i\nabla + \frac{\tilde{A}(\tilde{r})}{c})^2 + V_{eff}(\tilde{r}, \tilde{B})]\phi_n(\tilde{r}, \tilde{B}) = \epsilon_n(\tilde{B})\phi_n(\tilde{r}, \tilde{B}) \tag{3.96}$$

so that the typical definitions of the noninteracting kinetic energy, the total energies and the effective potential can be made, for closed shell systems,

$$T_s[\rho, \tilde{B}] = 2\sum_{i}^{N/2} \int d\tilde{r}\phi_n^*(\tilde{r}, \tilde{B})\frac{1}{2}(-i\nabla + \frac{\tilde{A}(\tilde{r})}{c})^2\phi_n(\tilde{r}, \tilde{B}) \tag{3.97}$$

$$F[\rho(\tilde{r}), \tilde{B}] = T_s[\rho, \tilde{B}] + E_{xc}[\rho(\tilde{r}), \tilde{B}] \tag{3.98}$$

$$V_{eff} = V\tilde{r} + \int d\tilde{r}' \frac{\rho(\tilde{r}, \tilde{B})}{|\tilde{r} - \tilde{r}'|} + \frac{\partial E_{xc}[\rho(\tilde{r}), \tilde{B}]}{\partial \rho(\tilde{r})} \tag{3.99}$$

thus one has a set of self-consistent equations to solve which require the approximation of $E_{xc}[\rho(\tilde{r})], \tilde{B}]$.

The second set of Kohn-Sham equations that can be constructed is atypical, but these equations have their own advantages,

$$[\frac{1}{2}(-i\nabla^2) + V_{eff}(\tilde{r}, \tilde{B})]\phi_n(\tilde{r}, \tilde{B}) = \epsilon_n(\tilde{B})\phi_n(\tilde{r}, \tilde{B}) \tag{3.100}$$

$$T_s[\rho, \tilde{B}] = 2\sum_{i}^{N/2} \int d\tilde{r}\phi_n^*(\tilde{r}, \tilde{B})\frac{1}{2}(-i\nabla)^2\phi_n(\tilde{r}, \tilde{B}) \tag{3.101}$$

$$F[\rho(\tilde{r}), \tilde{B}] = T_s[\rho, \tilde{B}] + E_{kxc}[\rho(\tilde{r}), \tilde{B}] \tag{3.102}$$

$$V_{eff} = V(\tilde{r}) + \int d\tilde{r}' \frac{\rho(\tilde{r}, \tilde{B})}{|\tilde{r} - \tilde{r}'} + \frac{\partial E_{kxc}[\rho(\tilde{r}), \tilde{B}]}{\partial \rho(\tilde{r})}. \tag{3.103}$$

The principle advantage of the latter is that the orbitals can be purely real and there is no separation into diamagnetic and paramagnetic. The price is the need to approximate a kinetic-exchange-correlation functional.

The most important piece left of the foundations is the proof of the second order property theorem, which allows one to avoid calculation of the first order corrections to the density in the computation of magnetic responses.

This theorem is for weak magnetic fields as it is based upon perturbation theory. In particular, first expand the energy to second order with respect to its explicit dependence upon the field,

$$F[\rho(\tilde{r}),\tilde{B}] = F[\rho(\tilde{r}),0] + B^2\frac{\partial^2 F[\rho(\tilde{r}),B]}{\partial B^2}. \tag{3.104}$$

The quadratic term is taken in the limit as the field goes to zero, and there are only even powers of B due to time reversal symmetry as discussed in Chapter 1. The energy is even under time reversal, but an external field is odd. Hence, fields can couple in with only even powers. Though if there are two fields present, such as a uniform field and a dipole field, each field could couple in linearly.

Although the energy has been expanded with respect to its explicit field dependence there still is an implicit field dependence through the density, as the electron density itself depends upon the field. Now expand out the energy with respect to this implicit dependence,

$$F[\rho(\tilde{r}),\tilde{B}] = F[\rho(\tilde{r}),0] + \int d\tilde{r}\rho^2(\tilde{r},\tilde{B})\frac{F[\rho^0,0]}{\delta\rho(\tilde{r})} + ... + B^2\frac{\partial^2 F[\rho^0(\tilde{r}),B]}{\partial B^2} \tag{3.105}$$

where the following are defined

$$\rho^0(\tilde{r}) = \rho(\tilde{r}, 0) \tag{3.106}$$

$$\rho^2(\tilde{r}, \tilde{B}) = B^2 \frac{d^2\rho(\tilde{r}, B)}{dB^2}. \tag{3.107}$$

Each series is stopped at second order due to the weak field, and the normalization of $\rho(\tilde{r})$ requires that

$$\int d\tilde{r} \rho^2(\tilde{r}, \tilde{B}) = 0. \tag{3.108}$$

As a result the energy to second order is

$$\begin{aligned} E[\rho(\tilde{r}), \tilde{B}] &= E^0[\rho^0(\tilde{r})] + B^2 \frac{\partial^2 F[\rho^0(\tilde{r}), B]}{\partial B^2} + \int d\tilde{r} \rho^2(\tilde{r}, \tilde{B}) [\frac{\partial F[\rho^0, 0]}{\partial \rho(\tilde{r})} \\ &+ V(\tilde{r}) + \int d\tilde{r}' \frac{\rho^0(\tilde{r})}{|\tilde{r} - \tilde{r}'|}] + \ldots \end{aligned}$$

The first term in the expansion is the zero field energy. The zero field density minimizes this. Applying this variational condition causes the last term to vanish for the true ground state electron density. Thus,

$$E[\rho(\tilde{r}), \tilde{B}] = E^0[\rho^0(\tilde{r})] + B^2 \frac{\partial^2 F[\rho^0(\tilde{r}), B]}{\partial B^2} \tag{3.110}$$

which completes the proof as only the ground state density is needed. Now if the full functional is used, rather than the Kohn-Sham equations, then the explicit B dependent term, which corresponds to the second term, can be found by examination. As the Kohn-Sham equations are used in any practical application, the problem seems to be more complicated as

$$E[\rho(\tilde{r}),\tilde{B}] = E^0[\rho^0(\tilde{r})] + B^2\frac{\partial^2 T_s[\rho^0(\tilde{r}),B]}{\partial B^2} + B^2\frac{\partial^2 E_?[\rho^0(\tilde{r}),B]}{\partial B^2} \tag{3.111}$$

where $E_? = E_{kxc}$ or $E_? = E_{xc}$ depending upon the Kohn-Sham equations used. Now the latter term can be obtained trivially by examination given some approximation to the functional. The explicitly field dependent portion of the noninteracting kinetic energy, however, cannot be found by examination because the orbitals are not known as functionals of $\rho(\tilde{r},\tilde{B})$.

The explicit field dependence of the kinetic energy, however, can be obtained. Consider T_s as an expectation value of a one-electron kinetic energy operator, as in coupled Hartee-Fock theory,

$$T_s = \sum_i^{N/2} < i|t|i > \tag{3.112}$$

then the explicitly field dependent portion becomes

$$\frac{\partial^2 T_s[\rho^0(\tilde{r}),B]}{\partial B^2} = 2\sum_i^{N/2}[< i^0|t^2|i^0 > + \frac{1}{2} < i^0|t^1|i^1 > + \frac{1}{2} < i^1|t^0 >]. \tag{3.113}$$

Now if the first set of Kohn-Sham equations is used then all the terms above are present, and one need calculate linear field corrections to the Kohn-Sham orbitals. The second order property theorem is still valid as these corrections can be calculated with the zero field electron density. Now if the second set of Kohn-Sham equations is used, then the one-electron kinetic energy operator is just

$$t = -\frac{1}{2}\nabla^2 \tag{3.114}$$

and hence, the energy to second order in the field is given by,

$$E[\rho(\tilde{r}), \tilde{B}] = E^0[\rho^0(\tilde{r})] + B^2 \frac{\partial^2 E_{kxc}[\rho^0(\tilde{r}), B]}{\partial B^2} \tag{3.115}$$

which means there is another advantage to the second formulation.

The basic and essential elements of density functional theory both with and without magnetic fields have been reviewed. The background has been laid for further development of Magnetic Field Density Functional Theory (BDFT) as discussed in the next few chapters.

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Chapter 4

Local Current Density Functionals

In this chapter, I present my work on local current density functionals. These functionals are used with the Biot-Savart integrals to obtain the magnetic responses as functionals of the zero field electron density. A gradient expansion of the electronic current density in the electron density is used to obtain these expressions for the magnetic susceptibility and chemical shielding. The first term in the expansion is the Thomas Fermi expression. All succeeding terms diverge for both properties. A renormalized functional is used which removes the divergences and gives asymptotic diamagnetism. This renormalized functional uses a single parameter that depends linearly on the number of electrons gives heavy rare gas susceptibilities to within 1% of exact calculations using electron densities calculated at the same level of theory. Similar results are found for the chemical shielding. Susceptibility and shielding calculations for the helium dimer and the hydrogen molecule in singlet and triplet states are presented. The results are compared with other calculations over a full range of internuclear distances.

4.1 Introduction

The earliest use of density functional theory as a means of calculating magnetic responses may be found in the work of Cina and Harris. [1] They used an electron gas, or Thomas-Fermi-Dirac, type theory to calculate the magnetic susceptibility tensor of the triplet state of H_2. Grayce and Harris then used a similar description of the electrons to calculate the shielding tensor of the same state of H_2. [2]

The above usage of density functional theory might be called a "pure density functional theory". That is, responses are obtained from an energy functional by invoking the Hellman-Feynman theorem and taking the appropriate derivatives. This method is in contrast to more recent calculations that solve the Kohn-Sham equations in a vector potential. [3]

In 1995, an entirely different theory of magnetic responses was advanced. [10] [11] This theory demonstrated that the magnetic responses are all related to a single tensor response functional. This functional is a universal functional of the electron density in the absence of the magnetic field. The functional is, of course, unknown. If one could find reasonable approximations to the functional, all field dependent methods of calculating magnetic responses could be dispensed with. This may well lead to a simpler way of obtaining and understanding the responses.

Locally uniform approximations to the functional have been developed. These were developed by Cina and Harris [1] and Grayce and Harris, [2], in what may be considered precursors to the general theory. In reality their work was a hybrid of ideas. As the functional was meant for application to interacting closed shell systems, additive densities were used. These additive densities were used as their work was based upon Gordon-Kim theory. [11] In Gordon-Kim theory, additive densities are used to obtain incremental responses. The full responses are obtained with the additive densities and then the atomic responses are subtracted away. The hope is that the incremental responses are modeled well. Gordon-Kim theory has been applied with some success to electrical responses. [12] In the work of Harris and Cina and Grayce and Harris, each atomic density was in the presence of the appropriate magnetic fields. Thus, terms in the functional, which would make no contribution if the exact nonadditive density were used, are manifestly present. This seeming contradiction to the tenets of the general theory is not a surprise. A similar result occurs in all linear responses via density functional theories of interacting closed shell systems: additivity in the presence of external fields is approximately equivalent to nonadditivity in the absence of the fields. [11]

In this chapter, an attempt is made to obtain the magnetic susceptibility and the chemical shielding directly from the total current density. [18],[19],[20] The resulting integral expressions, (sometimes called the "Biot-Savart integrals") [20], for the shielding and susceptibility are consequences of linear response theory. As such, the induced current density may be looked upon as a response. Hence, according to the general theorems of BDFT, the current density is a linear function of the external magnetic field and a functional of the unperturbed electron density.

The attempt to construct responses via the induced current density has a long history. [15], [16], [17] Such attempts usually involve bypassing perturbation theory or using a Dalgarno-Lewis version of perturbation theory. [16][17] Indeed there even has been attempts to construct currents from a form of quantum hydrodynamics. [16] None of these theories related the current density to the unperturbed electron density, although some came close. [15]

4.2 The Current Density

The current density, $\tilde{j}(\tilde{r})$, is not arbitrary. [12] For a bound stationary state it must be transverse,

$$\nabla \bullet \tilde{j}(\tilde{r}) = 0 \tag{4.1}$$

and so one must have,

$$\tilde{j}(\tilde{r}) = \nabla \times \tilde{M}(\tilde{r}). \tag{4.2}$$

As the chemical shielding and the magnetic susceptibility are the quantities of interest, the linear response regime may be considered. In this regime, the external magnetic field is constant and uniform. Hence, the most general form of $\tilde{M}(\tilde{r}))$, to within a gradient of a scalar, is

$$\tilde{M}(\tilde{r}) = M^{(0)}(\tilde{r})\tilde{B} + \tilde{M}^{(1)}(\tilde{r}) \times \tilde{B} + \tilde{\tilde{M}}^{(2)}(\tilde{r}) \bullet \tilde{B} \tag{4.3}$$

$M^{(0)}(\tilde{r})$, $\tilde{M}^{(1)}(\tilde{r})$ and $\tilde{\tilde{M}}^{(2)}(\tilde{r})$ are, respectively, irreducible zero, first and second rank tensors. The shielding and susceptibility tensors may be written in terms of the M tensors through use of the Biot-Savart integrals [12],[14]

$$\chi_{\gamma\beta} = -\frac{1}{2}\int d^3r(\tilde{r} \times \frac{\partial \tilde{j}(\tilde{r})}{\partial B_\beta})_\gamma \tag{4.4}$$

and

$$\sigma_{\gamma\beta} = \int d^3r(\frac{\tilde{r}}{r^3} \times \frac{\partial \tilde{j}(\tilde{r})}{\partial B_\beta})_\gamma. \tag{4.5}$$

Substitution of Eqn. (4.4) into Eqn. (4.5) gives a contribution from $\tilde{M}^{(1)}$ to χ that is a rank one tensor, so that the full $\tilde{\tilde{\chi}}$ tensor would be asymmetric. The $\tilde{\tilde{\chi}}$ tensor, however, is symmetric, hence $\tilde{M}^{(1)}$ must equal zero. $M^{(0)}$ contributes to the scalar component of both $\tilde{\tilde{\sigma}}$ and $\tilde{\tilde{\chi}}$, as well as the symmetric component of $\tilde{\tilde{\sigma}}$. $\tilde{\tilde{M}}^{(2)}$ contributes to all ranks of both responses.

Now the $\tilde{\tilde{M}}$ tensor will be determined as a functional of the unperturbed electron density. In order to orient oneself, begin with the only systems, besides the noninteracting uniform electron gas, where the current density and hence, M, are known exactly, given that the magnetic field is either constant or that due to a nuclear spin. [12] These systems are closed shell atoms, or more generally, any rotationally invariant bound system in a state of zero angular momentum. Here the current density is entirely diamagnetic. [12] That is, in the gauge where

$$\nabla \bullet \tilde{A}(\tilde{r}) = 0, \tag{4.6}$$

and, e.g.,

$$\tilde{A}(\tilde{r})) = \frac{1}{2}\tilde{B} \times \tilde{r}, \tag{4.7}$$

the current density is, in units where all constants are set equal to one,

$$\tilde{j}(\tilde{r}) = -\tilde{A}(\tilde{r})\rho(\tilde{r}). \tag{4.8}$$

Thus,

$$\tilde{j}(\tilde{r}) = \tilde{B} \times \nabla M^{0}(\tilde{r}). \tag{4.9}$$

From Equations (4.8) and (4.9) the scalar, $M^{(0)}$ may be determined, namely,

$$M^{(0)} = \frac{1}{2}\int_0^{r'} dr'\rho(r'). \tag{4.10}$$

Now the scalar susceptibility and shielding are given, respectively by,

$$\chi = -\int drM^{(0)}\rho(r) \tag{4.11}$$

and

$$\sigma = 8\pi M^{(0)}(0). \tag{4.12}$$

The $M^{(0)}(0)$ indicates evaluation at the nucleus whose shielding is to be calculated. In terms of the density, the well-known results are, [10]

$$\chi = -\int_0^{\infty} drr^4\rho(r) \tag{4.13}$$

and

$$\sigma = \int_0^{\infty} drr\rho(r) \tag{4.14}$$

As mentioned above, the starting point will be the locally uniform electron gas model. Here, as shall be seen , both the current density and $M^{(0)}(0)$ are local functions of the density. Hence, by comparing Eqn. (4.12) in the local electron gas limit with Eqn. (4.15), a failure of the local theory is immediately seen. The exact diamagnetic $M^{(0)}(0)$ is nonlocal. Hence the shielding is an integral over all space. The shielding in the local electron gas theory depends on the density at the nucleus (r=0). Thus, it should come as no surprise that a purely local theory may fail to predict shieldings well, but may generate reasonable susceptibilities. Nor should one be surprised if a "corrected" local theory requires different functionals for shieldings and susceptibilities.

4.3 The Gradient Expansion of The Current Density

The problem is how to obtain the current density as a functional of the density. It shall be assumed that the current density is that which arises from the solutions of the Kohn-Sham equations, e.g., Equations 3.36-3.69, in the presence of a vector potential. [7],[19] Thus, the current density constructed is not exact. If the Hellmann-Feynman theorem is used to derive the current density from the energy functional, there are additional terms. [9] The present approximation is the same approximation used in the work of Harris and Cina [18] and the path integral theory of Harris and Pratt. [19] The situation is not unlike the so-called "adiabatic approximation" in time-dependent density functional theory. [20]

Given the above approximation, the many-electron current density for a closed shell system may be expressed in terms of the propagator of a single electron in a scalar potential, $V(\tilde{r})$, and a vector potential, $\tilde{A}(\tilde{r})$. [1] Namely,

$$\tilde{j}(\tilde{r}) = \frac{-2}{2\pi i}\int_{-\infty-i\gamma}^{\infty-i\gamma}\frac{dt}{t}\lim_{\tilde{r}'\to\tilde{r}}[\frac{(\nabla'-\nabla)}{2i}+\tilde{A}(\tilde{r})] < \tilde{r}t|\tilde{r}'0 >, \tag{4.15}$$

in which

$$< \tilde{r}t|\tilde{r}'0 >=< \tilde{r}t|e^{-itH}|\tilde{r}'0 > \tag{4.16}$$

is the single electron propagator and H is the single electron Hamiltonian in the presence of a scalar potential, $V(\tilde{r})$, and vector potential, $\tilde{A}(\tilde{r})$. The Fermi energy has been absorbed as a constant in the Hamiltonian. The density, $\rho(\tilde{r})$, is also given by an integral over the propagator: [21] [22]

$$\rho(\tilde{r}) = \frac{2}{2\pi i}\int_{-\infty-i\gamma}^{\infty-i\gamma}\frac{dt}{t} < \tilde{r}t|\tilde{r}0 > . \tag{4.17}$$

Obtaining reasonable approximations for the propagator may be carried out via a generalization of the method of Makri-Miller. [23] Begin with the anzatz

$$< \tilde{r}t|e^{-itH}|\tilde{r}'0 >= e^{iW(\tilde{r},t)}(\frac{1}{2\pi it})^{3/2}e^{\frac{i(\tilde{r}-\tilde{r}')^2}{2t}}. \tag{4.18}$$

This ansatz starts with the free particle propagator in three dimensions and extends it using $W(\tilde{r}, t)$. The dependence of W on $\tilde{r}'$ is implicit. In the weak field limit, write W as

$$W(\tilde{r},t) = \tilde{B} \bullet \frac{\tilde{r} \times \tilde{r}'}{2} + W^0(\tilde{r},t) + W^1(\tilde{r},t) \tag{4.19}$$

$\tilde{B} \bullet \frac{\tilde{r}\times\tilde{r}'}{2} + W^0(\tilde{r},t)$ represents the propagator when, to lowest order, there is no coupling between the magnetic field and the scalar potential. [24] $W^1(\tilde{r},t)$ represents the coupling to first order in the field. $W^0(\tilde{r},t)$ has been calculated by Makri and Miller. [23]

An equation for $W^1(\tilde{r},t)$ shall be obtained by substituting Eqn. (4.19) and Eqn. (4.20) into the time-dependent Schrödinger equation and linearizing with respect to the magnetic field. The resulting equation for $W^1(\tilde{r},t)$ is

$$\frac{-\partial W^1(\tilde{r},t)}{\partial t} - (\tilde{r} - \tilde{r}') \bullet \nabla W^1(\tilde{r},t) + \frac{i}{2}\nabla^2 W^1(\tilde{r},t) = \tilde{B} \times \frac{(\tilde{r} - \tilde{r}')}{2} \bullet \nabla W^0(\tilde{r},t). \tag{4.20}$$

$W^0(\tilde{r},t)$ is symmetric in $\tilde{r}$ and $\tilde{r}'$, and $W^1(\tilde{r},t)$ is antisymmetric in these same variables. Upon using these symmetries in the equation for the current density, the following result is arrived at,

$$\tilde{j}(\tilde{r}) = \frac{2}{2\pi i}\int_{-\infty-i\gamma}^{\infty-i\gamma} \frac{dt}{t} e^{iW^0(\tilde{r},\tilde{r}',t)} \lim_{\tilde{r}'\to\tilde{r}} \frac{(\nabla' - \nabla)W^1(\tilde{r},\tilde{r}',t)}{2i}. \tag{4.21}$$

Both position variables, $\tilde{r}$ and $\tilde{r}'$, have been explicitly indicated. The diamagnetic contribution to the current density is exactly canceled by the $\frac{\tilde{B}\bullet\tilde{r}\times\tilde{r}'}{2}$ term in $W(\tilde{r},t)$ as $W((\tilde{r},t)$ is exponentiated in the propagator and derivatives are then taken.

A gradient expansion for $\tilde{j}(\tilde{r})$ is sought for in terms of the electron density. This may be accomplished by expanding both $W^0(\tilde{r},t)$ and $W^1(\tilde{r},t)$ as power series in time, and then expanding both the current density and the electron density in terms of the potential and inverting to obtain $\tilde{j}(\tilde{r})$ as a functional of the electron density, $\tilde{j}[\rho(\tilde{r})]$. Thus,

$$W^0(\tilde{r},t) = \Sigma_{n=2}^{\infty} W_n^0(\tilde{r})t^n \tag{4.22}$$

and

$$W^1(\tilde{r},t) = \Sigma_{n=3}^{\infty} W_n^1(\tilde{r})t^{n-1}. \tag{4.23}$$

The first nonvanishing contributions to the W's appear at t^2. This can be demonstrated by allowing for lower order terms and then substituting into the Schrödinger equation. All lower order terms are contained already in the free particle propagator, $(\frac{1}{2\pi it})^{3/2}e^{\frac{i(\tilde{r}-\tilde{r}')^2}{2t}}$. After substituting the $W^0(\tilde{r},t)$ power series into Eqn. (4.21) one obtains,

$$\begin{aligned}(n-1)W_n^1 &+ (\tilde{r}-\tilde{r}')\bullet\nabla W_n^1 - i\nabla^2 W_{n-1}^1 + \sum_{m=2}^{n}\nabla W_m^0\bullet\nabla W_{n-m}^1 \\ &= \frac{1}{2}(\tilde{r}-\tilde{r}')\times\tilde{B}\bullet\nabla W_{n-1}^0 \qquad (4.24)\end{aligned}$$

where $n = 3...\infty$. The lowest order contribution to the current density is W_3^1, which yields the current density

$$\tilde{\jmath}(\tilde{r}) = \frac{\tilde{B}\times\nabla W_2^0}{12\pi^2(2W_2^0)^{1/2}} \qquad (4.25)$$

Since $W_2^0 = -V(\tilde{r})$ after taking the limit, one can change the current density from a functional of the potential into a current density that is a functional of the electron density. This is done via the Thomas-Fermi relation, [20]

$$2W_2^0 = (3\pi^2\rho)^{2/3}. \qquad (4.26)$$

The resulting current density is identical to the Thomas-Fermi current density derived by Harris and Cina, as it should be. [18]

$$\tilde{\jmath}(\tilde{r}) = \frac{\tilde{B}\times\nabla\rho(\tilde{r})}{12(3\pi^2)^{2/3}} \qquad (4.27)$$

Their treatment is equivalent to the present one in lowest order.

Now the treatment is extended to fourth order in time. This gives the first gradient corrections to the Thomas-Fermi current density. The relevant part of the propagator is,

$$e^{i(W^0(\tilde{r},t)+W^1(\tilde{r},t))} \approx e^{itW_2^0}[1 + it^2W_3^1 + it^3W_4^1 + it^4W_5^1 - t^4(W_3^0W_3^1)]. \tag{4.28}$$

to third order in gradients the current density is,

$$\begin{aligned} \tilde{j}(\tilde{r}) &= \frac{\tilde{B} \times \nabla W_2^0}{12\pi^2(2W_2^0)^{1/2}} - \frac{\tilde{B} \times \nabla\nabla^2 W_2^0}{48\pi^2(2W_2^0)^{3/2}} + \frac{(\tilde{B} \times \nabla W_2^0)\nabla^2 W_2^0}{16\pi^2(2W_2^0)^{5/2}} \\ &+ \frac{\tilde{B} \times \nabla W_2^0(\nabla W_2^0)^2}{192\pi^2(2W_2^0)^{7/2}} - \frac{\tilde{B} \times \nabla\nabla W_2^0 \bullet \nabla W_2^0}{96\pi^2(2W_2^0)^{5/2}}. \end{aligned} \tag{4.29}$$

Inversion to obtain the current density as a functional of the electron density requires the use of the Thomas-Fermi relation for the last two terms. The first term requires gradient corrections to the electron density .[25]

Instead of writing the current density explicitly, it is written in terms of $\tilde{\tilde{M}}$. Only M^0 appears to second order in the gradients of the density.

$$M^0 = \frac{\rho^{1/3}}{4(3\pi^2)}^{2/3}[1 + \frac{1}{3(3\pi^2)^{2/3}}(\frac{4}{9}x^2 + \frac{\nabla \bullet \tilde{x}}{2\rho^{1/3}})], \tag{4.30}$$

where $\tilde{x} = \frac{\nabla\rho}{\rho^{4/3}}$. As the gradient expansion at this order contains only M^0, only the scalar component of the magnetic susceptibility can be calculated and the scalar and symmetric component of the chemical shielding. Tensor terms do not appear even to sixth order in time in the gradient expansions. It may very well be that no finite gradient expansion can ever give tensor terms.

An additional deficiency of the gradient expansion is the divergence of the terms. If the full gradient expansion is used to calculate the magnetic susceptibility, the result diverges. The reason is that atomic and molecular electron densities are exponential at long range. Since $(\nabla\rho)^2/(\rho)^{7/3} \rightarrow \rho^{-1/3}$ as does $\nabla^2\rho/(\rho)^{4/3}$, the resulting integrals over all space diverge. $\rho^{1/3}$ is still finite in this instance; although the decay is not fast enough to recover diamagnetism. This divergence is the same type as that which appears in gradient expansions of the kinetic energy at sixth order in the dimensionless variable x, and at fourth order for the exchange energy. [26] In the case of the current density, the divergence occurs at a lower order because the scale, $\rho^{1/3}$, is at a lower power of the density. Similarly, the expression for the shielding in the gradient expansion, Eqn. (4.13), is incorrect because the infinite surface integral has been neglected. This point shall be returned to in a little while.

4.4 Atomic Susceptibilities and Shieldings

Suppose that the current density is truncated at the Thomas-Fermi current density. What accuracy can be expected? Cina and Harris performed calculations for the susceptibility of the hydrogen atom and the triplet state of hydrogen molecule within the additive density approximation. They called their term "the direct term". Similar calculations were performed using the exact density of the hydrogen atom,

Table 4.1: Atomic Shieldings and Susceptibilities (atomic units)

Atom	Exact Shielding	Exact Susceptibility	TF Shielding	TF Susceptibility	TF +grad Shielding
H	0.333	-0.500	0.282	-0.958	0.294
He	1.127	-0.394	1.005	-0.841	1.058
Ne	10.7	-1.388	5.787	-1.064	6.017
Ar	22.9	-4.34	10.28	-2.576	11.96
Xe	106.2	-9.00	31.57	-4.308	32.8

$\frac{e^{-2r}}{\pi}$, and Hartree-Fock densities [27] for helium, neon, argon, and xenon. The shielding has also been calculated using the same approximations for the electron densities. The results are given in Table 4.1. The exact calculation of the diamagnetic susceptibilities and chemical shieldings, using the same densities as those used in the Thomas-Fermi calculations, is presented for comparison.

The Thomas-Fermi results for the susceptibility are within a factor of 2.2 in all cases. For hydrogen and helium Thomas-Fermi overestimates. For the remaining atoms, however, the results are too low. The reasons for the trend in the Thomas-Fermi magnetic susceptibility is that the Thomas-Fermi susceptibility density, i.e. the integrand in the susceptibility integral (Eqns. 4.12 and 4.14), decays far too slowly at long distances, but also is too small at short distances. For hydrogen and helium, the Thomas-Fermi underestimate at short distances is over-compensated by the slower decay at long distance. For the heavier elements, the short distance shell behavior is more important, and so the underestimate at short distances is not compensated by the long-term distance behavior. That neon is most accurately represented by the

Thomas-Fermi function is simply a manifestation of these two errors approximately canceling.

The behavior of the chemical shielding is harder to understand. In a local density functional theory, the shielding is a functional of the electron density at the origin alone, whereas in exact diamagnetism, the shielding still involves an integral over all space. The inconsistency here may be an indication that a local density functional theory cannot represent the chemical shielding accurately, or it could mean that different functionals are needed to represent the shielding.

As discussed earlier, the gradient expansion for the magnetic susceptibility diverges as does the gradient expansion for the shielding. For the shielding, the divergence appears in the infinite surface terms that must sum to zero as the exact result is finite. The local contributions are finite. Thus, gradient corrections to the Thomas-Fermi may be considered, if only the local terms are kept, disregarding the divergent surface terms. These surviving terms involve the electron density, the gradient of the electron density, etc., all evaluated at the nucleus.

The gradient-corrected calculations have been carried out for the noble gas atoms. Using the first correction to Thomas-Fermi,

$$M^0 = \frac{\rho^{1/3}}{4(3\pi^2)^{2/3}}[1 + \frac{4x^2}{27(3\pi^2)^{2/3}}]. \tag{4.31}$$

As may be seen in Table 4.1, the improvement is not great.

To improve on the Thomas-Fermi functional and its gradient corrections, inspiration was taken from the work of A. D. Becke. [28], [29],[30] The crucial idea is that to improve a Thomas-Fermi functional one should multiply it by a function of the dimensionless variable $x = \frac{|\nabla\rho|}{(\rho^{4/3})}$, such that in the limit of the gradients going to zero, the Thomas-Fermi function is recovered, and such that some exact constraint, or constraints, of bound systems is satisfied. Becke constructed an exchange functional in this manner by considering the exact expression for the exchange hole. The same is done for the current density.

At long distances, one should not be able to tell the difference between at atom and a molecule, as in both cases the electron density looks the same. Atoms are, of course, purely diamagnetic. Thus, the long-range behavior which one would like to recover is the one in which $M^0 \longrightarrow \rho(r)r^2/2$. This reproduces asymptotic diamagnetism in the susceptibility density. The susceptibility density is the integrand of the susceptibility integral. The functional $arcsinh[x]/x \longrightarrow r[\rho(r)]^{1/3}$ as the electron density becomes exponential at large distances. There are many functionals that could reproduce this behavior. The only one, which was found to be reasonably successful in reproducing both the susceptibility and the susceptibility density, was:

$$M^{(0)} = \frac{\rho(\tilde{r})^{1/3}}{4(3\pi^2)^{2/3}}[\frac{1 + Qxarcsinh[x]}{1 + x^2}]^2. \tag{4.32}$$

Q is a linear function of the number of electrons. Figures 4.1-4.4 show how well the modified functional reproduces the exact susceptibility density.

It must be pointed out that $M^{(0)}$ as represented by Equation 4.32 has a serious flaw. It can never give net paramagnetism because it is always positive. This is because the constraint of asymptotic diamagnetism was imposed without sufficiently flexibility. This restricted physical behavior is also true of the Thomas-Fermi $M^{(0)}$ and its first gradient correction. Hence, one must be satisfied with obtaining responses in the region of net diamagnetism.

These modified functionals have been used to calculate the magnetic susceptibilities and the chemical shielding of hydrogen, helium and the heavier noble gas atoms. Table 4.1 shows the atomic susceptibilities as given by the Thomas-Fermi approximation as well as the exact results. As the deviation between the exact results and the ones obtained by using the fit functional is 1% or less, the fitted results are not presented. Different Q's had to be used for the susceptibility and the shielding, Q_χ and Q_σ respectively. The Q_χ for hydrogen and helium is different from that for the heavier atoms and is given by 3.92 for hydrogen and 3.41 for helium. The Q_χ of the heavier atoms is fit to a functional of the form,$Q_\chi = .0067N + 4.26$, where N is the number of electrons. Q_σ for the three heavier atoms may also be fit to a linear function of N: $Q_\sigma = 0.0232N + 1.87$. For hydrogen and helium, the values of Q_σ are 1.79 and 1.65, respectively.

The modified functional corrects the shielding results from the Thomas-Fermi functional and the gradient corrected functional. As indicated above, the fitted shield-

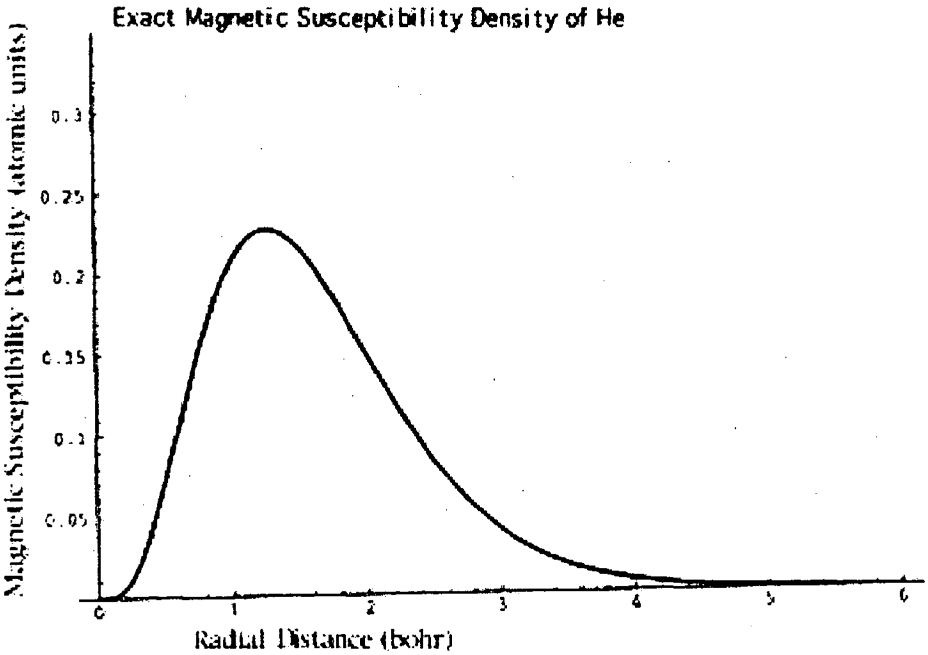

Figure 4.1: The exact magnetic susceptibility density of He is shown. The electron density is obtained from the wavefunctions in ref. 30.

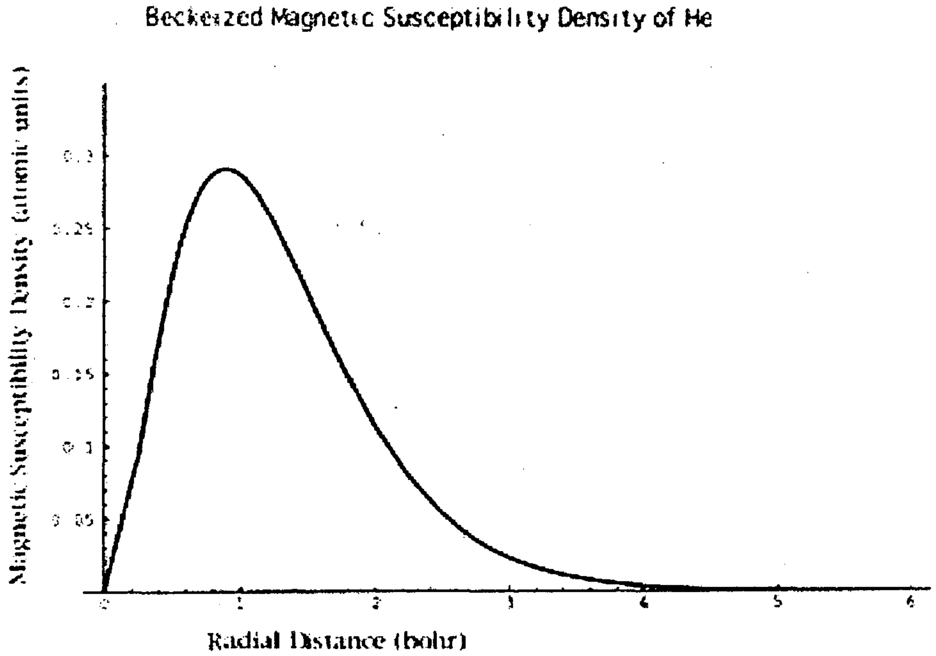

Figure 4.2: The magnetic susceptibility density of He obtained from the Beckeized functional is shown. The electron density is obtained from the wavefunctions in ref. 30.

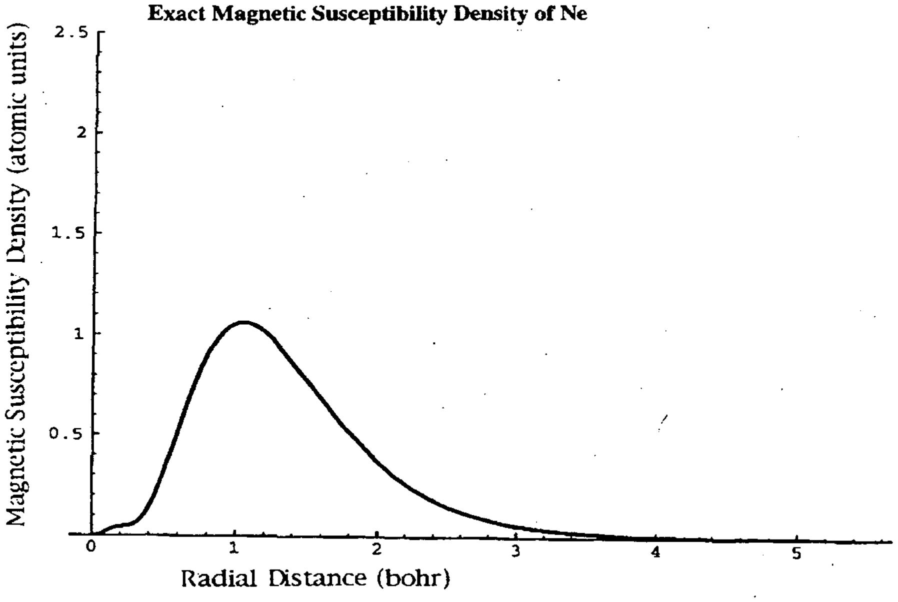

Figure 4.3: The exact magnetic susceptibility density of Ne is shown. The electron density is obtained from the wavefunctions in ref. 30.

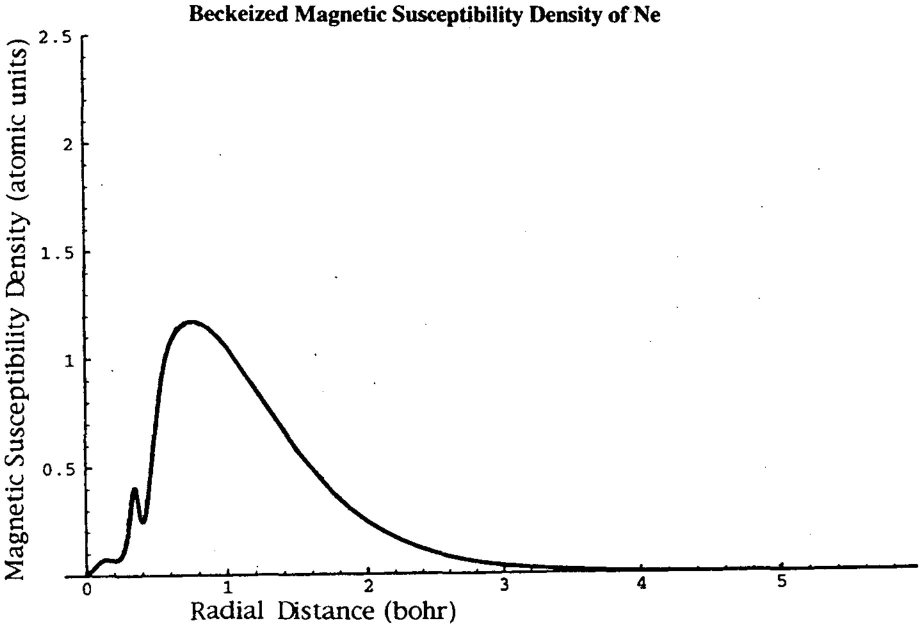

Figure 4.4: The magnetic susceptibility density of Ne obtained from the Beckeized functional is shown. The electron density is obtained from the wavefunctions in ref. 30.

ing functional requires different values of the parameter Q than does the susceptibility functional. The N dependence is much stronger for the shielding than for the susceptibility. This is because the functional does not correctly reproduce the short-range dependence of the shielding density. This problem requires a functional that reproduces diamagnetism close to the nucleus. Clearly the values of the parameter Q_σ which generate good values of the shielding for the atoms are those for which cancellation of error occurs.

4.5 Susceptibilities and Shieldings for H_2 and $(He)_2$

Calculations of susceptibilities and shieldings have also been performed for the hydrogen molecule in both the singlet and triplet states, and for the helium dimer. These calculations were carried out at a variety of internuclear distances. These calculations were carried out using Thomas-Fermi, gradient-corrected Thomas Fermi (for the shielding), and the modified $M^{(0)}$'s.

These results were calculated using Mathematica [31] with input densities from GAMESS. [32] The densities are constructed from finite superpositions of gaussians. Hence, the cusp condition at the nucleus is poorly satisfied. It is precisely the gradient at the origin that matters in the shielding calculations beyond Thomas-Fermi. The density at the origin is quite good. Instead of using the calculated radial derivative, the radial cusp condition is imposed, [33], [34]

$$\frac{d\rho(r)}{dr} = -2Z\rho(0). \tag{4.33}$$

$\rho(r)$ is the radial density; that is, the coefficient of the zeroth rank spherical harmonic in an expansion of the density in spherical harmonics. Direct calculation shows that the angular gradient contributes only a few tenths of a percent in all cases that have been considered.

Now consider these results in light of a few general considerations. The magnetic responses of the hydrogen singlet must be diamagnetic over the full range of internuclear distances. The reason is simply that a two-electron system in its ground state has no nodes. [15], [35] The triplet state of hydrogen and the He dimer do have nodes, hence, they may exhibit net paramagnetism in principle. Thus, these results are expected to be particularly poor when there is a region of internuclear distance near where net paramagnetism is obtained.

Consider first the He dimer. Van Wullen [36] has carried out a careful calculation of the chemical shielding. All three of the functionals give close agreement with Van Wullen's calculations near the united atom limit. At large internuclear distance, all of the functionals reach the separated atom limit; a limit that differs somewhat for each functional. The separated atom limit is so close for all three functionals because the Thomas-Fermi theory is rather accurate, as illustrated in Table 4.1. As

Table 4.2: Chemical Shielding of Helium Dimer (ppm)

Internuclear distance (Angs.) current chapter	Modified	T-F with gradients	V. W.	T-F	Internuclear distance (Angs.) Van Wullen
0.2	87.25	65.45	68.01	74.96	0.21
0.25	79.69	61.5	64.12	58.37	0.24
0.3	69.61	58.5	61.19	-15.24	0.29
0.35	66.81	56.28	59.04	-122.85	0.34
0.4	51.83	54.76	57.54	-119.94	0.40
0.45	63.91	53.8		-96.76	0.42
0.5	63.35	53.27	56.1	-53.06	0.48
0.55	63.04	52.98			-20.31
0.53					
0.6	62.65	52.83	55.68		
0.7	62.28	52.64	55.50	24.26	0.66
0.8	61.88	52.46	55.33	42.99	0.79
0.9	61.5	52.09	55.15	51.59	0.93
1	60.72	52.09	54.98	55.75	1.06
1.25	60.25	51.71	54.62	58.85	1.32
1.5	59.92	51.49	54.41	59.64	1.59
2	59.86	51.32		59.86	2.12
2.5	59.86	51.30		59.86	2.65
3	59.86	51.30	54.23	59.86	3.18
3.5	59.86	51.30	54.23		

expected, at intermediate distances, none of the shielding functionals exhibit net paramagnetism. The results are presented in Table 4.2 and Figure 4.5. The authors are not aware of any published calculation of the magnetic susceptibility of the helium dimer. Van Wullen [37], however, has commented that he expects the character of the susceptibility of the helium dimer to follow that of the shielding. Thus, in the intermediate region the calculations may be qualitatively incorrect.(see Table 4.3 and Figure 4.6).

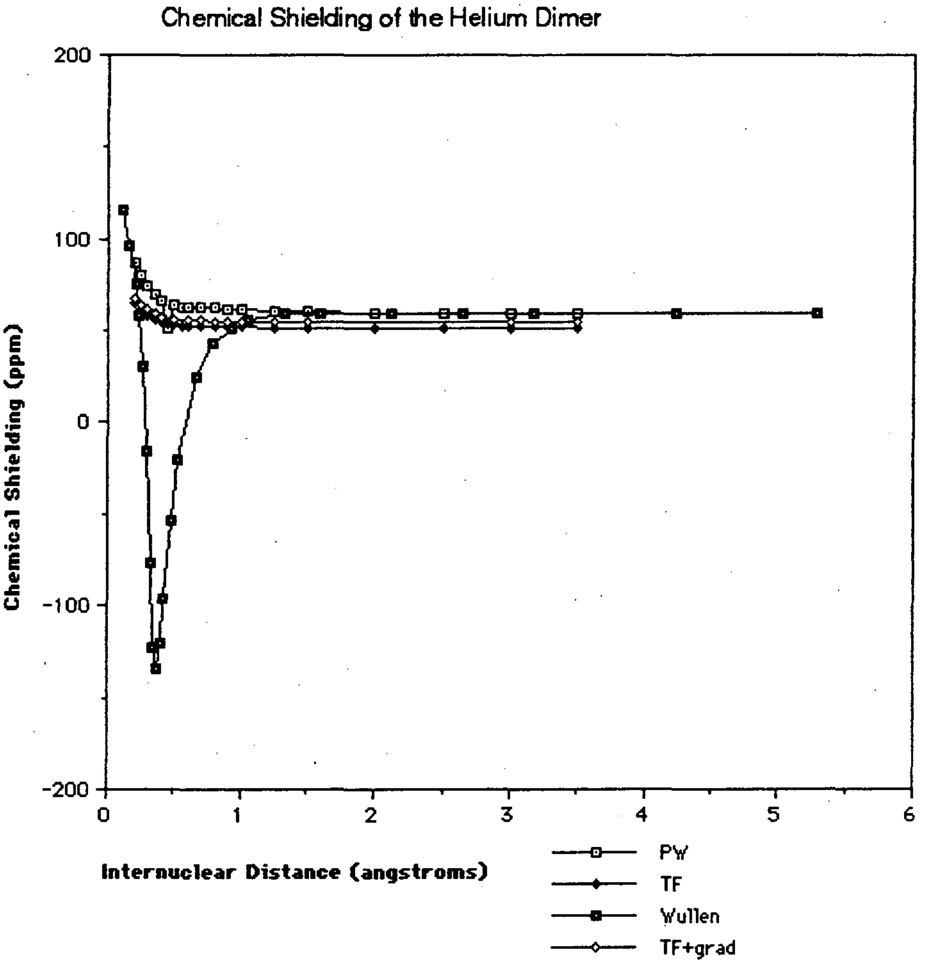

Figure 4.5: The results from the Beckized(PW) Thomas-Fermi (TF), and Gradient corrected Thomas-Fermi (TF + grad) functionals are presented along with the MC-SCF results of Van Wullen (ref. 36). The densities have been obtained from GAMESS using a 6-311* basis set.

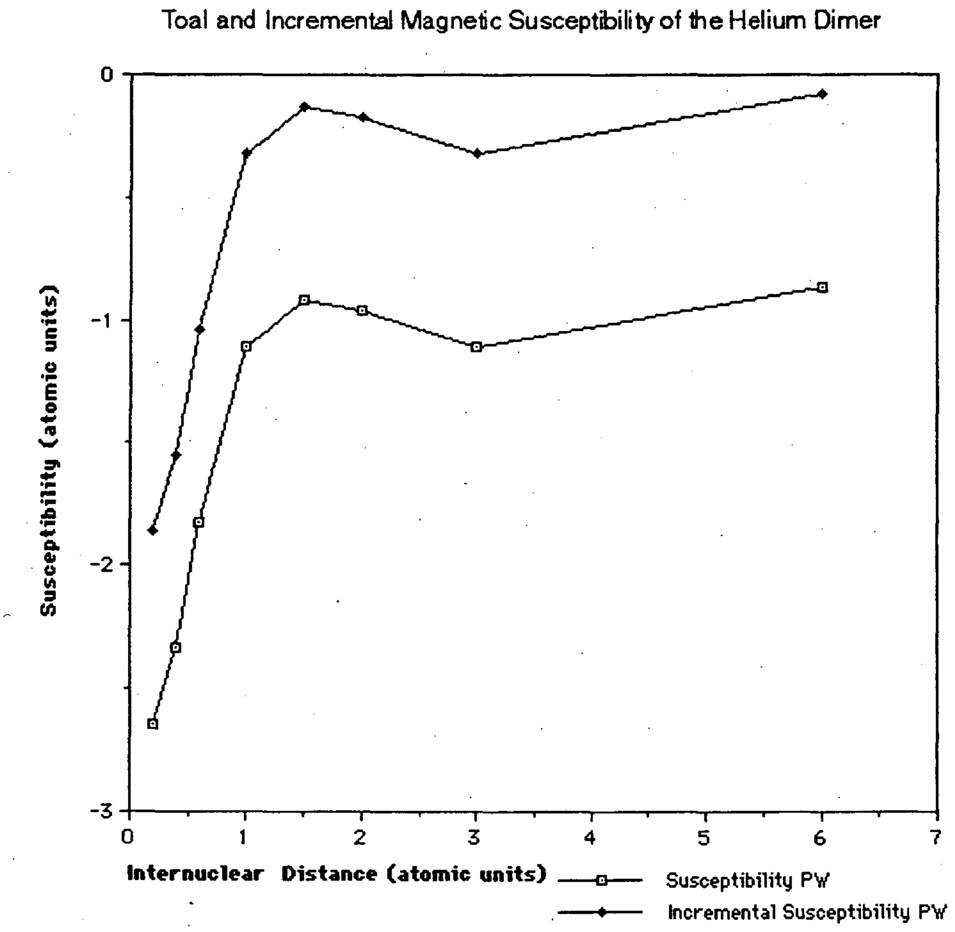

Figure 4.6: The magnetic susceptibility has been calculated using the Beckized functional referred to in the text. The densities have been obtained from GAMESS using a 6-311* basis set.

Table 4.3: Magnetic Susceptibility of Helium Dimer (atomic units)

Internuclear distance (Angs.)	Total	Incremental
0.2	-2.643	-1.855
0.4	-2.332	-1.544
0.6	-1.824	-1.036
1.0	-1.108	-0.320
1.5	-0.920	-0.132
2.0	-0.958	-0.170
3.0	-1.106	-0.318
6.0	-0.862	-0.074

Similar results to those of the helium dimer are found for the shielding of the hydrogen triplet (Table 4.4 and Figure 4.7), except that the agreement with the calculations of Grayce and Harris [2] is more qualitative.

One should note that the calculation of Grayce and Harris is an electron gas calculation and must be considered to be rather approximate especially as hydrogen molecule is far from an electron gas. This same accuracy is to be found in the calculations of Cina and Harris of the magnetic susceptibility of the hydrogen triplet. In this instance the results here differ qualitatively from those of Cina and Harris, as may be seen in Table 4.5 and Figure 4.8.

The calculations of the magnetic properties of the hydrogen singlet show closer agreement to literature values [38],[39] over the full range of interatomic distances. This agreement is exhibited in Tables 4.6-4.7 and Figures 4.9-4.11.

Table 4.4: Chemical Shielding of Hydrogen Triplet (ppm)

Internuclear distance (Angs.) Current Chapter	Beckeized	TF	TF +grad	G & H	Internuclear distance (Angs.) G & H
0.2	30.9	21.31	21.7		
0.3	26.5	19.1	19.72		
0.4	23.6	17.8	18.2	32.6	0.375
0.5	21.5	16.5	17.1		
0.6	20.2	15.7	16.36		
0.7	19.38	15.29	15.91	9.186	0.70
0.75	19.14	15.26	15.78		
0.8	18.97	15.07	15.69	6.053	0.79
0.9	18.79	14.98	15.60		
1.0	18.71	14.94	15.57	3.425	1.0
1.5	18.39	14.80	15.43	6.85	1.39
2.0	18.02	14.64	15.28	13.54	1.78

Table 4.5: Incremental Magnetic Susceptibility of Hydrogen Triplet (atomic units)

Internuclear distance (Angs.)	Current Chapter	Cina & Harris
0.2	-1.09	
0.4	-0.95	0.788
0.6	-0.80	
0.8	-0.64	0.568
1.0	-0.46	
1.5	-0.07	
2.0	0.538	
3.2	0.468	
4.0	0.394	

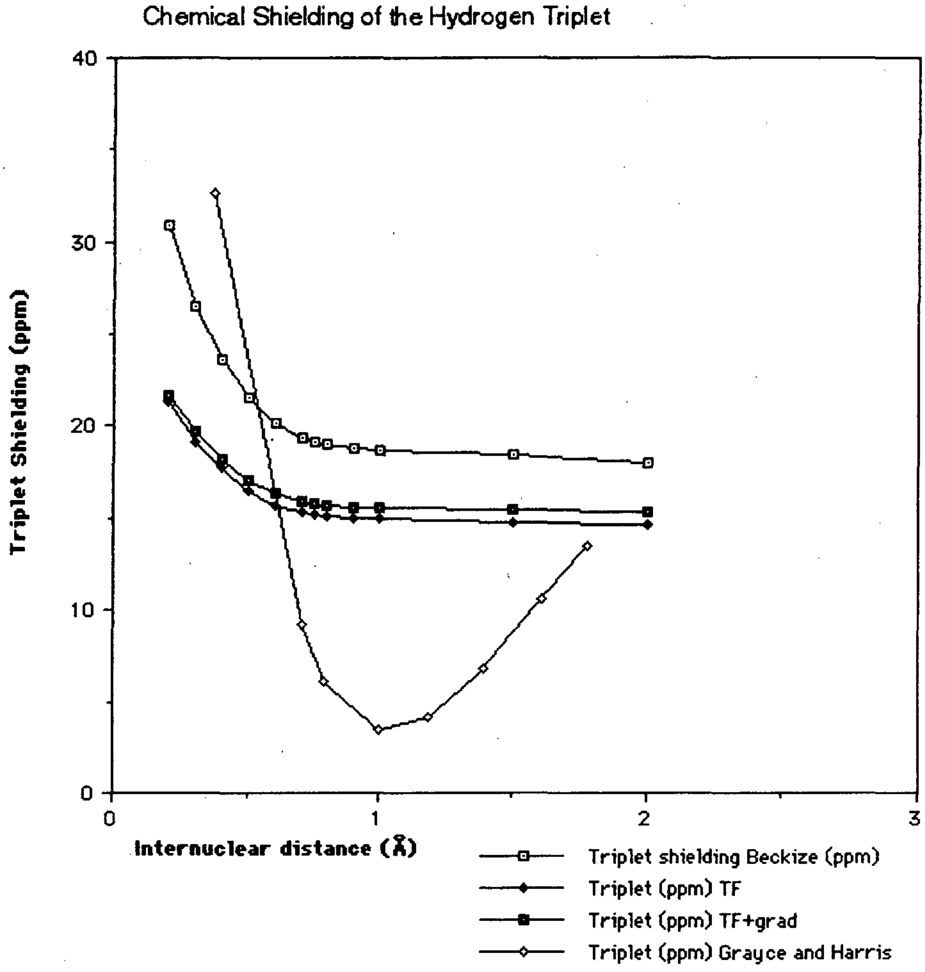

Figure 4.7: The shielding has been calculated using the Beckized, Thomas-Fermi (TF), and Gradient corrected Thomas-Fermi (TF + grad) functionals. The results of Grayce and Harris (ref. 2) are shown for comparison. The densities have been obtained from GAMESS using a 6-311* basis set.

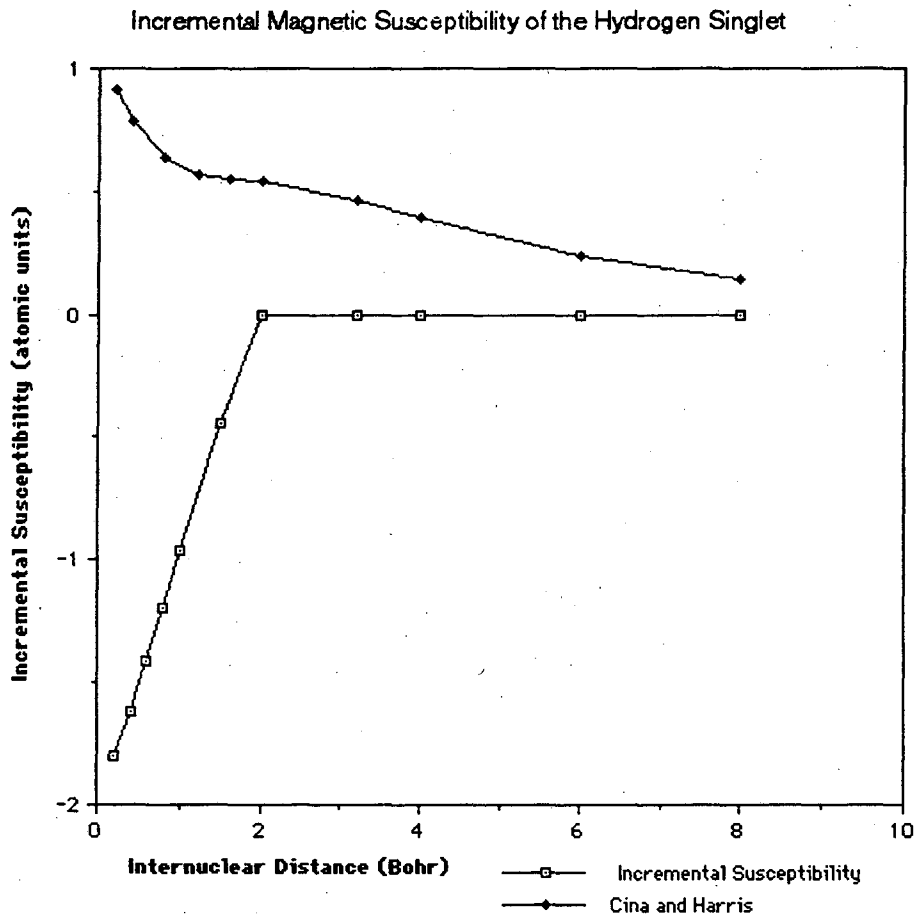

Figure 4.8: The susceptibility has been calculated using the Beckized functional by subtracting twice the atomic results from the total. The results of Cina and Harris are shown for comparison. (ref. 1) The densities have been obtained from GAMESS using a 6-311* basis set.

Table 4.6: Magnetic Susceptibility of Hydrogen Singlet (atomic units)

Internuclear distance (Angs.) Current Chapter	Cina & Harris	Internuclear distance (Angs.) Cina & Harris	
0.2	-0.543		
0.3	-0.593		
0.4	-0.655		
0.5	-0.723	-0.679	0.53
0.6	-0.795	-0.693	0.58
0.7	-0.867	-0.806	0.69
0.8	-0.941	-0.893	0.79
1.0	-0.990	-1.026	0.95

Table 4.7: Incremental Magnetic Susceptibility of Hydrogen Triplet (atomic units)

Internuclear distance (Angs.)	Current Chapter	Cina & Harris
0.2	-1.09	
0.4	-0.95	0.788
0.6	-0.80	
0.8	-0.64	0.568
1.0	-0.46	
1.5	-0.07	
2.0	0.538	
3.2	0.468	
4.0	0.394	

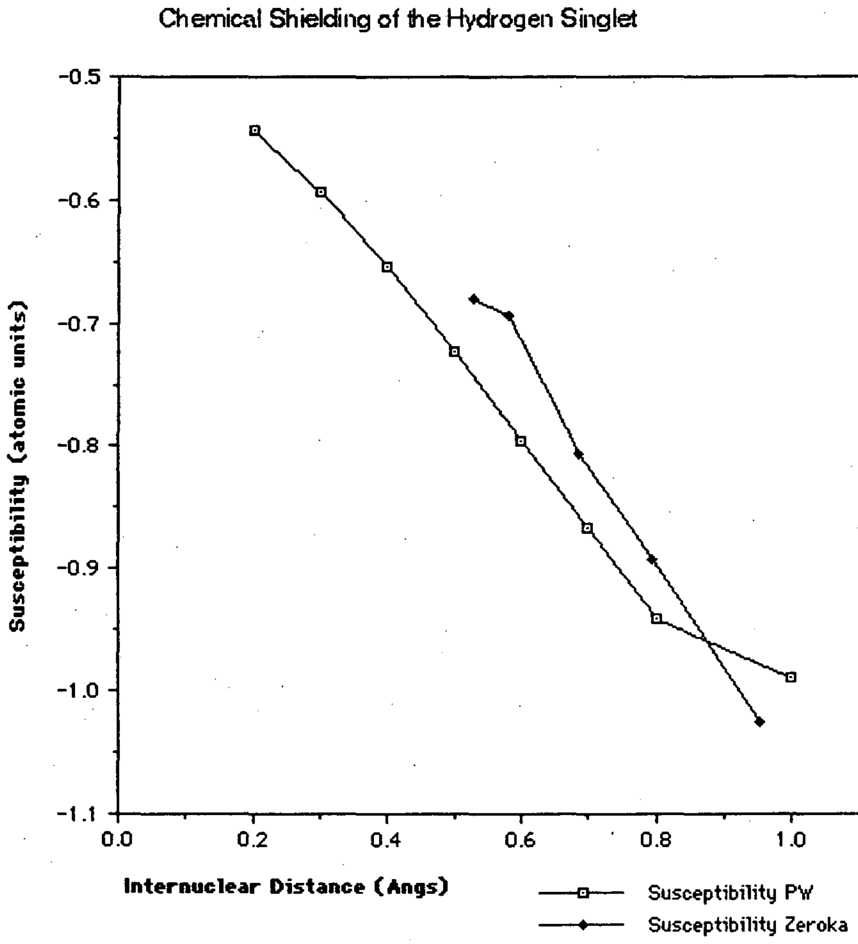

Figure 4.9: The magnetic susceptibility has been calculated using the Beckized functional referred to in the text. The densities have been obtained from GAMESS using a 6-311* basis set. The results of Zeroka (ref.38) are shown for comparison. The density has been obtained from GAMESS using a 6-311* basis set.

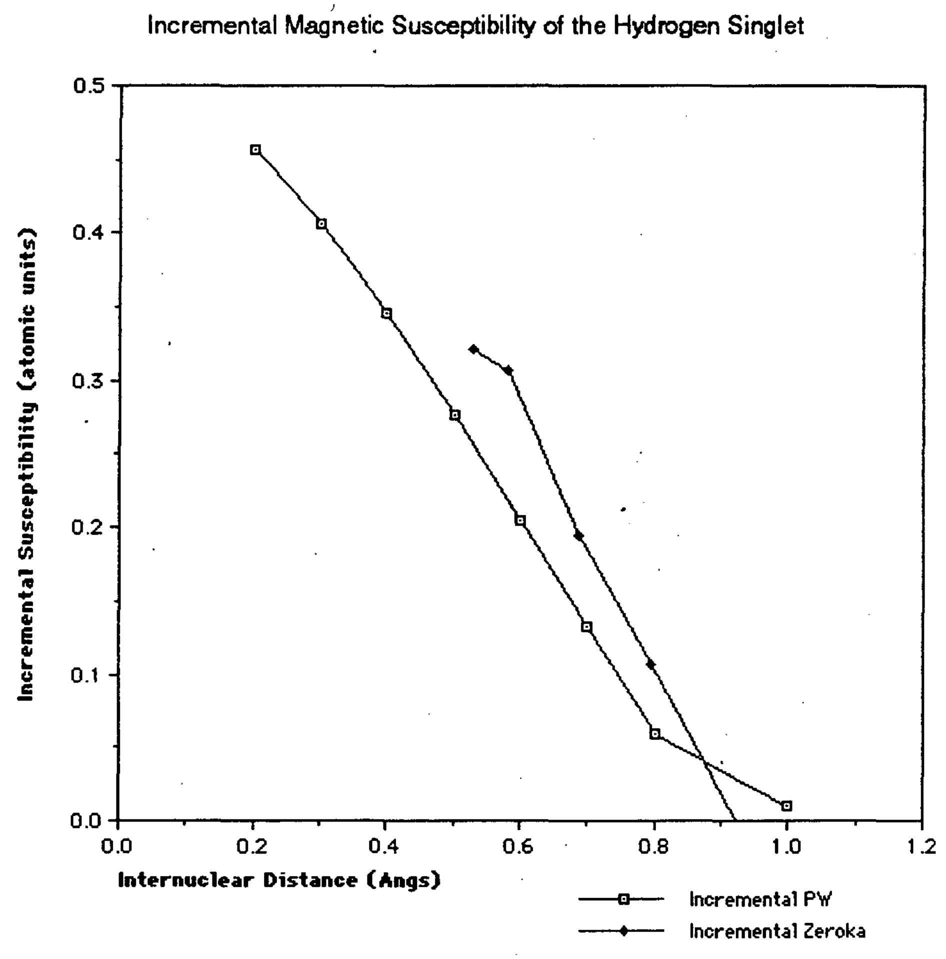

Figure 4.10: This is the susceptibility from Figure 4.7 minus twice the atomic result. Incremental results have been calculated using the Beckized functional by subtracting twice the atomic results from the total. The results of Zeroka (ref. 38) are shown for comparison. The densities have obtained from GAMESS using a 6-311* basis set.

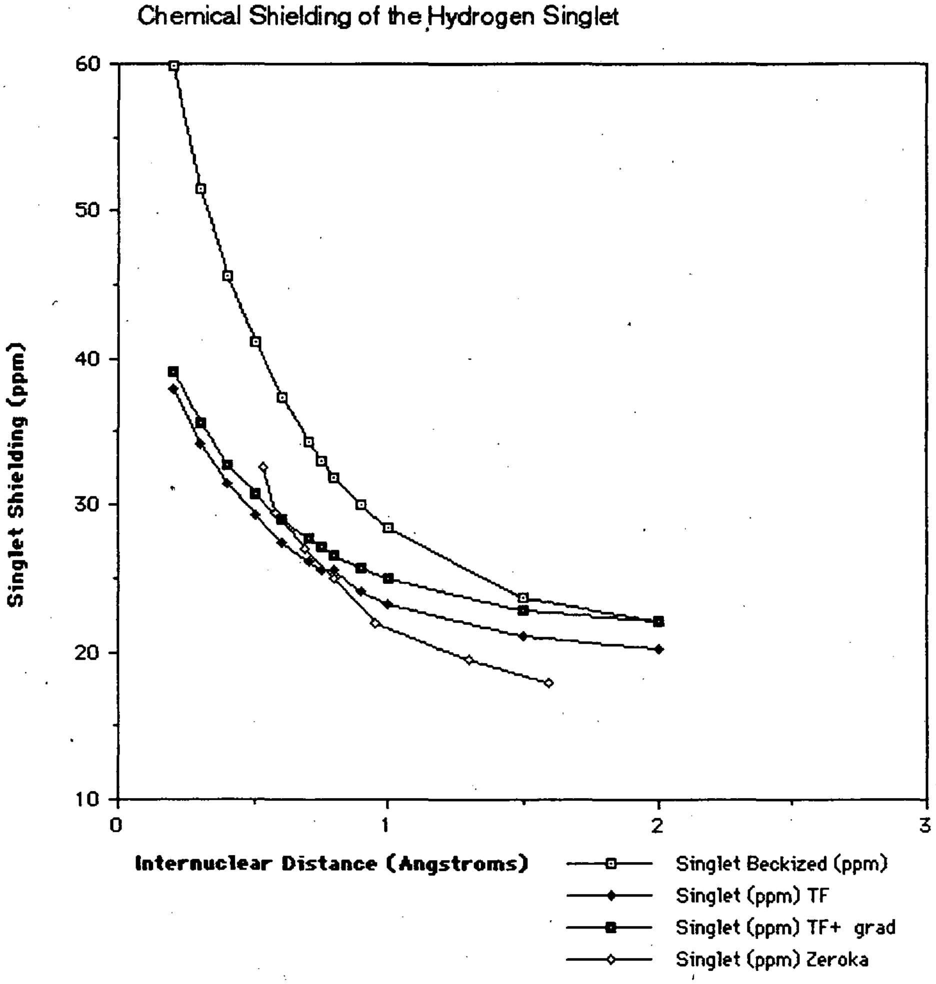

Figure 4.11: The shielding has been calculated using the Beckized, Thomas-Fermi (TF), and Gradient corrected Thomas-Fermi (TF + grad) functionals. The results of Zeroka (ref. 38) are shown for comparison. The densities have obtained from GAMESS using a 6-311* basis set.

4.6 Conclusions

The theory constructed in this chapter, is approximate at two levels. First, the explicit magnetic field-dependent corrections to the Kohn-Sham equations have been ignored. Their presence is expected and is explored in Chapter 7. The size of this error has not been investigated.

Secondly, the current density has been expanded in a gradient expansion in the unperturbed electron density. This expansion is transverse and gauge invariant. However, as discussed earlier in this chapter, this expansion has huge flaws. To reiterate: a finite sum of gradients can never give pure diamagnetism, the tensor character of the magnetic susceptibility does not appear, and the low order terms in the expansion only give diamagnetism, that is, negative magnetic susceptibilities and positive shieldings. And to top it off, for any exponentially decreasing electron density, each term in the magnetic susceptibility and chemical shielding diverges beyond the Thomas-Fermi approximation.

Thus, an approximate density functional theory of the magnetic susceptibility and chemical shielding has been constructed. The theory is based on the Biot-Savart integrals and a density functional expression for the ground state current density induced by a homogeneous magnetic field.

An attempt has been made to ameliorate at least some of the above problems. The calculations have been limited to the scalar responses. Two attempts have been made to deal with the divergences. The first, which holds only for the chemical shift, is to transform the divergences to infinite surface integrals that must sum to zero. Hence, the shielding is left as a power series in the density, its gradients, etc., at the nucleus whose shielding is being measured. The second way to correct the current, as well as to give diamagnetism asymptotically, is to modify the current functional using ideas developed by A. D. Becke. Both of the above methods are still incapable of giving net paramagnetism. In spite of the failings of the approximations, a single parameter modified functional, linear in the number of electrons, is shown to be capable of giving magnetic susceptibilities and chemical shieldings of the rare gas atoms to within 1% of the best calculated values.

The calculations on the two states of the hydrogen and the helium dimer show that qualitative accuracy can be obtained for hydrogen and helium chemical shifts when the system is not paramagnetic or near paramagnetic. The calculations of the magnetic susceptibility show that qualitatively accurate results can be obtained for at least one system that is always diamagnetic: ground state H_2. This reinforces the idea that this method in its present form will work best for molecules that are not paramagnetic or nearly so.

Some progress has been made in mitigating the titanic shortcomings of the theory presented in this chapter. Recapitulating 25 years of density functional theory history in order to obtain magnetic responses of chemical accuracy should not be necessary. [42] Indeed, the next chapter shows calculation of the hydrogen shieldings of a number of small molecules using this new theory. [40]

The current is a strongly nonlocal functional of the density. [41] The shielding and the susceptibility measure different aspects of this functional in physical space. It is remarkable that such simple, highly local functionals of the density give such good results in the regions of a priori applicability.

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Chapter 5

Hydrogen Chemical Shieldings

In this chapter, three approximations to the isotropic chemical shielding functional are used to calculate isotropic hydrogen chemical shieldings in small molecules. The approximations require, at most, the electron density and its angular derivative at the hydrogen nucleus. Results are compared to a variety of theoretical calculations and/or experiments. Deviations from these calculations are at worst off by 40%, and at best off by a few percent.

5.1 Introduction and Theory

Calculations of molecular chemical shieldings are becoming routine [1]. Methods used range from coupled Hartree-Fock calculations [2], through many-body theory, [3] [4] [5] ending up with density functional theories [6] [7] [8]. All of the calculations involve the determination of single particle and/or many particle wavefunctions.

Recently a new theory of the chemical shieldings was advanced [9]. The theory is based upon magnetic field density functional theory and is explicated is this thesis [10]. A result of this theory is that the chemical shielding is a universal functional of the ground state electron density. Hence, if one could find the functional, one could dispense with all of the above methods that involve calculations at the field-dependent level. In addition, one could, perhaps, develop methods for using the chemical shielding to obtain aspects of the electron density itself, as well as its familiar usage in determining molecular structure.

Previously, in what is a precursor to the present work, the chemical shielding tensor was calculated from an energy functional in a generalized Thomas-Fermi-Dirac approximation [11]. This functional is bilinear in the external magnetic field and the magnetic moment of the nucleus.

Because of the difficulty of constructing an energy functional that goes beyond the generalized Thomas-Fermi-Dirac approximation, the chemical shielding tensor was determined in Chapter 4 via the Biot-Savart integral [9]. This required obtaining the current density in a weak and uniform magnetic field. According to the general theory, from chapter 3, the current density itself is a universal functional of the ground state electron density, i.e.,

$$\tilde{J}(\tilde{r}) = \tilde{J}[\rho(\tilde{r})]. \tag{5.1}$$

Accordingly, a functional can be constructed which is linear in the external magnetic field, and more amenable to corrections beyond the Thomas-Fermi approximation [12]. For a stationary state the current density, $\tilde{J}(\tilde{r})$, is transverse. Hence, [13]

$$\tilde{J}(\tilde{r}) = \nabla \times \tilde{M}(\tilde{r}) \tag{5.2}$$

where $\tilde{M}(\tilde{r})$ is defined in the previous chapter.

The shielding tensor may be written in terms of the M tensors through use of the Biot-Savart integral. The nuclear spin is taken to be at the origin. Upon integration of the Biot-Savart integral by parts, an expression arrived at for the scalar component of the shielding tensor,

$$\sigma = 8\pi M^{(0)} + \int d\tilde{r} \nabla\nabla \frac{1}{r} : M^{(2)} + (surfaceterms). \tag{5.3}$$

In Chapter 4, M was constructed at three levels [9]. These three levels are truly an example of ontogeny recapitulates phylogeny in density functional theory [14]. The current density was expanded in gradients and higher derivatives of the electron density. Beyond the Thomas-Fermi level, e.g., the lowest-order contribution to the shielding, the surface terms each diverge. They,however, must sum to zero, so they may be ignored. This leads to a remarkable conclusion. To at least a rather high order, the isotropic chemical shielding is a function of the density, the gradient of the density, the curvature of the density, and so on, all localized at the position of the nuclear spin.

As the method of obtaining the gradient expansion is given in great detail in our previous chapter, only the results are repeated here. The lowest order contribution to the chemical shielding is the Thomas-Fermi approximation. The shielding is given by,

$$\sigma(TF) = \frac{2\pi(\rho(0))^{1/3}}{(3\pi^2)^{2/3}}. \tag{5.4}$$

The Thomas-Fermi isotropic chemical shielding plus its first gradient correction has the form,

$$\sigma(TF+G) = \frac{2\pi(\rho(0))^{1/3}}{(3\pi^2)^{2/3}}[1 + \frac{4\tilde{x}(0)^2}{27(3\pi^2)^{2/3}}] \tag{5.5}$$

where as usual,

$$\tilde{x} = \frac{\nabla\rho}{\rho^{4/3}} \tag{5.6}$$

is the dimensionless gradient and $\tilde{x}(0)$ indicated evaluation at the nucleus. We note that $\sigma > 0$ when the density does not vanish at the nucleus. Hence, the isotropic chemical shielding must be net diamagnetic in this instance. The third approximation to σ will also have this character. Paramagnetic contributions appear in the gradient expansion at higher order.

The third approximation is carried out by a process that is called "Beckeization." In the late 1980s, A. D. Becke intuitively corrected the Dirac exchange potential such that a number of physical conditions in bound systems were satisfied [15]. This began the leap of density functional theory into quantum chemistry. Here a form of Beckeization is performed.

Since a gradient expansion can never give pure diamagnetism, the current density is constrained to be asymptotically diamagnetic; a quality that is shared by all molecular systems. In addition, the current density is required to reduce to the Thomas-Fermi current density in the absence of gradients. Finally, a single parameter that is a linear function of the number of the electrons of the magnetic nucleus is introduced.

The Beckeized isotropic chemical shielding is written as,

$$\sigma(B) = \frac{2\pi(\rho(0))^{1/3}}{(3\pi^2)^{2/3}}\left[\frac{1 + Q|\tilde{x}(0)|arcsinh|\tilde{x}(0)|}{1 + \tilde{x}(0)^2}\right]^2 \tag{5.7}$$

Q is the single parameter defined in the previous chapter. σ depends upon two molecular parameters: the electron density and the angular gradient of the electron density at the nucleus. The absence of the radial gradient as an independent parameter is due to the exact cusp condition, namely [16],

$$\frac{\partial \rho(\tilde{r})}{\partial r} = -Z\rho(0) \tag{5.8}$$

The derivative is evaluated at the nucleus.

In this chapter, the isotropic hydrogen chemical shieldings for an assortment of small molecules are calculated using the three isotropic chemical shielding functionals. There is no free parameter in any of the functionals, as the hydrogen atom Q=1.79 is used. So the chemical shielding of the hydrogen atom is fit to its exact value. It is shown that one can obtain qualitative and sometimes quantitative agreement with the most sophisticated theories as well as with experiment, with the Beckeized shielding function. The theory's failures shall also be discussed.

5.2 Methods and Results

All three isotropic chemical shielding functionals require as input the electron density at the nucleus. Two of the shielding functions require the angular gradient of the density at the nucleus. That is all. The electron densities are calculated at the Hartree-Fock level using the GAMESS program [17]. As the exact cusp condition is rigorously enforced, the flaw in a finite gaussian representation of the density gradients at the origin is not an issue.

A simpler approximation to all three functions would be to neglect the small angular gradients and consider the functions as depending only on the electron density at the nucleus. An examination of the effect of the angular gradient shows that it actually contributes little to the gradient corrected Thomas-Fermi results. Neglecting the angular gradients changes these results by between 0.04 and 0.62 ppm in all instances [18]. The angular gradients play a more substantial role in the Beckeized functional. The change upon neglecting them varies from 0.4 ppm to 2.8 ppm with the change usually around 1 ppm [18].

The results of the calculations, as well as other theoretical calculations and some experimental shieldings are presented in Table 5.1. When comparing experimental and theoretical results, one must keep in mind that the theoretical results are at the equilibrium position of the nucleus. The experimental results are averaged by nature. Of course, the theoretical results could easily be averaged.

The best functional overall in comparison with experiment is the Thomas-Fermi with gradient correction. The root mean square deviation is only 2.55%, this is only slight worse than the GIAO SCF method that has a root mean square deviation of 1.71%. The Thomas-Fermi method by itself has a root mean square deviation of 3.49%, and the Beckeized functional has a root mean square deviation of 4.83%. The root mean square deviation of the Beckeized functional so large because of its inadequate treatment of the hydrogen molecule, ethylene and benzene. If one omits these three molecules, the root mean square deviation of the Beckized functional is only 2.01%. Unlike GIAO SCF which always overestimates the isotropic chemical shielding, the methods presented here can either over- or underestimate the shieldings Thus, one cannot simply scale our results in order to obtain better correlation with experiment.

Table 5.1: Isotropic Hydrogen Chemical Shieldings of Small Molecules (ppm)
* Indicates the hydrogen for which the shielding was calculated. a Full Configuration Interaction (FCI) result from Ref. 19. b Ref 20. c Ref 9. d Exact Result e Ref 21 interpolated to R=Re. f Ref 22. g Ref 23 h Ref 24. i Ref 25. j Ref 26. k Ref 27. Coupled Cluster Singles Doubles (Triples) (CCSD(T)) results from Ref. 20. Moller-Plesset Fourth order Perturbation Theory (MP(4)) results from Ref. 4. Multi-Configurational Self Consistent Field (MCSCF) results from Ref. 28. Salahub's Sum Over States Density Functional Theory results are from Ref. 29. Gauge-Including Atomic Orbital (GIAO) SCF results from Ref. 30.

	CCSD(T)	MP(4)	MCSCF	Salahub	GIAO	TF	TF+grad	Beckeized	E
H				14.97	^{c}15.61		^{c}17.7	^{d}17.7	
H_2	^{a}26.68	26.67			^{b}26.49	26.10	27.69	34.36	^{e}26
H_2O	30.9	30.9		31.1	32.11	25.87	27.70	29.73	^{f}3
C_2H_2	30.62				30.99	25.87	27.41	31.96	^{g}2
CH_4	31.6	31.5	31.13	31.1	31.94	26.33	27.76	33.68	^{f}3
HF	29.2	29.1	29.26	30.3	30.31	25.30	28.89	29.06	^{f}2
H_2S			31.01	30.54		24.79	26.31	30.27	^{h}3
NH_3		31.6		31.1	32.67	26.30	28.02	31.34	^{i}3
C_2H_4					26.78	26.40	27.92	33.09	^{g}2
C_2H_6					31.50	26.13	27.93	31.96	^{g}2
CH_3^*OH					29.26	24.78	26.59	28.14	^{j}27
Benzene					24.81	26.49	27.95	33.64	^{k}2
HCN	29.0				29.93	25.66	27.45	31.20	^{i}27
HNC		^{b}29.29				25.41	27.09	30.09	

5.3 Conclusions

The failure to reproduce accurately the equilibrium shieldings of H_2 and the two sp^2 hybridized molecules appears to be a consequence of the localized nature of our present functionals, as well as their overemphasis on asymptotic diamagnetism. Indeed, the results of ethylene and benzene may be accurately reproduced with a single negative Q.

It is remarkable that such simple functions of the electron density and its gradient at the origin is able to give such a variety of hydrogen isotropic chemical shielding to within a few ppm of the results of very sophisticated calculations. It will be certainly necessary to build more sophisticated functionals, including the explicit role of correlation in the current density functional.

Finally, it is noteworthy that GIAO SCF and DFT methods are the only ones that currently are being applied to large biomolecules. As the method presented here should be readily applicable to arbitrarily large molecular systems, further developments in the theory are surely warranted.

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Chapter 6

A Nonlocal Current Density Functional

A nonlocal current density that is a gauge invariant functional of the electron density in the absence of the magnetic field is constructed. Unlike local functionals, which reduce to the Thomas-Fermi current density in the limit of zero gradients, the new functional treats diamagnetism exactly. Additionally, unlike earlier local functionals, the new functional has the capacity to support net paramagnetism. The full magnetic susceptibility and chemical shielding tensor density functionals are also derived.

6.1 Introduction

There has been a blossoming of density functional calculations of magnetic responses. Most of these calculations have been based on generalizations of the Kohn-Sham equations. Recent developments in exchange-correlation functionals have made these methods viable alternatives to those of conventional quantum chemistry. Indeed, density functional theory combines the promise of accurate results with cheaper computation. There is the added bonus that systems too large to be examined by conventional methods are now studied routinely. [1]

As was discussed in Chapter 3, there is a theoretical difficulty in using density functional theory to calculate magnetic responses. The original Hohenburg-Kohn theorem is valid only for a scalar potential. If the system is in the presence of a vector potential, then one needs a generalization of the Hohenburg-Kohn theorem. This generalization was first performed by Rajagopal and Callaway. They showed that one could include vector potentials in density functional theory, if one considered functionals of the current and electron densities. [2]. Rajagopal and Callaway's generalization was in the form of an existence theorem. It was left to Vignale and Rasolt to put what is now known as current density functional theory (CDFT) on firm footing. [3] Of particular importance, Vignale and Rasolt showed that by solving the Kohn-Sham equations, appropriately generalized exactly, then by definition, the exact current and electron densities would be obtained. For molecular systems, however, implementation of their theory has proven to be difficult. [4]

In $\tilde{B}$DFT, however, the energy functionals depend on the magnetic field and on the electron density. As the magnetic field is fixed by the physical problem, the functionals for a given magnetic field depend solely on the electron density. In particular, for the calculation of chemical shifts, and magnetic susceptibilities, one need only consider the magnetic field produced by a constant applied field and a single magnetic dipole.

A concomitant of $\tilde{B}$DFT is that the current density is a functional of the electron density. In the linear response regime, the current density functional depends on the zero field electron density. As a consequence, magnetic responses in the linear regime are functionals solely of the electron density in the absence of the magnetic field. At present, generalizations of Kohn-Sham density functional theory (KSDFT) are used to obtain magnetic responses. These methods use perturbation theory to obtain the responses. The magnetic responses are not obtained as functionals of the zero field density alone. As a result, magnetic responses should be simpler to calculate and interpret in $\tilde{B}$DFT than in ordinary KSDFT based methods.

Unlike in CDFT, the current density obtained from the Kohn-Sham equations is not exact. This is the equivalent of saying that the total energy obtained from the Kohn-Sham equations is not exact. The explicit exchange-correlation contributions to the current must be obtained via coupling constant integration. In this chapter, these corrections shall be ignored, but they will be considered in Chapter 7.

The first steps in constructing current density functionals within $\tilde{B}$DFT are discussed in Chapter 4. [6] The dependence of the current density upon the electron density was exploited to show that one could construct density functionals for the chemical shift and the magnetic susceptibility via the Biot-Savart law.

While the application of this method to the hydrogen chemical shieldings of some small molecules showed that qualitative accuracy could be obtained by calculations that were trivial, given a ground state electron density. [7] The local functionals do have deficiencies that need to be remedied. As such the development of a nonlocal current density functional would be useful as was discussed in Chapter 4. [6], [8] In this chapter, the first such functional is constructed and discussed.

6.2 Review of $\tilde{B}$DFT

A key point from Chapter 4 is that a finite gradient expansion does not allow for pure diamagnetism. The diamagnetic term has been canceled out prior to the expansion, and no finite sum of gradients can recover it. This gradient expansion obtains, after inversion, a $\tilde{\jmath}[\rho_0(\tilde{r})]$ of the form,

$$\tilde{\jmath}[\rho(\tilde{r})] = \tilde{B} \times \nabla \left[\frac{(\rho(\tilde{r})^{1/3})}{4(3\pi^2)^{2/3}} \left(1 + \frac{2(\nabla\rho(\tilde{r}))^2}{27(3\pi^2)^{2/3}\rho^{8/3}} \right) \right] + ... \tag{6.1}$$

To this order, $\tilde{\jmath}[\rho(\tilde{r})]$ may be written as,

$$\tilde{\jmath}[\rho(\tilde{r})] = \tilde{B} \times \nabla M^0. \tag{6.2}$$

This form of the current density has several consequences:

(1) To second order in derivatives the current density can never be net paramagnetic, i.e. the responses are always diamagnetic.

(2) At this level of truncation, the current density from Equation 6.1 does not allow for the appearance of all the tensor elements of χ and σ.

In addition, for finite systems, the gradient expansion of the current density diverges term by term after the first, or Thomas-Fermi, term. This divergence may be removed by considering a resummation of the gradient expansion subject to the condition of asymptotic diamagnetism. [6] This resummation is similar to the one which A.D Becke performed on the exchange energy density [12].

Even when M^0 is not local, a further consequence of the form of $\tilde{j}[\rho(\tilde{r})]$ from Equation 6.2 is that after integration by parts, one can rewrite the isotropic susceptibility and isotropic shielding as respectively,

$$\chi = -\int d\tilde{r} M^0 \tag{6.3}$$

$$\sigma = 8\pi M^0(\tilde{r}_i) \tag{6.4}$$

where r_i is the position of nucleus i. The local form of M^0 reduces calculation of σ to the evaluation of a local functional at the nuclear position. [7]

Equations 6.3 and 6.4 have the advantage of being particularly easy to use. Specifically, they were used in calculations of hydrogen chemical shieldings for some small molecules. [7] Extending this work to other elements, however, has proved problematic because of the necessity of including higher derivatives in the gradient expansion that diverge because of the nuclear radial cusp. As a result, a nonlocal current density functional may be useful in alleviating some of the less desirable aspects of the local current density functional.

6.3 Construction

In this section, a nonlocal current density functional is constructed. The functional which was used in our previous work is automatically gauge invariant, has the correct Thomas-Fermi limit, and is asymptotically diamagnetic. Here the starting point is the opposite limit. A current density that is automatically purely diamagnetic in the appropriate limits is constructed. Of course, the current density must be transverse, gauge invariant, support net paramagnetism and support tensor terms in the chemical shielding and the magnetic susceptibility. [13]

In constructing the current density, the Coulomb gauge shall be used, $\tilde{A}(\tilde{r}) = \frac{1}{2}(\tilde{B}\times\tilde{r})$. In this gauge, the current density of atoms is purely diamagnetic. In another gauge, there would be a paramagnetic contribution that would be exactly cancelled by an additional diamagnetic component. As the results are gauge invariant, a sensible approach is to pick the simplest gauge possible. [14]

As in the last section, the density matrix is constructed to first order in $\tilde{B}$. The first order contribution in $\tilde{B}$ to the density matrix must vanish when $[\tilde{L}, V(\tilde{r})] = 0$. The propagator is now used in a new way to realize this commutation relation. The assumption here is that the ground state electron density has the same symmetry as $V(\tilde{r})$.

To first order in $\tilde{B}$, the Hamiltonian is,

$$H_B = H - \tilde{L} \bullet \tilde{B} \tag{6.5}$$

which implies that the unitary operator,

$$U(t,0) \approx \exp(-iHt) + i \exp(-iHt) \int_0^t \tilde{L}(t') \bullet \tilde{B} dt' \tag{6.6}$$

where $\tilde{L}(t')$ is the interaction representation of the angular momentum operator. When $[L, H] = 0$, e.g. a locally free electron, then $L(t') = \tilde{L}$ and

$$U(t,0) = \exp(-iHt) + i \exp(-iHt) \tilde{L} \bullet \tilde{B} t \tag{6.7}$$

If one stopped here, there would have zero current density as the diamagnetic current would be canceled and nothing would remain. The important point is that this term does not contribute to the density matrix for bound systems, assuming that there is a gap between the ground state and the lowest excited state.

This term shall be ignored by looking at the equation of motion for $\tilde{L}(t')$. Namely,

$$i\frac{\partial}{\partial t'}L(t') = [L(t'), H]. \tag{6.8}$$

Integrating up, the following is obtained

$$L(t') = L(0) - i\int_0^{t'} dt''[L(t''), H]. \tag{6.9}$$

Ignoring the first term gives

$$L(t') = -i\int_0^{t'} dt''[L(t''), H]. \tag{6.10}$$

The latter, Equation 6.10, is the approximation that shall be used. Now

$$[\tilde{L}(t''), H] = \exp(iHt'')[\tilde{L}, H]\exp(-iHt'') \tag{6.11}$$

And critically, since,

$$[\tilde{L}, H] = [\tilde{L}, V] = \tilde{r} \times [\tilde{p}, V] \tag{6.12}$$

then,

$$L(\tilde{t}') = -i\int_0^{t'} \exp(iHt'')\tilde{r} \times [\tilde{p}, V]\exp(-iHt'')dt''. \tag{6.13}$$

After integrating once over time,

$$\begin{aligned} U(t,0) &= \exp(-iHt) + i\exp(-iHt) \\ &\times \int_0^t dt'(t-t')\exp(iHt')r \times [\tilde{p}, V]\exp(-iHt') \bullet \tilde{B}. \end{aligned} \tag{6.14}$$

Therefore in physical space,

$$\begin{aligned} <\tilde{r}|U(t,0)|\tilde{r}'> = <\tilde{r}t|\tilde{r}'0> &+ \int_0^t (t-\tau) \int <\tilde{r}t-\tau|\tilde{r}''> \\ &\times (\tilde{r}'' \times \nabla V(\tilde{r})) \bullet \tilde{B} <\tilde{r}''\tau|\tilde{r}'0> d\tilde{r}''. \end{aligned} \tag{6.15}$$

The resulting density matrix is,

$$\rho(\tilde{r},\tilde{r}') = \rho(\tilde{r},\tilde{r}')_0 + \int d\tilde{r}'' f(\tilde{r},\tilde{r}',\tilde{r}'')r'' \times \nabla V(\tilde{r}'') \bullet \tilde{B}, \tag{6.16}$$

with

$$f(\tilde{r},\tilde{r}',\tilde{r}'') \propto \frac{1}{2\pi i}\int \frac{dt}{t}\int_0^t d\tau(t-\tau) <\tilde{r}t-\tau|\tilde{r}''><\tilde{r}''\tau|\tilde{r}'0>. \tag{6.17}$$

When $V(\tilde{r}) = V(r)$, or some other suitable symmetry, then $\tilde{r} \times \nabla V = 0$. Thus, when the system is purely diamagnetic in an exact treatment, it is in this treatment as well.

In order to actually construct a nonlocal current density functional, approximations must be made to the propagators and then some nontrivial integrations performed.

The Makri-Miller approximation to the zero field propagator, Equations 4.18-4.21, shall be used as in Chapter 4 [6],

$$f(\tilde{r},\tilde{r}',\tilde{r}'') = i\left(\frac{1}{2\pi}\right)^4 \int \frac{dt}{t} \int_0^t d\tau (t-\tau)^{-1/2}(\tau)^{-3/2} \exp\left(\frac{i(\tilde{r}-\tilde{r}'')^2}{2(t-\tau)}\right) \times \exp\left(\frac{i(\tilde{r}''-\tilde{r}')^2}{2\tau}\right) \exp(iW^0(\tilde{r},\tilde{r}'',(t-\tau))) \exp(iW^0(\tilde{r}'',\tilde{r}',\tau)). \tag{6.18}$$

In lowest order the result is:

$$f(\tilde{r},\tilde{r}',\tilde{r}'') = i\left(\frac{1}{2\pi}\right)^4 \int \frac{dt}{t} \int_0^t d\tau (t-\tau)^{-1/2}(\tau)^{-3/2} \exp\left(\frac{i(\tilde{r}-\tilde{r}'')^2}{2(t-\tau)}\right) \times \exp\left(\frac{i(\tilde{r}''-\tilde{r}')^2}{2\tau}\right) \exp(iW_2^0(\tilde{r},\tilde{r}'')(t-\tau)) \exp(iW_2^0(\tilde{r}'',\tilde{r}')\tau). \tag{6.19}$$

Where, explicitly, [11]

$$W_2^0 = -\int_0^1 d\epsilon V(\bar{x}), \tag{6.20}$$

with

$$\bar{x} = (\tilde{r} + (\tilde{r}'' - \tilde{r})\epsilon). \tag{6.21}$$

Taking gradients and then the limit, both before integrating over time, gives,

$$
\begin{aligned}
&\frac{i}{2}\lim_{\tilde{r}'\to\tilde{r}}(\nabla-\nabla')f(\tilde{r},\tilde{r}',\tilde{r}'') = \\
&-\left(\frac{1}{2\pi}\right)^4\int_{-\infty}^{\infty}\frac{dt}{t}\int_0^t d\tau(t-\tau)^{-1/2}(\tau)^{-3/2}\exp\left(\frac{i(\tilde{r}-\tilde{r}'')^2}{2(t-\tau)}\right)\exp\left(\frac{i(\tilde{r}''-\tilde{r})^2}{2\tau}\right) \\
&\times\exp(iW_2^0(\tilde{r},\tilde{r}'')(t-\tau))\exp(iW_2^0(\tilde{r}'',\tilde{r})\tau) \\
&\times\left[\frac{i(\tilde{r}-\tilde{r}'')}{t-\tau}+i\nabla W_2^0(t-\tau)+\frac{i\ (\tilde{r}''-r)}{\tau}-i\nabla W_2^0\tau\right]. \qquad (6.22)
\end{aligned}
$$

Equation 6.22 yields the paramagnetic current density.

$$
\begin{aligned}
\tilde{j}_p(\tilde{r}) = &-\left(\frac{1}{2\pi}\right)^4\int d\tilde{r}''\int_{-\infty}^{\infty}\frac{dt}{t}\int_0^t d\tau(t-\tau)^{-1/2}\tau^{-3/2}\exp\left(\frac{i(\tilde{r}-\tilde{r}'')^2}{2(t-\tau)}\right) \\
&\times\exp\left(\frac{i(\tilde{r}''-\tilde{r})^2}{2\tau}\right)\exp(iW_2^0(t-\tau))\exp(iW_2^0\tau)[\frac{i(\tilde{r}-\tilde{r}'')}{t-\tau} \\
&+i\nabla W_2^0(t-\tau)+\frac{i(\tilde{r}''-r)}{\tau}-i\nabla W_2^0\tau]\times[r''\times\nabla V(\tilde{r}'')]\,d\tilde{r}''\bullet\tilde{B} \qquad (6.23)
\end{aligned}
$$

When the total current density is substituted into the Biot-Savart integrals, Equations 4.4 and 4.5, then the terms in the paramagnetic current, Equation (6.23), which involve $\tilde{r}$'s do not contribute to the magnetic responses. This is because, if the nuclear position is the origin, the result would be $(\tilde{r}\times\tilde{r})$. For completeness, the full current density functional shall be quoted in the Appendix, but for now the focus is on the quantity that manifests itself in the responses.

The integral, $f'(\tilde{r}, \tilde{r}, \tilde{r}'')$, the relevant portion of $f(\tilde{r}, \tilde{r}, \tilde{r}'')$ is,

$$f'(\tilde{r},\tilde{r},\tilde{r}'') = -\left(\frac{1}{2\pi}\right)^4 \int_{-\infty}^{\infty} \frac{dt}{t} \int_0^t d\tau (t-\tau)^{-1/2} (\tau)^{-3/2} \exp\left(\frac{i(\tilde{r}-\tilde{r}'')^2}{2(t-\tau)}\right)$$
$$\times \exp\left(\frac{i(\tilde{r}''-\tilde{r})^2}{2\tau}\right) \exp(iW_2^0(t-\tau)) \exp(iW_2^0\tau)$$
$$\times \left[i\nabla W_2^0(t-\tau) - i\nabla W_2^0\tau\right]. \tag{6.24}$$

The integrals are quite involved and the details are sketched out in the Appendix. [15] Here the resulting portion of the current density is just quoted,

$$\tilde{j}(\tilde{r})_p = -\left(\frac{1}{2\pi}\right)^3 \int d\tilde{r}''[\nabla''V(\tilde{r}) \times \tilde{r}''] \bullet \tilde{B}\nabla W_2^0 \left[\frac{\sqrt{2}\cos[2\sqrt{2}\sqrt{W_2^0}|\tilde{r}-\tilde{r}''|]}{\sqrt{W_2^0}|\tilde{r}-\tilde{r}''|}\right] \tag{6.25}$$

To make the symmetries and the dimensions abundantly clear, the relevant current density can be written as,

$$\tilde{j}(\tilde{r})_p = -\left(\frac{1}{2\pi}\right)^3 \int d\tilde{r}''[\nabla''V(\tilde{r}'') \times \tilde{r}''] \bullet \tilde{B}\nabla W_2^0 G[z], \tag{6.26}$$

in which

$$G[z] = \left[\frac{\sqrt{2}\cos[2\sqrt{2}z]}{z}\right], \tag{6.27}$$

with

$$z = \sqrt{W_2^0}|\tilde{r} - \tilde{r}''|. \tag{6.28}$$

G[z] is completely symmetric in $\tilde{r}$ and $\tilde{r}''$, and is dimensionless. Hence, all symmetries and dimensions are determined by the term which multiples G[z].

6.4 Discussion

When one uses the Biot-Savart integrals, Equations (4.4) and (4.5), the paramagnetic contributions to the magnetic susceptibility and chemical shielding are:

$$\chi^p_{\alpha\beta} = \frac{1}{2}\left(\frac{1}{2\pi}\right)^3 \int d\tilde{r} \int d\tilde{r}''[\nabla''V(\tilde{r}'') \times \tilde{r}'']_\alpha[\nabla W_2^0 \times \tilde{r}]_\beta G[z], \tag{6.29}$$

and

$$\sigma^p_{\alpha\beta} = -\left(\frac{1}{2\pi}\right)^3 \int d\tilde{r} \int d\tilde{r}''[\nabla''V(\tilde{r}'') \times \tilde{r}'']_\alpha \left[\nabla W_2^0 \times \frac{\tilde{r}}{r^3}\right]_\beta G[z], \tag{6.30}$$

respectively. The physical responses are,

$$\begin{aligned}\chi_{\alpha\beta} &= -\frac{1}{2}\left(\int d\tilde{r}(r^2\delta_{\alpha\beta} - r_\alpha r_\beta)\frac{\rho(\tilde{r})}{2}\right) \\ &+ \frac{1}{2}\left(\left(\frac{1}{2\pi}\right)^3 \int d\tilde{r}''[\nabla''V(\tilde{r}'') \times \tilde{r}'']_\alpha[\nabla W_2^0 \times \tilde{r}]_\beta G[z]\right) \qquad (6.31)\end{aligned}$$

$$\begin{aligned}\sigma_{\alpha\beta} &= \int d\tilde{r}((r^2\delta_{\alpha\beta} - r_\alpha r_\beta)\frac{\rho(\tilde{r})}{2r^3}) \\ &- \left(\frac{1}{2\pi}\right)^3 \int d\tilde{r}''[\nabla''V(\tilde{r}'') \times \tilde{r}'']_\alpha[\nabla W_2^0 \times \frac{\tilde{r}}{r^3}]_\beta G[z] \qquad (6.32)\end{aligned}$$

The χ tensor is a symmetric tensor. The σ tensor has both symmetric and anti-symmetric components. These are the correct forms. The symmetries can be seen by integrating Equations 6.31 and 6.32 by parts. After doing so,

$$\begin{aligned}\chi^p_{\alpha\beta} &\propto \int\int d\tilde{r}d\tilde{r}'V(\tilde{r})[([\tilde{r}' \times \nabla']_\alpha[\tilde{r} \times \nabla]_\beta W_2^0)\, G[z] \\ &+ [\tilde{r}' \times \nabla' W_2^0]_\alpha[\tilde{r} \times \nabla W_2^0]_\beta \frac{dG[z]}{dz}\frac{|r - r'|}{2(W_2^0)^{1/2}}] \qquad (6.33)\end{aligned}$$

$$\begin{aligned}\sigma^p_{\alpha\beta} &\propto \int\int d\tilde{r}d\tilde{r}'V(\tilde{r})[((\tilde{r}' \times \nabla')_\alpha \nabla \left(\left(\frac{1}{\tilde{r}}\right) \times \nabla\right)_\beta) W_2^0 G[z] \\ &+ (\tilde{r}' \times \nabla' W_2^0)_\alpha \left(\frac{1}{\tilde{r}} \times \nabla W_2^0\right)_\beta \frac{dG[z]}{dz}\frac{|r - r'|}{2(W_2^0)^{1/2}}]. \qquad (6.34)\end{aligned}$$

Hence, there is a nonlocal current density that generates the full tensorial aspects of the magnetic responses. Also, note that the sign in front of the paramagnetic component is the opposite of that in front of the diamagnetic term. Thus this nonlocal current may support net paramagnetism. By construction, the paramagnetic term also vanishes for symmetries which result in pure diamagnetism.

The expressions for the responses are not explicitly functionals of the density. This can be remedied and the expressions placed into a density functional form using the definition of G[z] from Equations 6.27 and 6.28, and with the Thomas-Fermi relation between $V(\tilde{r})$ and $\rho(\tilde{r})$ as,

$$V(\tilde{r}) = (3\pi^2\rho(\tilde{r}))^{\frac{2}{3}}. \tag{6.35}$$

Hence,

$$W_2^0 = \int_0^1 d\epsilon(3\pi^2\rho(\bar{x}))^{\frac{2}{3}}. \tag{6.36}$$

This implies that

$$\begin{aligned}\chi_{\alpha\beta} &= -\frac{1}{2}(\int d\tilde{r}(r^2\delta_{\alpha\beta} - r_\alpha r_\beta)\frac{\rho(\tilde{r})}{2} \\ &- \left(\frac{1}{2\pi}\right)^3 \int d\tilde{r} \int (d\tilde{r}''[\nabla''(3\pi^2\rho(\bar{r}''))^{\frac{2}{3}} \times \tilde{r}'']_\alpha \\ &\times \left[\nabla \int_0^1 d\epsilon(3\pi^2\rho(\bar{x}))^{\frac{2}{3}} \times \tilde{r}\right]_\beta G[z]))\end{aligned} \tag{6.37}$$

$$\begin{aligned}&\sigma_{\alpha\beta} = \int d\tilde{r}(r^2\delta_{\alpha\beta} - r_\alpha r_\beta)\frac{\rho(\tilde{r})}{2r^3} - \left(\frac{1}{2\pi}\right)^3 \int d\tilde{r} \int (d\tilde{r}''[\nabla''(3\pi^2\rho(\bar{r}''))^{\frac{2}{3}} \times \tilde{r}'']_\alpha \\ &\left[\nabla \int_0^1 d\epsilon(3\pi^2\rho(\bar{x}))^{\frac{2}{3}} \times \frac{\tilde{r}}{r^3}\right]_\beta G[z]).\end{aligned} \tag{6.38}$$

The use of the Thomas-Fermi relation changes z into a density functional,

$$z = \sqrt{\int_0^1 d\epsilon (3\pi^2 \rho(\bar{x}))^{\frac{2}{3}} |\tilde{r} - \tilde{r}''|}. \tag{6.39}$$

6.5 Conclusions

A current density functional that gives all the properties that a current density should has been constructed. The price is nonlocality. The functionals not only have different r's which must be integrated over, but also an integrated version of the electron density appears in the functional. All these nonlocal aspects may make practical implementation of this functional difficult. However, that these functionals use the zero field electron density to obtain magnetic responses could make usage of this functional profitable and interesting. Another advantageous property of this functional is that the treatment of pure diamagnetism is exact; it is the treatment of paramagnetism that is approximate. This places the calculation of the current density, the shielding and the susceptibility into a situation analogous to that of the energy in KSDFT. In KSDFT, one calculates the kinetic energy of a noninteracting system exactly, which obtains most of the energy of the system. The approximations lie in the treatment of correlation and exchange that are small energetically, but which change the most in chemical reactions. Here there is the capacity to treat the diamagnetic component exactly, and hence, calculate the larger component of the responses exactly. The approximation lies in the treatment of the paramagnetic component, the part that changes the most upon bonding.

Thus, while this functional may be difficult to implement, or to further approximate, it will be valuable to do so.

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[13] It is important to understand that allowing tensor terms and supporting net paramagnetism are seperate issues. One and two electron systems are diamagnetic, but may have tensor terms.

[14] Pure diamagnetism should be contrasted with the diamagnetism of one and two electron systems. In one and two electron systems, regardless of symmetry, $\tilde{j}_p(\tilde{r}) = \rho(\tilde{r})\nabla\phi(\tilde{r})$. Thus, one can perform a gauge transform such that $\tilde{j}_{d'}(\tilde{r}) = \rho(\tilde{r})[\tilde{A}(\tilde{r}) + \nabla\phi(\tilde{r})]$. Three or more electron systems must have a node in physical space and so the paramagnetic component cannot be gauge transformed away. See A.D. McLachlan and M.R. Baker, Mol. Phys. 4, 255 (161).

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6.6 Appendix

In this appendix, the solution of the integrals is sketched out and the full nonlocal paramagentic current reported.

From Equation 6.37, one can see that the integrals which must be solved are in the form of a convolution, in particular

$$\tilde{j}_p(\tilde{r}) = \int \frac{dt}{t} e^{(iW_2^0 t)} \int_0^t d\tau F_1(i(\tilde{r}-\tilde{r}''))F_1 + (i\nabla W_2^0)F_2) + F_3((i(\tilde{r}''-\tilde{r}))F_4 - i\nabla W_2^0 F_3) \tag*{(A1),}$$

where

$$F_1 = x^{-3/2} \exp\left(\frac{i(\tilde{r}-\tilde{r}'')^2}{2x}\right)$$

$$F_2 = x^{1/2} \exp\left(\frac{i(\tilde{r}-\tilde{r}'')^2}{2x}\right),$$

$$F_3 = x^{-1/2} \exp\left(\frac{i(\tilde{r}-\tilde{r}'')^2}{2x}\right),$$

$$F_4 = x^{-5/2} \exp\left(\frac{i(\tilde{r}-\tilde{r}'')^2}{2x}\right), \tag*{(A2)}$$

where $x = t$ or $x = t - \tau$.

By the convolution theorem we have,

$$L^{-1}[L(F_i)L(F_j)] = \int_0^t d\tau F_i * F_j \tag{A3}$$

where L denotes the Laplace transform, and L^{-1}, the inverse Laplace transform. The Laplace transforms and the inverse Laplace transforms can be found in the Bateman Manuscript Project [15]. This leaves only one time integral to perform. This can be readily done analytically via integral tables or a symbolic mathematics program. Performing these integrations leads to the portion of the current density which contributes to the magnetic responses, Equation 6.25, plus the following terms, $\tilde{j}_p^o(\tilde{r})$,

$$\tilde{j}_p^o(\tilde{r}) = -\left(\frac{1}{2\pi}\right)^3 \int d\tilde{r}'' \sqrt{2}\frac{(\tilde{r}''-\tilde{r})}{W_2^0}\left(\sin\left[4\sqrt{W_2^0}|\tilde{r}-\tilde{r}''|\right] + \frac{\cos\left[4\sqrt{W_2^0}|\tilde{r}-\tilde{r}''|\right]}{\sqrt{W_2^0}|\tilde{r}-\tilde{r}''|}\right). \tag{A4}$$

Equation (A4), can be written in a simpler form as:

$$\tilde{j}_p^o(\tilde{r}) = -\left(\frac{1}{2\pi}\right)^3 \tilde{r}\int d\tilde{r}''\left(1-\frac{\tilde{r}\bullet\tilde{r}''}{r^2}\right)F[\tilde{r},\tilde{r}''], \tag{A5}$$

with

$$F[\tilde{r},\tilde{r}''] = \left(\sin\left[4\sqrt{W_2^0}|\tilde{r}-\tilde{r}''|\right] + \frac{\cos\left[4\sqrt{W_2^0}|\tilde{r}-\tilde{r}''|\right]}{\sqrt{W_2^0}|\tilde{r}-\tilde{r}''|}\right)\frac{1}{W_2^0}. \tag{A6}$$

Chapter 7

The Exchange Energy Functional for a Uniform Magnetic Field

A density functional theory for the Kohn-Sham exchange energy of a bounded, closed shell system in a weak and uniform magnetic field is presented. The form obtained vanishes when the electron density is radial. Unlike the unscreened exchange energy of a locally uniform electron gas, it does not diverge due to the Coulomb interaction. The role of the exchange-correlation functional in the context of magnetic response theory is also examined.

7.1 Introduction

Kohn-Sham density functional theory is on center stage in quantum chemistry. The emergence of this development after decades of hovering at the edges has been due to remarkable progress in obtaining approximations to the exchange-correlation functional. These approximations reflect the localized nature of most molecular systems. [1]

In order to rigorously calculate magnetic responses, e.g., the parameters of NMR, it is necessary to examine how the exchange-correlation functional changes in the presence of weak magnetic fields. In particular, the exchange energy functional in a weak magnetic field shall be investigated in this chapter.

Using ordinary perturbation theory, the exchange energy never appears. This is because one starts with wavefunctions determined in the absence of the magnetic field. The perturbation then has two terms: one linear in the vector potential and one quadratic in the vector potential. The linear term requires one to carry out perturbation theory to first order in the field. This is the paramagnetic term. The quadratic term just requires the electron density without the field. This is the diamagnetic component. The magnetic responses are then obtained from the sum of the two terms via the Hellman-Feynman theorem. [2]. This is discussed in more detail in Chapter 1.

It is only with theories that begin with Hartree-Fock, or its correlation generalizations, that the exchange potential appears. [3], [4], [5] The reason is that these theories are nonlinear. If one starts with the field in the nonlinear part of the Hamiltonian then the appearance of the exchange potential with an explicit dependence on the vector potential is a necessity for gauge invariance.

In this chapter, the exchange energy, and in passing the exchange-correlation energy, shall be investigated in the context of Kohn-Sham theory and its corrections. The bound nature of the system is explicitly taken into account. It is also considered that such a system in general possesses symmetries that are not isotropic and homogeneous. It will be shown that writing the energy as the sum of Kohn-Sham orbitals plus a coupling constant integration is crucial for the analysis. This analysis is based upon gauge invariance and the properties of bound state systems.

The theoretical underpinning of this analysis is magnetic field density functional theory. [6] This theory indicates, through the variational theorem, that the energy in a weak magnetic field, such as those used in NMR/MRI experiments, is a functional of the ground state electron density obtained in the absence of the field. In this thesis, the Kohn-Sham approximation to the theory has been used to calculate the current in two limits: the locally uniform electron gas plus gradient corrections, and the fully bound state limit. [7],[8],[9] As will be seen, the method used in the latter case shall be exploited here.

The correlation energy of a uniform electron gas diverges order by order in perturbation theory. The sum, however, is convergent. The exchange energy does not diverge in the absence of an applied magnetic field. In the presence of a weak and uniform magnetic field, however, the long range of the coulomb interaction is manifested earlier: the exchange energy diverges and the divergence of the correlation remains when exchange and correlation are considered separately. The removal of the divergence involves the screening of exchange by the correlation. [10],[11],[12]

The divergences of the exchange energy in a locally uniform electron gas in a weak magnetic field was noted by Cina and Harris. [13] They were attempting to calculate molecular magnetic susceptibilities using density functional theory. They, however, did not screen the exchange; they ignored it. Grayce and Harris calculated the exchange energy functional in the bilinear presence of a constant magnetic field and that due to a nuclear spin. [14] By not treating the field due to the dipole as locally uniform, they were able to obtain a finite exchange energy functional for a bound electronic system. So it appears that obtaining a finite exchange energy without screening may require boundness.

In this chapter, two important conclusions are presented. First, it is proven that the Kohn-Sham exchange as well as the total exchange-correlation energy vanishes when the electron density is spherical. Although self evident for a bound system, this result is totally absent in the local electron gas approximation. Secondly, a general form for the exchange energy functional that explicitly manifests the above result, and has a natural cut-off is obtained. The latter renders the exchange energy finite. This cut-off is due to the quantum mechanics of a localized electronic system, not electron correlation. The simplest explicit exchange energy functional will also be derived and its properties discussed.

7.2 Theory

First, begin with density functional theory from the point of view of magnetic field density functional theory. [6] Recall from previous chapters, that this theory states that for each magnetic field the total energy is a universal functional of the density. By the usual arguments, the total energy in the presence of a magnetic field, B, may be written as,

$$E_B[\rho] = E_B^{KS}[\rho] + E_B^{XC}[\rho] \tag{7.1}$$

The term $E_B^{KS}[\rho]$ is from the sum of the Kohn-Sham orbital energies and $E_B^{XC}[\rho]$ is the exchange-correlation functional. This energy also contains the correlation correction to the kinetic energy. An explicit correlation correction to the kinetic energy may be avoided by carrying out a coupling constant integration over ground state wavefunctions which give the exact density. [1] That is, in second quantization, and in terms of the coupling-constant-dependent ground state wavefunction, $|\psi_B(\lambda)>$,

$$E_B^{XC}[\rho] = \frac{1}{2}\int_0^1 d\lambda < \psi_B(\lambda) \int d\tilde{r} \int d\tilde{r}' \sum_{\sigma,\sigma'} \psi_\sigma^+(\tilde{r})\psi_{\sigma'}^+(\tilde{r}')\frac{1}{|\tilde{r}-\tilde{r}'|}\psi_\sigma(\tilde{r}')\psi_{\sigma'}(\tilde{r})|\psi_B(\lambda) > \tag{7.2}$$

The densities depend upon the magnetic field, of course. The energy $E_B^{KS}[\rho]$ is the sum of the orbital energies, $\epsilon_i(\tilde{B},\rho)$, of the Kohn-Sham equation,

$$[-\frac{1}{2}(\nabla+\tilde{A})^2+\nu_{T,\tilde{B}}]\phi_i=\epsilon_i(\tilde{B},\rho)\phi_i \tag{7.3}$$

A change in the gauge, $\tilde{A}\longrightarrow\tilde{A}+\nabla\lambda$, manifests itself only in the kinetic energy, as the potential, $\nu_{T,\tilde{B}}$, depends upon B. This means that the coupling constant integral is gauge invariant.

Now consider weak magnetic fields and one of the central results of this paper. In the weak field limit, it has been shown that only the zero field electron density, ρ_0, appears in the energy. [6],[15] Thus, to second order in B, the energy may be written as,

$$\begin{aligned} E_{\tilde{B}}^{XC}(\rho_0) = \frac{1}{2}\int_0^1 d\lambda < \psi_{\tilde{B}}^{\lambda}(\rho_0)| \int d\tilde{r}\int d\tilde{r}'\sum_{\sigma,\sigma'}\psi_\sigma^+(\tilde{r})\psi_{\sigma'}^+(\tilde{r}')\frac{1}{|\tilde{r}-\tilde{r}'|} \\ \psi_\sigma(\tilde{r}')\psi_{\sigma'}(\tilde{r})|\psi_{\tilde{B}}^{\lambda}(\rho_0)> -\frac{1}{2}\int d\tilde{r}\int d\tilde{r}'\rho_0(\tilde{r})\frac{1}{|\tilde{r}-\tilde{r}'|}\rho_0(\tilde{r}'). \end{aligned} \tag{7.4}$$

The above results shall now be used assuming that the magnetic field is constant. The ground state energy may be written as,

$$E_B(\rho_0)=E_0(\rho_0)+2\tilde{B}\bullet\chi[\rho_0]\bullet\tilde{B} \tag{7.5}$$

Here, $\chi[\rho_0]$ is the magnetic susceptibility tensor. It is a universal functional of the magnetic field independent density. From the previous analysis,

$$\chi[\rho_0] = \chi^{KS}[\rho_0] + \chi^{XC}[\rho_0]. \tag{7.6}$$

Now to an important point in the analysis. Suppose the system is purely diamagnetic, such as a closed shell atom, or a cluster in a J=0 electronic ground state. It is clear that the Kohn-Sham contribution to the energy contains the exact diamagnetic energy. This is because the Kohn-Sham density is the exact density. This result is gauge invariant. A change in the gauge manifested in the diamagnetic term will be canceled by a change in the paramagnetic contribution to the Kohn Sham energy. In other words, the exchange-correlation energy contributes nothing here. It is also clear that if the system is in a state with vanishing angular momentum along certain symmetry axes, the exchange-correlation contribution also vanishes.

The situation is not unlike that which occurs for the current density. [9] Here, within Kohn-Sham, the current is exact when the system is diamagnetic. The paramagnetic portion is constructed to explicitly vanish when the system is purely diamagnetic. Indeed, the method of constructing the exchange functional is closely related to the construction of the Kohn-Sham current density.

The $\lambda = 0$ contribution to the exchange-correlation energy is called the KS exchange. It is constructed from the single particle density matrix made up of Kohn-Sham orbitals. It is a functional of the exact density. Here consider the density matrix in a constant B field and keep terms to $O(B^2)$. The exchange energy itself is given by,

$$E_B^X = -\int d\tilde{r} \int d\tilde{r}' \frac{|\rho_B(\tilde{r},\tilde{r}')|^2}{|\tilde{r}-\tilde{r}'|}, \tag{7.7}$$

where the density matrix is given by

$$\rho_B(\tilde{r},\tilde{r}') = \sum_i \eta(\epsilon_F - \epsilon_i)\phi_i(\tilde{r})\phi_i^*(\tilde{r}'). \tag{7.8}$$

The orbitals, $\phi_i(\tilde{r})$, and the energies, ϵ_i, are solutions of the Kohn-Sham equation,

$$[-\frac{1}{2}\nabla^2 - \tilde{I} \bullet \tilde{B} + \nu_e(\tilde{r}) + \int d\tilde{r}\frac{|\rho_0(\tilde{r})|}{|\tilde{r}-\tilde{r}'|} + \nu_{xcB}(\rho_0(\tilde{r})) + \frac{1}{4}(\tilde{r}\times\tilde{B})^2]\phi_i(\tilde{r}) = \epsilon_i\phi_i(\tilde{r}). \tag{7.9}$$

$\tilde{I}$ is the single electron angular momentum operator, $\nu_e(\tilde{r})$ is the external potential and $\nu_{xcB}(\rho_0(\tilde{r}))$ is the exchange-correlation potential.

Because the density in the absence of the magnetic field appears, the potential is the explicit magnetic-field-dependent exchange-correlation potential,

$$\frac{\delta E_B^{XC}}{\delta\rho(\tilde{r})} = \nu_{xcB}(\rho_0(\tilde{r})). \tag{7.10}$$

The derivative is evaluated at $\rho_0(\tilde{r})$.

Hence, to $O(B^2)$, the diamagnetic and explicit B dependent parts of the exchange-correlation manifest themselves in the ordinary exchange-correlation energy through a B^2 dependent density.

However, magnetic field density functional theory states that the only density that appears to lowest order in B is the ordinary, field independent, density. Hence, only the paramagnetic term is to be used when constructing the exchange and correlation energy. Note that a change of gauge does not affect the energy; it changes the density matrices by a phase.

Now the Kohn-Sham exchange is formally constructed such that it explicitly vanishes, if the system possesses the proper symmetries. As stated before, the method is the same as that used to construct a current density with the proper diamagnetic limit.[9] Begin by writing the density matrix in terms of the single electron propagator. That is,

$$\rho_B(\tilde{r},\tilde{r}') = \frac{1}{2\pi i}\int_c \frac{dt}{t} < \tilde{r}|e^{-iHt}|\tilde{r}' >, \tag{7.11}$$

where

$$H = -\frac{1}{2}\nabla^2 - \tilde{l} \bullet \tilde{B} + \nu(\tilde{r},\rho_0) - \epsilon_F. \tag{7.12}$$

Here $\nu(\tilde{r},\rho_0)$ is the total potential in the absence of the B field. Henceforth, ϵ_f is absorbed into the potential. The propagator is expanded to second order in the magnetic field. So that the density matrix retains its idempotency, the propagator is constrained to be unitary. Unitarity is preserved in exact time dependent perturbation theory, order by order. The unitary operator, e^{-iHt}, to second order, is

$$e^{-iHt} = (1 - i\tilde{B} \bullet \int_0^t \tilde{l}(t')dt' - \tilde{B} \int_0^t \tilde{l}(t')dt' \tilde{B} \bullet \int_0^{t'} \tilde{l}(t'')dt'' + ... \tag{7.13}$$

As in the derivation of the current density in Chapter 6, [9] $\tilde{l}(t)$ is replaced by a commutator,

$$\tilde{l}(t) \approx -i \int_0^t [\tilde{l}, H_0](t')dt'. \tag{7.14}$$

The commutator is given by,

$$[\tilde{l}, H_0] = -i\tilde{r} \times \nabla\nu. \tag{7.15}$$

Now substitute Equation (7.14) into Equation (7.15) and go into the position representation. The resulting propagator is,

$$\begin{aligned} < \tilde{r}|e^{-iHt}|\tilde{r}' > \;&=\; < \tilde{r}t|\tilde{r}'0 > -i \int_0^t d\tau(t-\tau) \int < rt-\tau|\tilde{r}''0 > \tilde{B} \bullet \tilde{r}'' \times \nabla\nu(\tilde{r}'')d\tilde{r}'' \\ &- \int_0^t dt'' \int_0^t dt' [\frac{(t-t')^2}{2} - \eta(t''-t')\frac{(t-t'')^2}{2}] \int d\tilde{r}''d\tilde{r}''' \\ &\quad < \tilde{r}t-t''|\tilde{r}''0 > \tilde{B}\tilde{r}''' \times \nabla\nu(\tilde{r}''') < \tilde{r}'''t'|\tilde{r}'0 > . \end{aligned} \tag{7.16}$$

$< \tilde{r}t|\tilde{r}0 >$ is the single electron propagator in the absence of the magnetic field. Thus, upon carrying out the time integration, the density matrix must have the form,

$$\rho_b(\tilde{r},\tilde{r}') = \rho_0(\tilde{r},\tilde{r}') - i\int d\tilde{r}'' f_1(\tilde{r}\tilde{r}'\tilde{r}'')\tilde{B} \bullet \tilde{r}'' \times \nabla\nu(\tilde{r}'')d\tilde{r} \tag{7.17}$$

$$-\int d\tilde{r}''d\tilde{r}'''\tilde{B} \bullet \tilde{r}'' \times \nabla\nu(\tilde{r}'')f_2(\tilde{r}\tilde{r}'\tilde{r}''\tilde{r}''')\tilde{B} \bullet \tilde{r}''' \times \nabla\nu(\tilde{r}'''). \tag{7.18}$$

Given the above, the exchange energy functional must have the form,

$$E_B^X = E_0^X + \int d\tilde{r}d\tilde{r}'\tilde{B} \bullet \tilde{r} \times \nabla\nu(\tilde{r})F(\tilde{r}\tilde{r}')\tilde{B} \bullet \tilde{r}' \times \nabla\nu(\tilde{r}'). \tag{7.19}$$

Here $F(\tilde{r}\tilde{r})$, a universal functional of the density, may be derived from particular forms of the propagator, or may be constructed phenomenologically.

From the form of the integral, some comments for the case of a neutral bounded electronic system may be made. The total potential, $\nu(\tilde{r})$, is a functional of the density. Thus, the long range behavior of $\nu(\tilde{r})$ is governed by the long range behavior of $\rho(\tilde{r})$ or some functional of $\rho(\tilde{r})$. The long range behavior of $\rho(\tilde{r})$ is exponential and radial. Thus, $\tilde{r} \times \nabla\nu(\tilde{r})$ vanishes beyond the distance where the radial behavior dominates. Hence, any divergence in the $\tilde{r}$ and $\tilde{r}'$ integrals is naturally cut-off at the distance where the density becomes radial. Of course, as shall be seen, this natural cut-off does not prevent the integrand from diverging in certain approximations. These divergences will not be due to the long range of the coulomb interaction. Thus, there is a natural convergence for the exchange energy functional that need not involve screening. The convergence is due to the nature of the bound states of finite electronic systems.

Now consider the locally uniform electron gas approximation, but in such a way that it preserves the structure given above. There is no free lunch. The density matrix that is constructed does not have vanishing diagonal elements to first order. Also, the integral diverges; not from the long range of the coulomb interaction, but from a variant of the divergence of the gradient expansions of the ordinary kinetic and exchange energy functionals. [16]

Suppose the presence of the exponential time dependence is ignored in Equation (7.13) Then with,

$$l(t) \approx -i\tilde{r} \times \nabla \nu t \tag{7.20}$$

and

$$e^{-iHt} = e^{-iH_0 t}[(1 - \tilde{B} \bullet \tilde{r} \times \nabla \nu)\frac{t^2}{2} - (\tilde{B} \bullet \tilde{r} \times \nabla \nu)^2 \frac{t^4}{8} + ...]. \tag{7.21}$$

In physical space, to lowest order in the gradients, in center of mass and relative coordinates, the propagator is,

$$\begin{aligned} < \tilde{R} + \frac{\tilde{x}}{2}|e^{-iHt}|\tilde{R} - \frac{\tilde{x}}{2} > &\approx \frac{1}{(2\pi i t)^{3/2}} e^{ix^2/2t} e^{-i\nu(\tilde{R})t}[(1 - \tilde{B} \bullet \tilde{R} \times \nabla \nu(\tilde{R}))\frac{t^2}{2} \\ &- (\tilde{B} \bullet \tilde{R} \times \nabla \nu(\tilde{R}))^2 \frac{t^4}{8}]. \end{aligned} \tag{7.22}$$

Rather than explicitly write out the density matrix, one may go straight to the exchange energy itself. Namely,

$$\begin{aligned} E_B^X &\approx \frac{1}{(2\pi i)^2}\int d\tilde{R}\int d\tilde{x}\int_c \frac{dt}{t}\frac{1}{(2\pi i t)^{3/2}}\int_c \frac{dt'}{t'}\frac{1}{(2\pi i t')^{3/2}} e^{ix^2/2t}e^{-i\nu(\tilde{R})t}e^{ix^2/2t'}e^{-i\nu(\tilde{R})t'}[1 \\ &+ \frac{t^2t'^2-t^4}{4}(\tilde{B}\bullet\tilde{R}\nabla\nu(\tilde{R}))^2]. \end{aligned} \tag{7.23}$$

Now the potential, $\nu(\tilde{R})$ will be scaled out. The first term is the Dirac expression for the field-independent exchange energy. The Dirac exchange plus the field-dependent part of the exchange energy is,

$$E_B^X = E_0^X + \alpha \int d\tilde{R}(\tilde{B}\bullet\tilde{R}\times\nabla\ln\nu(\tilde{R}))^2 \tag{7.24}$$

where α is a constant that has been omitted for the sake of clarity. Substituting the Thomas-Fermi relation between potential and density, the result is

$$E_B^X = E_0^X + \alpha \int d\tilde{R}(\tilde{B}\bullet\tilde{R}\times\nabla\ln\rho(\tilde{R}))^2, \tag{7.25}$$

β is another constant again omitted for the sake of clarity. It is immediately seen that the natural cut-off appears as $\nabla\ln\rho(\tilde{R}) \to \tilde{R}/R$ at large distances.

There is, however, a fly in the ointment: the constants diverge. This divergence is derived in the Appendix. As is shown there, the source of the divergence is not the long range of the coulomb interaction, but the time integrals. These ordinarily arise in propagator derivations of gradient expansions. Thus, the source of the divergence is from the gradients. A "conjoint" [17] expression for the B field exchange may exist which is of the form,

$$E_B^X = E_0^X + \alpha \int d\tilde{R}(\tilde{B} \bullet \tilde{R} \times \nabla \ln \rho(\tilde{R}))^2 G(x(\tilde{R})), \tag{7.26}$$

with the usual definition of,

$$x(\tilde{R}) = \frac{|\nabla \rho(\tilde{R})|}{\rho(\tilde{R})^{4/3}} \tag{7.27}$$

as a "bounding" function introduced by A. D. Becke. [1],[7],[8],[17] This function removes the divergence and has the correct asymptotic behavior while preserving the fundamental character of the energy functional.

7.3 Conclusions and a Conjecture

The coupling constant integrated exchange-correlation energy in a uniform magnetic field has been shown to vanish when the ground state density is spherical. It also vanishes when the field is parallel to certain symmetry axes as manifested in the density. Next the $\lambda = 0$, or Kohn-Sham exchange energy functional was examined. It was shown that an explicit functional could be obtained which satisfied the above criteria. Unlike the exchange energy of a locally uniform electron gas, the divergence that occurs can be cured without invoking electron correlation. it was also shown that the most general form of the exchange energy is, for the field-dependent part,

$$E_B^X - E_0^X = \int d\tilde{r}\tilde{r}'\tilde{B} \bullet \tilde{r} \times \nabla\nu(\tilde{r})F[\tilde{r}\tilde{r}'\rho]\tilde{B} \bullet \tilde{r}' \times \nabla\nu(\tilde{r}'). \tag{7.28}$$

It is worth a conjecture that the full exchange-correlation energy has the same form.

7.4 Appendix

The divergence from the space integrals of Equations (7.21) and (7.22) is demonstrated.

The exchange energy density is the sum of three terms,

$$E_X = E_X^0 + E_X^1 + E_X^2. \tag{7.29}$$

The first term is the exchange energy density in the absence of the magnetic field. Defining,

$$g(x,t) = \frac{1}{(2\pi it)^{3/2}} e^{ix^2/2t} e^{iVt}, \tag{7.30}$$

Then the terms are explicitly

$$E_X^0 = \int dx \int \frac{dt}{2\pi i t} \frac{dt'}{2\pi i t'} g(x,t) g^*(x',t'), \tag{7.31}$$

$$E_X^1 = \int dx \int \frac{dt}{2\pi i t} \frac{dt'}{2\pi i t'} t^2 t'^2 g(x,t) g^*(x',t'), \tag{7.32}$$

$$E_X^2 = \int dx \int \frac{dt}{2\pi i t} \frac{dt'}{2\pi i t'} t^4 g(x,t) g*(x',t'). \tag{7.33}$$

After performing the time integrations, one obtains the following, [18]

$$E_X^0 = \int dx (\frac{\sqrt(2V)}{2\pi i x})^3 (J_{3/2}[\sqrt(2V)x])^2, \tag{7.34}$$

$$E^1 \propto (\frac{1}{2\pi})^4 \int dx (\frac{2\pi i x}{\sqrt(2V)} (J_{-12}[\sqrt(2V)x])^2, \tag{7.35}$$

$$E^2 \propto (\frac{1}{2\pi})^4 \int dx (\frac{2\pi i x}{\sqrt(2V)} (J_{3/2}[\sqrt(2V)x])(J_{-5/2}[\sqrt(2V)x]) \tag{7.36}$$

$J_{\frac{2n+1}{2}}$ are spherical Bessel functions.

Upon scaling out the potential, V, and performing the final integration, the first term remains finite and proportional to $V(x)^2$, which is correct for the Dirac exchange. The remaining integrals, however, diverge both separately and when summed. The source of the divergence is the behavior of the Bessel functions of negative order near x=0. Hence, the exchange energy still diverges, but this divergence is of the kind typically found in gradient expansions. [16]

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Chapter 8

Estimation of Intermolecular Xenon J Couplings

8.1 Introduction

In Nuclear Magnetic Resonance (NMR), improving sensitivity is a major concern of researchers. The use of optically pumped noble gases is one means of obtaining signal enhancement in order to observe signals that ordinarily would be too small to measure [1]. Optical pumping produces a very large, nonthermal, nuclear spin polarization. This large spin polarization is equivalent to having a very low spin temperature. Optically pumped xenon, in particular, may be used as a spin probe. Signals can be observed signals that previously were too small to observe, either through direct observation of the xenon, or by transferring the nuclear polarization to other spins. [2].

One of the more useful NMR parameters in obtaining structures is the J or indirect spin-spin, coupling. The J coupling is a second rank tensor. The Fermi contact contribution, however, usually dominates and is a scalar. Hence, only this scalar term shall be estimated. These J couplings are widely used to determine connectivity in directly bonded systems [3]. The small size of J couplings between systems that are not chemically bound such as Van der Waals complexes have rendered intermolecular J couplings unobservable until now, and hence, uninteresting. More recent experiments, however, using laser polarized xenon have lead us to consider indirect spin-spin, or J, couplings of xenon in Van der Waals clusters. These small couplings may be observable in the near future using laser polarized.

As the J coupling is linear in each nuclear spin, a large enhancement of the nuclear spin polarization could allow for observations of very small J couplings. These large enhancements could be obtained via optical pumping of the nuclear spins of xenon or helium. The xenon-hydrogen and xenon-xenon J couplings that are calculated in this chapter are on the order of mHz-μHz in regions of physical interest. More conventional techniques allow for the trivial observation of J couplings on the order of a few Hz. Due to the factors of 10,000 or more enhancement in the xenon spin polarization that may potentially be obtained with optical pumping, the small xenon J couplings which one would expect in Van der Waals complexes may be experimentally observable.

This potential for the observation of small Xe-H J couplings is exciting as xenon often binds biomolecules via Van der Waals interactions. Observing J couplings could provide more structural information than measuring the chemical shift as there are potentially multiple Xe-H J couplings present in a biomolecule. In addition, the possibility of observing Xe-Xe J couplings in cavities provides an impetus for their calculation. [4], [5]

In this chapter, the Fermi contact contribution to the J coupling of Xe-H and Xe-Xe is estimated using a variant of density functional theory. The Xe-Xe coupling may be between Xe_{129} and Xe_{131} or between xenon atoms of the same isotope in chemically different environments.

8.2 Previous Theoretical Frameworks

The J coupling tensor has been studied previously in both wavefunction and density functional frameworks [3]. The work presented in this paper is based upon Magnetic Field Density Functional theory [6].

Grayce and Harris showed that a consequence of magnetic density functional theory is that the energy to second order in field strength may be written as

$$E_2 = \int \tilde{B}(\tilde{r}) \bullet F(\rho_0, \tilde{r}, \tilde{r}') \bullet \tilde{B}(\tilde{r}') d^3r d^3r,' \tag{8.1}$$

where the functional, $F(\rho_0, \tilde{r}, \tilde{r}')$, is a universal functional of the unperturbed electron density, ρ_0. The magnetic field due to the nuclear spins A and B is,

$$\tilde{B}(\tilde{r}) = \Sigma_{\alpha=A,B}\frac{4\pi}{3}\delta^3(\tilde{r} - \tilde{R}_a)\tilde{\mu}_\alpha \tag{8.2}$$

in which $\tilde{\mu}_\alpha$ is the magnetic moment of the α spin, and $\tilde{R}_\alpha$ is the position of the α spin.

$$J_{ab} = \frac{8\pi}{3}Tr[F(\rho_0, \tilde{R}_a, \tilde{R}_b)] \tag{8.3}$$

Grayce and Harris also showed that one could obtain the Fermi contact contributions to the J coupling without knowing $F[\tilde{r}, \tilde{r}', \rho_0]$, by using spin density functional theory [8]. The resulting equation required one to obtain the electronic spin polarization, $\chi(\tilde{r})$, from a density functional generalization of the Dalgarno-Schwartz equation for the hyperfine coupling in one-electron atoms.

Both the above methods are unnecessarily complex for the estimate, as the interest is in weakly bound electronic systems. The method used here is referred to as an electron gas theory, e.g., a Gordon-Kim theory as applied to responses. This theory uses the sum of the atomic electron densities in the presence of the external fields, that is, the additive density approximation [9]. For the Fermi contact coupling constant, like earlier theories of electrical responses, only the usual forms of spin density functionals are needed. [10] That is, there is no need to know $F[\rho_0, \tilde{R}_\alpha, \tilde{R}_\beta]$ explicitly.

8.3 Present Theoretical Framework

Given the weakly bound nature of the complexes, it is a reasonable to consider only two atoms as a prototype for the entire complex. Atom A is at the origin and atom B is at R. Two situations shall be considered. In the first instance, the atom at R has only one electron, e.g., a hydrogen atom, and the atom at the origin is a closed shell system, e.g., xenon. In the second case, both atoms are electronically identical closed shell atoms, for example, a pair of xenon atoms. In zeroth order, the total electron density of the closed shell atoms is twice that of its spin up component. Thus, only the change of the spin up component need be considered in both scenarios.

$$\rho_\uparrow(\tilde{r}) = \rho^B_{0\uparrow}(\tilde{r} - \tilde{R}) + \rho^A_{0\uparrow}(\tilde{r}) + \Delta_\uparrow(\tilde{r}) \tag{8.4}$$

The first term is the spin up density of atom B, the second the spin up density of atom M, and $\Delta_\uparrow(\tilde{r})$ is the spin up density change induced by the Fermi contact perturbation to the ground state. The Fermi contact perturbation due to both nuclear spins. $\Delta_\uparrow(\tilde{r})$ is included within the additive density approximation upon which Gordon-Kim theory is based as,

$$\Delta_\uparrow(\tilde{r}) = \frac{m_e}{m_p}\mu_B^2\frac{8\pi}{3}[g_a I_a \delta^\uparrow_A(\tilde{r}) + g_b I_b \delta^\uparrow_B(\tilde{r} - \tilde{R})], \tag{8.5}$$

where $g_i I_i$ is the gyromagnetic ratio for nucleus i times the spin for nucleus i, $\delta^\uparrow_i$ is the dimensionless perturbation of the density via the Fermi contact interaction, m_e is the mass of the electron, m_p the mass of the proton, and μ_B is the nuclear bohr magneton. Details of the calculation of $\delta_i^\uparrow$ are deferred to the next section. A similar expression exists for spin down,

$$\Delta_\downarrow(\tilde{r}) = \frac{m_e}{m_p}\mu_B^2\frac{8\pi}{3}[g_a I_a \delta_A^\downarrow(\tilde{r}) + g_b I_b \delta_B^\downarrow(\tilde{r} - \tilde{R})] \tag{8.6}$$

For the Xe-H interaction, the hydrogen atom at $\tilde{R}$ is chosen to have a spin up electron. The electron could have been picked to be spin down without changing the results. Hence, only need the deviation of the spin up electron density is needed,

$$\rho_\uparrow(\tilde{r}) = \rho_{0\uparrow}^{H}(\tilde{r} - \tilde{R}) + \rho_{0\uparrow}^{Xe}(\tilde{r}) + \Delta_\uparrow(\tilde{r}) \tag{8.7}$$

According to spin density functional theory, the relevant portion of the energy may be written as

$$\begin{aligned} E = E_{kinetic}[\rho_\uparrow] + E_{kinetic}[\rho_\downarrow] + E_{exchange}[\rho_\uparrow] + E_{exchange}[\rho_\downarrow] + E_{correlation}[\rho_\downarrow, \rho_\uparrow] \\ + \frac{m_e}{m_p}\frac{8\pi}{6}\mu_B^2[g_A I_A(\rho_\uparrow(0) - \rho_\downarrow(0)) + g_B I_B(\rho_\uparrow(\tilde{R}) - \rho_\downarrow(\tilde{R}))] \end{aligned} \tag{8.8}$$

where $E_{correlation}$,$E_{kinetic}$, and $E_{exchange}$ are the correlation, kinetic energy and exchange energy functionals, respectively, and the last term is the explicit Fermi contact energy. As the J tensor can be obtained from as an energy derivative, the J tensor is divided into two terms. The first term is the direct term which with our approximations depends only on the perturbed densities at the nuclear positions.

$$J_{direct} = \frac{{m_e}^2}{m_p}\frac{\mu_B^4}{2}(\frac{16\pi}{3})^2 g_a g_b I_a I_b[\delta_A^{\uparrow}(\tilde{R}) - \delta_B^{\uparrow}(0)] \tag{8.9}$$

This term is obtained solely from the Fermi contact perturbation. The second term, the indirect term, requires derivatives of the energy functionals. In order to estimate the indirect term, the simplest density functionals extant are used: namely the Thomas-Fermi-Dirac (TFD) functional. In the TFD approximation, the total energy, with neglect of correlation, is expressed as [10],

$$E = C_k \int d\tilde{r}\rho^{5/3}(\tilde{r}) - C_x \int d\tilde{r}\rho^{4/3}(\tilde{r}). \tag{8.10}$$

C_k and C_x are constants which for closed shell systems are 2.871 and 0.7386 respectively in atomic units. The density is now placed into the energy functional. The "indirect" term is obtained by differentiation of the TFD energy functional. This term contains products of the perturbed densities of atom A and atom B due to their own hyperfine interactions.

The off center perturbation is neglected as being significantly smaller than the on center one. Carrying out the required functional differentiation gives the indirect J as,

$$J_{indirect} = \frac{m_e}{m_p}^2 \frac{\mu_B^4}{2} (\frac{16\pi}{3})^2 \int d\tilde{r} (\frac{\delta^2 E_{kin}}{\delta(\rho_\uparrow(\tilde{r}))^2} + \frac{\delta^2 E_x}{\delta(\rho_\uparrow(\tilde{r}))^2}) g_a g_b I_a I_b [\delta_a^\uparrow(\tilde{r}) \delta_b^\uparrow(\tilde{r} - \tilde{R})]. \tag{8.11}$$

Thus, the present method requires only functional evaluations at two points for the direct term, but requires an integral over all space for the indirect term. Performing the latter requires a numerical integration program. Note that, the terms direct and indirect here refer to different portions of the Fermi contact contribution to the J coupling. This usage should not be confused with the use of direct and indirect spin-spin coupling to refer to the dipolar spin-spin and the total spin-spin couplings, respectively. This chapter is only concerned with a portion of the J coupling.

8.4 Fermi Contact Perturbation

The problem of solving for $\delta_i^\uparrow(\tilde{r})$ remains. In order to determine the effect of the Fermi contact interaction on the electron density, perturbation theory and hydrogenic orbitals are used. The results are correct to first order for hydrogenic orbitals. However, the use of hydrogenic orbitals requires that the density for xenon and hydrogen be expressed in terms of hydrogenic orbitals with effective Z's. This will be discussed in more detail later in the chapter. Other work has been done on perturbation theory of the Fermi contact interaction such as the work of Harris and Pitzer. [11] The method used here is similar, though with slight differences. Additionally, the method is generalized to arbitrary quantum number, n, and effective charge, Z.

For the Fermi contact interaction, only the ns states need be considered as only s states penetrate to the nucleus. The differential equation that must be solved from perturbation theory is,

$$(H^0 - E_n^0)\psi_{ns}^1 = (E_n^1 - H^1)\psi_{ns}^0 \tag{8.12}$$

The various terms in Equation 8.12 are,

$$H^0 = \frac{-\nabla^2}{2} - \frac{Z}{r} \tag{8.13}$$

$$H^1 = 4\pi\delta(\tilde{r})) \tag{8.14}$$

$$E_n^0 = \frac{-Z^2}{2n^2} \tag{8.15}$$

$$E_n^1 = 4\pi(\psi_{ns}^0(0))^2 \tag{8.16}$$

The following amplitude is also defined,

$$\psi_{ns} = \frac{Z^{3/2} exp(-Zr/n)}{\zeta}, \tag{8.17}$$

where ζ is the normalization constant for the ψ^0_{ns} state, such that

$$\psi^0_{ns} = P^n[rZ]\psi_{ns}. \tag{8.18}$$

The assumption is also made that,

$$\psi^1_{ns} = ZF^n[rZ]\psi_{ns}. \tag{8.19}$$

$F^n[rZ]$ is, of course, not the same as $P^n[rZ]$. The spirit of this approach is the same as in Dalgarno-Lewis perturbation theory. [12] The precise details, however, are not the same. In Dalgarno-Lewis theory, one would assume a form of $\psi^1_{ns} = G^n[rZ]\psi^0_{ns}$. In this particular instance, the form from Delgarno-Lewis perturbation theory is not the most facile approximation.

The differential equation is solved in more detail in the appendix. The only remaining issue that must be dealt with to obtain perturbed densities is the role of effective Z's. As estimated of the J coupling is all that is desired, first use Slater's rules to obtain Z effectives for all but the 5s and 5p orbitals. [13] The Z's for the n=5 shell are obtained by first calculating the electron density at R, the position of the second nucleus, via a Hartree-Fock calculation and then fitting. Obviously a possible improvement would be to do a more global fit, but for this estimate it was believed to be unnecessary.

8.5 Results

After obtaining the perturbed densities, solving for the J couplings becomes a matter of numerical evaluation for the direct term, and numerical integration for the indirect. These results are quoted in Table 8.I, and Figures 8.1-8.5. From an inspection of the figures one can see several trends. Figure 8.1 indicates that the Xe-Xe J coupling decays roughly as an exponential, though with some slight oscillations as indicated in Figure 8.2. In the region of physical interest, 8-12 bohr, the coupling is of the order of millihertz. The Xe-Xe coupling is dominated by the indirect term. The direct term is never more than 1% of the indirect. A plot of the Xe-Xe interaction potential is included to illustrate the region of significant overlap [14]. In the case of Xe-H, the prototype for Xe in a cage molecule, the direct and indirect terms are of roughly equal magnitude as demonstrated in Figures 8.3 and 8.4. The total J couplings has an approximately exponential decay, as demonstrated by the plot of the ln[J] in Figure 8.5. The region of physical interest for xenon contained in a cage molecule is 6-8 bohr where the couplings are of the order of 10-100 microhertz.

Table 8.1: J Couplings

Internuclear	Xe-Xe		Xe-H Total	Xe-H Indirect
Xe-H direct				
Distance (Bohr)	J Coupling	J Coupling	J Coupling	J Coupling
4.5		63.0	4.80	58.2
5.0	1.59	3.32	1.79	1.53
5.5	8.60	0.758	0.178	0.580
6.0	13.6	0.149	0.114	0.0350
6.5	6.50	0.089	0.074	0.0155
7.0	4.86	0.045	0.037	0.0083
7.5	2.53			
8.0	1.18			
8.5	0.373			
9.0	0.0732			
9.5	0.00429			
10.0	-0.0149			
10.5	-0.00147			
11.0	0.00657			
11.5	0.00902			
12.0	0.00752			
12.5	0.00481			

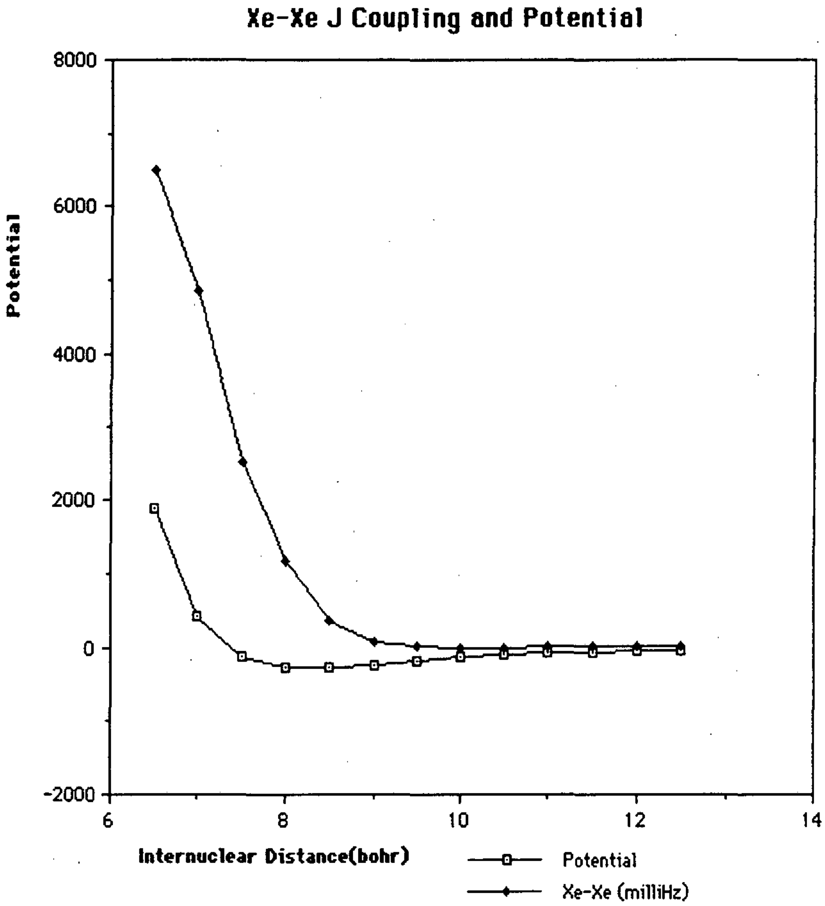

Figure 8.1: The Xe-Xe Fermi Contact J coupling is shown along with the Xe-Xe interatomic potential. The latter is obtained from ref. 16.

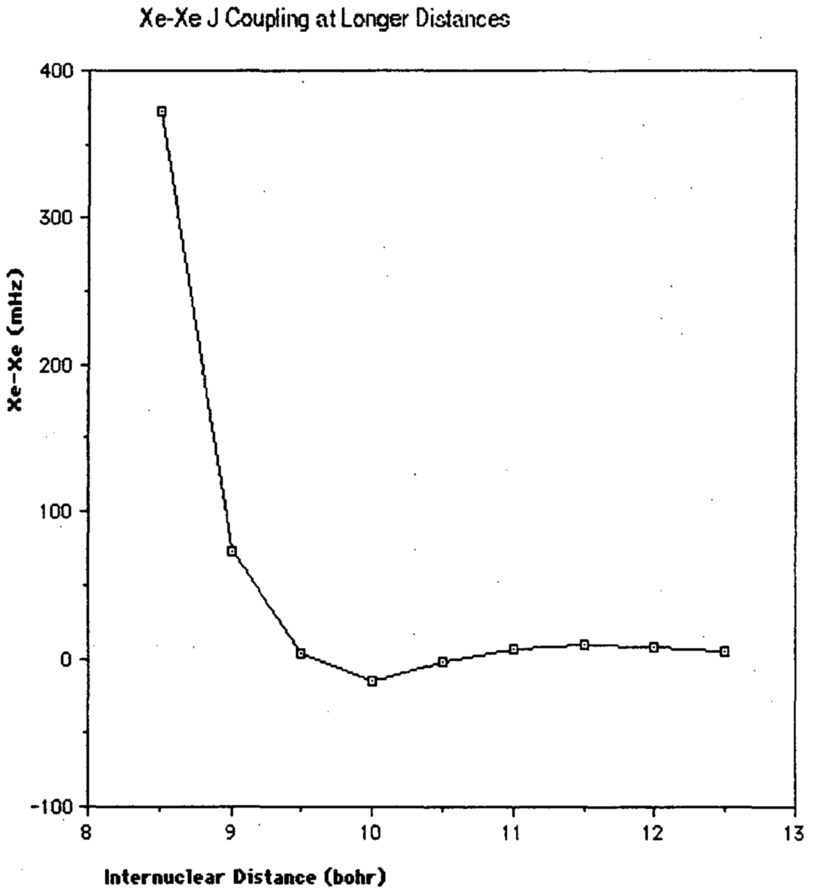

Figure 8.2: A blowup of the tail of Fig 8.1 to illustrate the oscillations in the coupling.

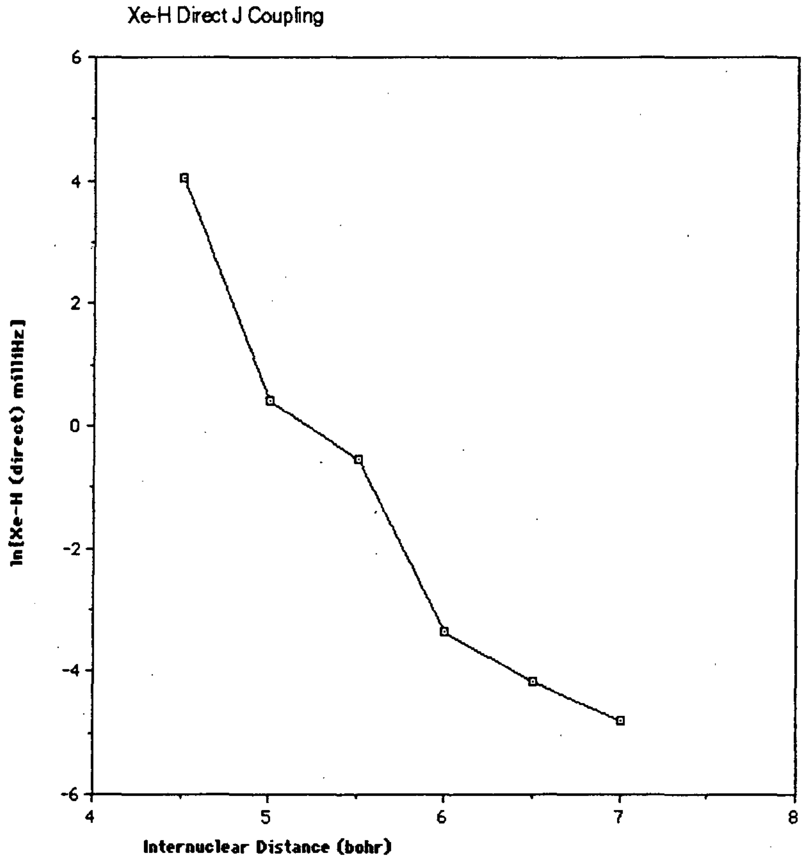

Figure 8.3: The direct portion of the Xe-H Fermi contact J coupling is shown.

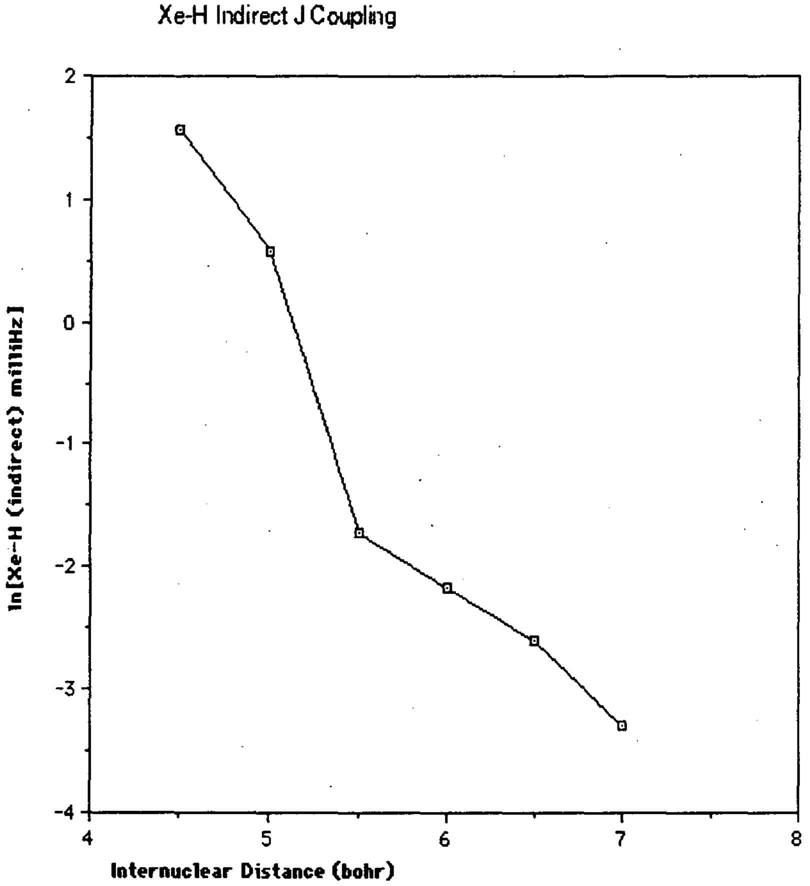

Figure 8.4: The indirect portion of the Xe-H Fermi contact J coupling is shown.

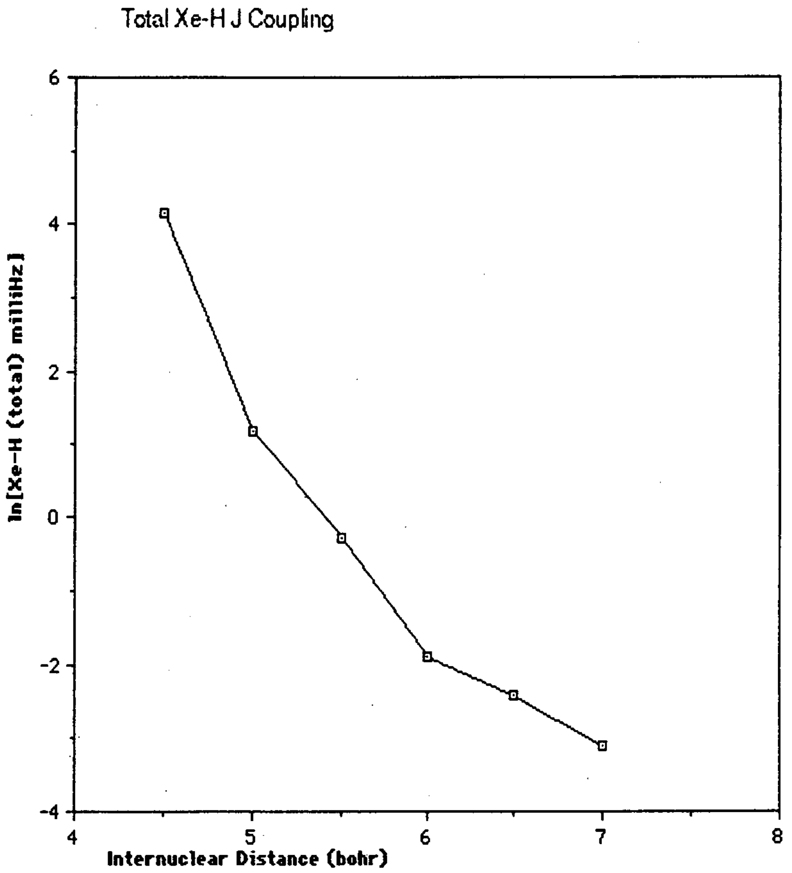

Figure 8.5: The entire Xe-H Fermi contact J coupling is shown. This is the sum of Fig. 8.3 and Fig 8.4

8.6 Conclusions

Using an electron gas theory, the J couplings between two inequivalent Xe atoms and between a xenon and a hydrogen atom are estimated. The latter is a prototype for the xenon-hydrogen coupling in a cage molecule. An approximately exponential dependence on internuclear distance in these parameters in the region of weak overlap was found. The values estimated are within the potential ability of experimentalists to measure with the techniques of optical pumping. Hopefully, these estimates will provoke experimentalists to measure these quantities.

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8.7 Appendix

The simplification and solution of the Fermi contact differential equation are exhibited in this appendix. In order to solve for $F[\tilde{r}]$, an approximation needs to be made. When r=0, the left hand side of equation (4.12) diverges because of the delta function. Assume that it suffices to only consider the divergence to first order. So that the divergence can be approximated by a/r. One can immediatly simplify the Z dependence of the differential equation. Define r'=rz. Then the differential equation becomes,

$$[\frac{-\nabla'^2}{2} - \frac{1}{r'} + \frac{1}{2n^2}]\psi^1_{ns}(\tilde{r}') = 4\pi Z(P^n(0))^2\psi^0_{ns}(\tilde{r}'). \tag{8.20}$$

Thus, this equation can be for arbitrary Z. For the remainder of the discussion, Z shall be set equal to one, and generalizations made when appropriate. The differentiation equation for the Fermi contact perturbation in the 1s state becomes,

$$[\frac{-\partial^2}{2\partial r^2} - \frac{\partial}{r\partial r} - \frac{1}{r} + \frac{1}{2}]F[r]\psi^0_{1s}(r) = 4\psi^0_{1s}(r). \tag{8.21}$$

Hence, if one lets $F[r] = a/r$, then the first two terms cancel, leaving the following,

$$[\frac{-a}{r^2} + \frac{r}{2}]\psi^0_{1s}(r) = 4\psi^0_{1s}(r) \tag{8.22}$$

Hence, $F[r] = a/r$ is not correct, and two more terms are necessary in order to obtain the full F[r] from Equation 8.21. Additionally, a constant term must appear so that orthogonality is preserved,

$$\int drr^2\psi^0_{1s}(r)\psi^1_{1s}(r) = 0. \tag{8.23}$$

The end result is an expression which has 4 terms,

$$F[r] = \frac{a}{r} + b + cr + d\ln[2\gamma r], \tag{8.24}$$

where a,c, and d are obtained from the differential equation using Mathematica and b is obtained from the orthogonality constraint. Euler's constant, γ introduced so that the coefficents are all rational. The crucial step in realizing how to solve for higher n states is to note that the left hand side of the differential equation (4.12) changes at higher n merely by the multiplication of an nth order polynomial, i.e.,

$$\psi^0_{ns}(r) = P^n(r)\psi_{ns}(r). \tag{8.25}$$

So the F[r]'s for higher n states, $F^n[r]$, must have the form

$$F^n[r] = \frac{a_n}{r} + b_n + \Sigma^n_{j=1} C_{jn} r^j + \Sigma^{n-1}_{i=0} d_{in} r^{i-1} \ln[2\gamma r], \tag{8.26}$$

where the coefficents can be obtained readily using Mathematica or some other symbolic mathematics program. Some explict solutions for a few s states include, s=1

$$\psi^1_{1s} = (\frac{-2}{r} - 10 + 4r + 4ln[2\gamma r])\frac{exp(-r)}{\pi^{1/2}}, \tag{8.27}$$

s=2

$$\psi^1_{2s} = (\frac{-4}{r} - 6 + 13r + 8ln[\gamma r] - r^2 - 4rln[\gamma r])\frac{exp(-r/2)}{32\pi^{1/2}}, \tag{8.28}$$

s=3

$$\psi^1_{3s} = (\frac{-48}{r} - \frac{454309}{6561} + \frac{1610806}{19683}r - \frac{40844062}{1778257}r^2 + 96ln[\gamma r] + \frac{64}{81}r^3 - 64rln[\gamma r] + \frac{64}{9}r^2 ln[\gamma r])\frac{exp(-r/3)}{81(12\pi)^{1/2}}. \tag{8.29}$$

There are similar but more complicated expressions for the n=4 and n=5 states which were used in the calculations. Subsitution of rz for r allowed the useage of effective Z's.

Chapter 9

The Magnetic Field Dependent Quadrupolar Splitting

In this chapter, it is confirmed that the recently discovered field dependent nuclear quadrupolar splitting of Xe^{131} arises from a distortion of the electron density due to the applied magnetic field. [1] Ordinarily, the spherical symmetry of the electron density would result in a vanishing quadrupolar splitting even in the spin $\frac{3}{2}$ Xe^{131} isotope. In a high enough magnetic field, however, the electron density can be slightly distorted causing a break in the spherical symmetry. The distortion depends both linearly and quadratically on the applied field. The existence of the former is due to the coupling to the field and the nuclear spin. The latter is a manifestation of the quadratic Zeeman effect. In addition to confirming the order of magnitude for the observed effect, it is shown that there should be an asymmetry introduced in the spectra due to the linear coupling with the nuclear spin. This effect has not been seen experimentally.

9.1 Introduction

Recently, evidence has been found for the existence of a magnetic field dependent quadrupolar splitting in gaseous ^{131}Xe. [1] The precise nature of the effect was not anticipated. However, previously in unpublished work, Rex Gerald III had speculated that a measurable quadratic effect would exist, and that the linear effect would be unmeasurably small. [2] Earlier experimental work had failed to observe any such effect. [3] In this work, a theory is presented which confirms the sign and magnitude of the experimentally observed linear and quadratic effects.

The intuitively obvious explanation of this behavior is that a magnetic field distorts the electron density. As expected, this distortion and hence, the quadrupole, is very small due to the weak interaction of the field and the electrons. There are two terms in this field induced nuclear quadrupolar Hamiltonian: a term linear in the field and a quadratic term. The sources of the two terms are respectively, the coupling of electrons to both the nuclear magnetic moment and the external field, and the ordinary diamagnetic coupling of the electrons to the external magnetic field. In the absence of the quadrupole, these terms generate respectively the ordinary chemical shielding and magnetic susceptibility. Hence, the description may be reversed so that the nuclear quadrupole distorts the electron density. The chemical shielding and magnetic susceptibility of an isolated atom would then become dependent on the orientation of the nucleus relative to the applied field. For a molecule there would be additional paramagnetic contributions to the induced quadrupole moment. These terms shall not be considered here as the atomic case is the one of interest.

The calculation of the two effects is presented here. Then the sign and magnitude are calculated exactly for a fake H like system. By fake hydrogren, an atom identical to hydrogen with nuclear spin 3/2 and ^{131}Xe nuclear magnetic and quadrupole moments is meant. Finally, an estimate of the size of the effect in real ^{131}Xe is given and the results are compared to the experiments.

9.2 General Theory

An isolated atom does not possess a field gradient at the nucleus because the electron density depends only upon the radial distance from the nucleus. When the atom is placed in an environment in which the electron density is perturbed and the expansion of the perturbation in spherical harmonics contains Y_{2m} components amongst others, a field gradient is generated. In the present situation, the perturbations are an applied magnetic field and a nuclear magnetic moment.

The relevant electronic Hamiltonian for an atom in the presence of both a nuclear quadrupole and a magnetic field may be decomposed into four pieces,

$$H = H_0 + H_Q + H_D + H_\sigma \tag{9.1}$$

H_0 is the zero field Hamiltonian for the electrons. H_Q, the ordinary quadrupolar Hamiltonian, is in atomic units,

$$H_Q = Q\Sigma_i 4\sqrt{\frac{\pi}{5}}Y_{20}(\theta_i)\frac{1}{r_i^3}\frac{(3I_z^2 - I(I+1))}{(3I^2 - I(I+1))} \tag{9.2}$$

$Y_{mn}(\theta_i)$ denotes spherical harmonics and, θ_i, r_i the electron coordinates. H_D is the diamagnetic interaction,

$$H_D = \alpha^4 \Sigma_i \frac{(B \times r_i)^2}{4} \tag{9.3}$$

B is in the atomic unit of 12.5 Tesla, and α is the fine structure constant which in atomic units is $\frac{1}{c} \approx \frac{1}{137}$. Finally there is the diamagnetic coupling, H_σ, of the nuclear spin, I, to the magnetic field that would give rise to the chemical shielding in the absence of the quadrupole. [4]

$$H_\sigma = \alpha^4 g \frac{m_e}{m_p}\frac{(B \times r_i)}{2} \bullet \frac{(I \times r_i)}{r_i^3} \tag{9.4}$$

The nuclear g factor may be positive or negative and $\frac{m_e}{m_p} \approx \frac{1}{1800}$.

Instead of calculating the distorted electron density, the contribution to the ground state electronic energy that is linear in H_Q and linear in each H_D and H_σ is calculated. This nonvanishing energy is proportional to the field induced electric quadrupole coupling hamiltonian.

As the atoms are in the gas phase, only the irreducible second rank terms in H_D and H_σ are kept. Due to the high field, only one component remains namely $Y_{20}(\theta_i)$. Thus,

$$H_D = -B^2\alpha^4\Sigma_i r_i^2 \frac{1}{6}\sqrt{\frac{\pi}{5}}Y_{20}(\theta_i) \tag{9.5}$$

and

$$H_\sigma = -Bg\alpha^4\frac{m_e}{m_p}I_z\Sigma_i\frac{1}{r_i}\frac{1}{6}\sqrt{\frac{\pi}{5}}Y_{20}(\theta_i). \tag{9.6}$$

The resulting energy, bilinear in H_Q and H_D and H_σ is,

$$\begin{aligned} E^{(2)} &= \frac{Q4\alpha^4\frac{\pi}{15}\Sigma_n' < 0|\Sigma_i\frac{Y_{20}(\theta_i)}{r_i^3}|n > \frac{(3I_z^2-I(I+1))}{(3I^2-I(I+1))}\frac{B^2}{3} < n|\Sigma_j r_j^2 Y_{20}(\theta_j)|0 >}{E_{no}} \\ &- \frac{Q4\alpha^4\frac{\pi}{15}\Sigma_n' < 0|\Sigma_i\frac{Y_{20}(\theta_i)}{r_i^3}|n > \frac{(3I_z^2-I(I+1))}{(3I^2-I(I+1))}I_z\frac{Bg}{3}\frac{m_e}{m_p}\Sigma_j < n|\frac{Y_{20}(\theta_j)}{r_j}|0 >}{E_{no}} \end{aligned} \tag{9.7}$$

E_{no} is the energy difference between the ground state, $|0>$ and the excited state $|n>$. The terms linear and quadratic in the field have different dependencies on the nuclear spin. In particular, the quadratic term depends as $(3I_z^2 - I(I+1))$, whereas the linear term is $I_z(3I_z^2 - I(I+1))$, the latter leads to a splitting of the nuclear spin degeneracy. Additionally, the signs of the linear and quadratic terms may be different. Indeed, the Hamiltonian may be written as,

$$H = g(1-\sigma)BI_z + QA_D B^2 \frac{(3I_z^2 - I(I+1))}{(3I^2 - I(I+1))} - gQA_\sigma B \frac{(3I_z^2 - I(I+1))}{(3I^2 - I(I+1))} I_z, \quad (9.8)$$

in which σ is the chemical shielding. The signs of A_D and A_σ may be proven to be the same in a simple Kohn-Sham approximation. The signs are conjectured to be the same in the exact theory.

Now specialize to the specific case of I=3/2. In particular, the spectra of a fake spin 3/2 hydrogen will be examined. In the absence of the quadrupole terms all the energy transitions are equal. Hence, there is only one line, assuming equal populations of the four m levels and neglecting induced emission. With the two additional terms the degeneracy is broken in a field dependent manner with different dependencies for each line. In experimental situations it may be necessary to track the lines relative to the center line, so the relative energies would be,

$$\Delta E(-\frac{3}{2} \rightarrow -\frac{1}{2}) \propto -2[A_D B^2 - gA_\sigma B] \quad (9.9)$$

$$\Delta E(-\frac{1}{2} \rightarrow \frac{1}{2}) \propto gA_\sigma B \quad (9.10)$$

$$\Delta E(\frac{1}{2} \rightarrow \frac{3}{2}) \propto 2[A_D B^2 + gA_\sigma B]. \quad (9.11)$$

The transition energies as a function of field for two different ratios of A_D to A_σ are plotted in Figures 9.1 and 9.2.

Notice that there is a B for which the 3 lines collapse into 2. This B_c is given by

$$B_c = \frac{3gA_\sigma}{2A_D} \tag{9.12}$$

which could experimentally provide the ratio of the two coupling effects. The coupling constants could be obtained experimentally by fitting results from a variety of field strengths.

A bound for $E^{(2)}$ can now be calculated assuming that the ground state is from a single determinant, e.g., from Kohn-Sham theory,

$$|E^{(2)}| \leq \frac{Q4\alpha^4\frac{\pi}{5} < 0|\Sigma_i \frac{Y_{20}^2(\theta_i)}{r_i^3}[\frac{B^2}{3}r_i^2 + \frac{\mu_z B}{3r_i}]|0 >}{E^*} \tag{9.13}$$

$$= \frac{Q4\alpha^4\frac{\pi}{5}\int d^3r\frac{\rho(r)}{r^3}[\frac{B^2}{3}r^2 + \frac{\mu_z B}{3r}]}{E^*}, \tag{9.14}$$

where $\rho(r)$ is the electron density.

An explicit calculation can be performed for this bound with fake hydrogen, given an estimate for E^*. Simple evaluation of the first term obtains,

$$|E_D^{(2)}| \leq \alpha^4\frac{QB^2 4\pi}{15E^*} \tag{9.15}$$

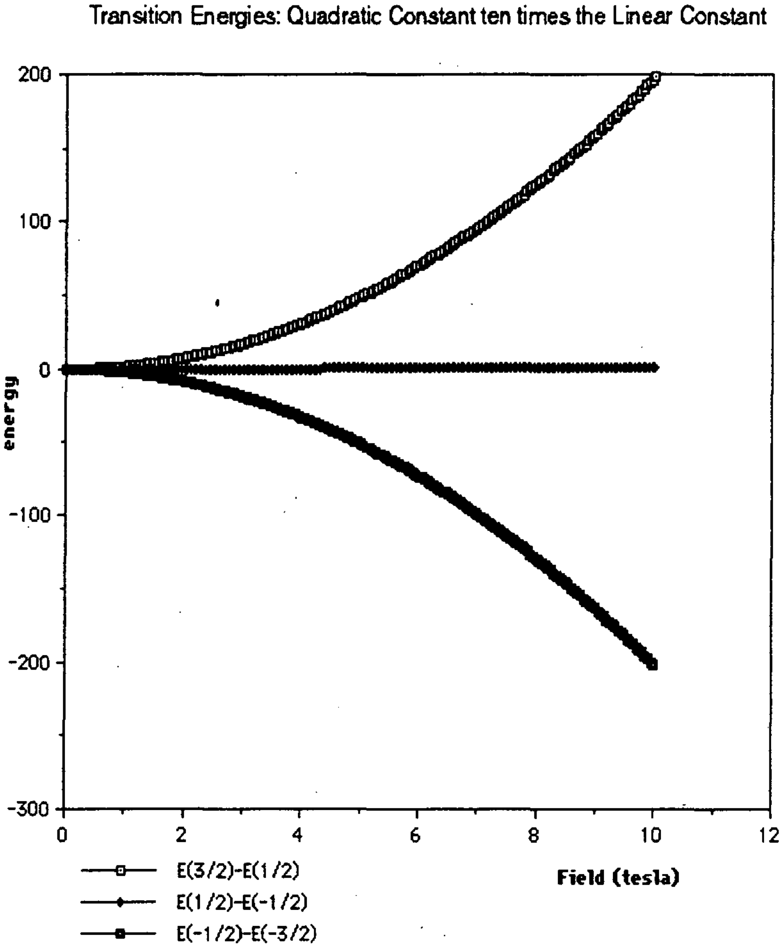

Figure 9.1: The transition Energies as a function of magnetic field strength for the case in which the quadratic coefficient is ten times the linear coefficient.

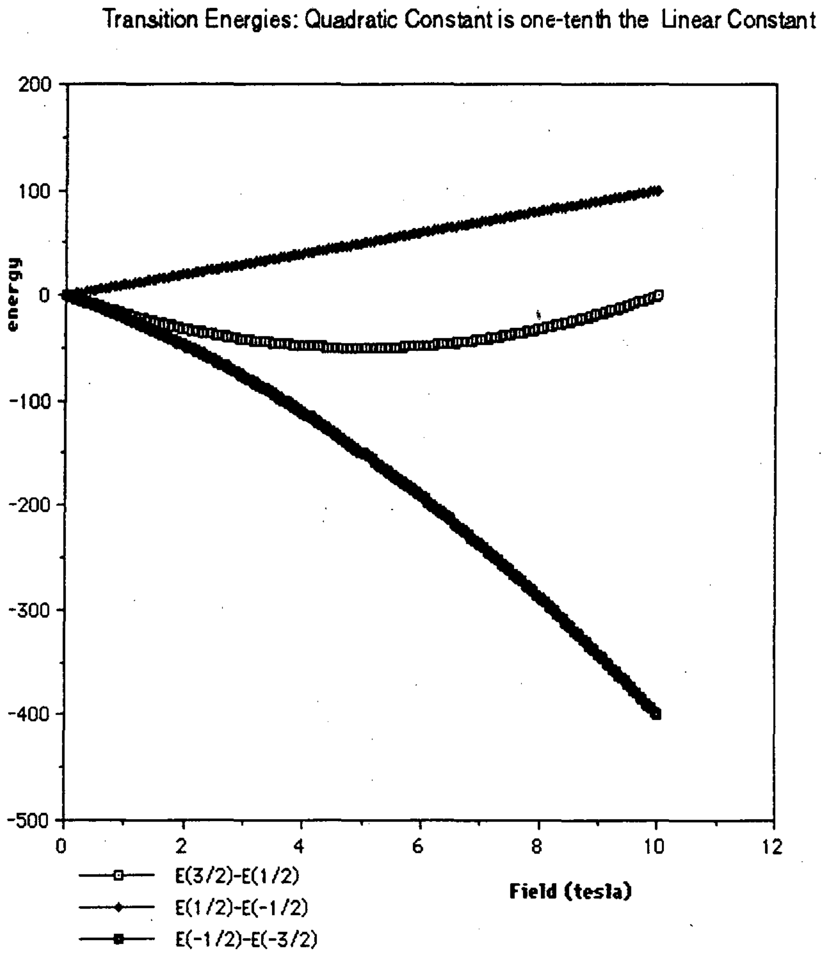

Figure 9.2: The transition Energies as a function of magnetic field strength when quadratic coefficient is one-tenth the linear coefficient.

which with $E^* = 3/8$, the excitation energy to $l = 2$, yields

$$|E_D^{(2)}| \leq 9.57 * 10^{25} Q B^2 \tag{9.16}$$

in units of hertz with QB^2 in units of (tesla-meter)^2. The bound for the second term linear in B is much less useful as it diverges.

In order to quantitatively examine the magnitude of the two terms they are calculated exactly for "fake" hydrogen. First, the energy of fake hydrogen with charge Z, quadrupole moment Q, and gryromagnetic ratio g is related to the energy of fake hydrogen with unit charge. Simple scaling obtains the results.

$$E_D^2(Z) = Z E_D(1) \tag{9.17}$$

$$E_\sigma^2(Z) = Z^4 E_\sigma(1) \tag{9.18}$$

Next an elementary calculation using Dalgarno-Lewis-Schwartz perturbation theory is performed. [5] The results of an earlier calculation of the quadrupolar induced dipole moment in HD may be used. [6] The second order energy is,

$$E^{(2)} = 2[< 0|H_D|\psi_q > + < 0|H_\sigma|\psi_q >]. \tag{9.19}$$

$|\psi_q>$ is the wavefunction perturbed to first order by the quadrupole. Explicitly,

$$\psi_q(r) = Q4\sqrt{\frac{\pi}{5}}Y_{20}f_q\psi_0(r) \tag{9.20}$$

with f_Q the solution of,

$$(\frac{-1}{2}\frac{d^2}{dr^2} + (1 - \frac{1}{r})\frac{d}{dr} + \frac{3}{r^2})f_Q = -\frac{1}{r^3} \tag{9.21}$$

A particular solution to equation (21) is,

$$f_Q = -(\frac{1}{3r} + 19) \tag{9.22}$$

As the ground state wavefunction is simply

$$\psi^0 = \frac{1}{\sqrt{\pi}}e^{-r} \tag{9.23}$$

with,

$$E^{(2)} = E_D^{(2)} + E_\sigma^{(2)}, \tag{9.24}$$

where

$$E_D^{(2)} = \frac{-5Q}{6\pi}\int r^4 dr e^{-2r}(\frac{1}{3r}+\frac{1}{9})B^2 Z\frac{(3I_z^2 - I(I+1))\alpha^4}{(3I^2 - I(I+1))} \tag{9.25}$$

$$E_\sigma^{(2)} = \frac{5Q}{6\pi}\int r dr^{-2r}(\frac{1}{3r}+\frac{1}{9})BZ^4 g I_z\frac{(3I_z^2 - I(I+1))\alpha^4}{(3I^2 - I(I+1))}. \tag{9.26}$$

Elementary integration yields,

$$E_D^{(2)} = -QB^2 * 5.6 * 10^{-2} Z\frac{(3I_z^2 - I(I+1))\alpha^4}{(3I^2 - I(I+1))} \tag{9.27}$$

$$E_\sigma^{(2)} = QB^2 * 5.2 * 10^{-5} Z^4 g I_z\frac{(3I_z^2 - I(I+1))\alpha^4}{(3I^2 - I(I+1))} \tag{9.28}$$

in atomic units.

9.3 Comparison with Experiment

The experimental splittings were fit as linear plus quadratic terms in the magnetic field. These results, in hertz per Tesla^2, and hertz per Tesla respectively, are [1] :

$$\frac{E_D^{(2)}}{B^2} = 0.016986 \tag{9.29}$$

and

$$\frac{E_\sigma^{(2)}}{B} = -0.077511. \tag{9.30}$$

The comparison to theory is not entirely straightforward as the peaks were assumed to split symmetrically about the center peak. While the experimental spectra do look asymmetric at low field, it is difficult to determine how much of this is from experimental artifacts. It is clear, however, that the experiments found a field dependent splitting that has both linear and quadratic dependencies. Moreover, the experiment found that the fitting constants for the two effects are comparable in magnitude. These results shall now be shown to be reasonable.

For fake hydrogen, substitute the parameters for Xe into equations (9.9), (9.10) and (9.11) to obtain the following results in units of hertz and tesla,

$$\Delta E(-\frac{3}{2} \rightarrow -\frac{1}{2}) = -3.08 * 10^{-3} B^2 + 7.09 * 10^{-6} B \tag{9.31}$$

$$\Delta E(-\frac{1}{2} \rightarrow \frac{1}{2}) = -3.55 * 10^{-6} B \tag{9.32}$$

$$\Delta E(\frac{1}{2} \rightarrow \frac{3}{2}) = 3.08 * 10^{-3} B^2 + 7.09 * 10^{-6} B. \tag{9.33}$$

Experimentally the only available reference is the center line, and so relative to that line, the transition energies become,

$$\Delta E(-\frac{3}{2} \rightarrow -\frac{1}{2}) = -3.08 * 10^{-3} B^2 + 1.06 * 10^{-5} B \tag{9.34}$$

$$\Delta E(-\frac{1}{2} \rightarrow \frac{1}{2}) = 0 \tag{9.35}$$

$$\Delta E(\frac{1}{2} \rightarrow \frac{3}{2}) = 3.08 * 10^{-3} B^2 + 1.06 * 10^{-5} B. \tag{9.36}$$

For fake hydrogen, the quadratic term dominates by almost 2 orders of magnitude. In fact $B_c = 0.0034$ Tesla. Clearly, for any reasonable experimental field, such as the 7.05 to 16.92 Tesla fields used in the xenon experiments, one would see a symmetric splitting quadratic in the field. For atoms other than hydrogen, one would have two changes. The first is that the nuclear charge changes. So Z is no longer one and effective Z's may be introduced into equations (9.27) and (9.28). These Z effectives may even be different for the linear and quadratic term, as one would find in the ordinary chemical shielding and magnetic susceptibility. [7] The second change is that there is more than one electron present. This causes an additional change in the constants beyond the change in the Z's. The latter change may be estimated by scaling by the change in the chemical shielding and the magnetic susceptibility in going from hydrogen to xenon. The shielding increases by a factor of about 300, whereas the susceptibility increases only by a factor of 20. Applying these arguments, one obtains the following,

$$\Delta E(-\frac{3}{2} \rightarrow -\frac{1}{2}) = -6.16 * 10^{-2} B^2 Z_{eff} + 3.18 * 10^{-3} B Z_{eff}^4 \tag{9.37}$$

$$\Delta E(-\frac{1}{2} \rightarrow \frac{1}{2}) = 0 \tag{9.38}$$

$$\Delta E(\frac{1}{2} \rightarrow \frac{3}{2}) = 6.16 * 10^{-2} B^2 Z_{eff} + 3.18 * 10^{-3} B Z_{eff}^4. \tag{9.39}$$

This estimate overestimates the quadratic term versus the linear term when compared to the experimental results. The agreement, however, is not bad for a simple scaling argument. One could also attempt to reproduce the experimental results by adjusting the effective Z's. The linear coefficient would be reproduced by an effective Z of 9.2 whereas the quadratic coefficient would require an effective Z of 5.5. The different r-dependencies of the operators would require the use of different effective Z's. Attempting to adjust the effective Z's to reproduce the experimental data is not necessarily sensible as one must consider that the experimental data was interpreted as being symmetric whereas the theory predicts an asymmetry. Additionally, this is only meant as an estimate of the effect not as a precise calculation.

9.4 Conclusions

The estimates presented in this chapter confirm the supposition that a magnetic field dependent quadrupole splitting in ^{131}Xe is due to a diamagnetic distorted atomic electron density. This distortion is primarily quadratic in the field for light atoms, but may have a substantive linear component in heavier atoms. Additional motivation for continued experimental work in this area is also presented as the predicted asymmetry in the spectra requires more conclusive experiments. It would also be fruitful to develop an experiment in which the reference is not the central transition as one could then see if the central transition also moves linearly with the field. Experiments in which this effect is sought for in other systems, i.e. other atoms, molecules, and solids, are likely to occur in the near future.

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[7] The chemical shielding should scale as $\frac{1}{Z}$, and the magnetic susceptibility as Z^2. In going from hydrogen to xenon, however, the shielding actually increases by about 300 fold and the susceptibility by about 20 times.

Chapter 10

Conclusions and Future Work

The major focus of this thesis has been on developing functionals for the magnetic susceptibility and the chemical shielding within the context of magnetic field density functional theory (BDFT). These functionals depend on the electron density in the absence of the field, which is unlike any other treatment of these responses. Additional work has also been done on intermolecular J couplings and the magnetic field-induced quadrupole splitting.

There are several developments reported in this dissertation. First, is the development of local density functionals for chemical shieldings and magnetic susceptibilities. These are the first such functionals ever proposed. In order to examine their advantages and disadvantages, they were tested numerically on some small molecules.

In order to mitigate some of the difficulties encountered with local functionals, nonlocal functionals of the electron density were also developed. The examination of the local current density functionals led to consideration of the field dependent portion of the exchange-correlation. The examination of nonlocal current density functionals generated the method used. In order to avoid divergence every other treatment of the exchange has required the screening of the exchange by correlation. The first exchange functional in which this divergence was avoided because of the bound state nature of the electronic system was then constructed. Additionally, a conjecture was given for the full form of the exchange-correlation energy functional. In both instances, the functionals depend on the ground state electron density in the absence of any magnetic field.

Additionally, the J, or indirect spin-spin coupling, was considered. An estimate was made of some intermolecular xenon J couplings, which have provided motivation for some experimentalists. These coupling are of interest because they could be used to study cage molecules or even xenon-protein complexes. This estimate was done using BDFT, but the approach was different from that used for the chemical shielding and the susceptibility. In particular, an energy approach was used within the additive density approximation. The use of the additive density approximation was justified as all that was desired was an estimate.

The recently discovered magnetic field-dependent quadrupole splitting was also investigated. The physical origin and magnitudes of both the linear and quadratic dependencies on the magnetic field were explained. The existence of a linear dependence had been particularly troubling as experimentally it had the larger coefficient in xenon, whereas previous researchers had claimed that it would not exist at all! Of course, at higher magnetic fields the quadratic effect does dominate despite its smaller coefficient. The small size of this effect makes it difficult to observe, however, there are some interesting effects that I have predicted, which have yet to be observed experimentally. In particular, the peaks should have slightly different dependencies on the magnetic field strength. In lighter atoms, the quadratic effect should have the larger coefficient. Hence, neon would be an ideal system to examine to test this effect. It is not surprising that these effects have yet to be observed. The experiments in which the gross effect was observed are at the cutting edge of NMR in 1998. The varying dependence of the lines is simply too fine a detail to be observed at the present. Additionally, this effect has only been observed in gaseous xenon, an ideal system for these studies. In order to test how the linear and quadratic dependencies vary from system to system, more experimental work is needed on other systems that may be beyond the state of the art at the present. However, creation of higher and higher strength magnets is an ongoing and intensive field of research. As such, these predictions should be tested in the near future.

Hence, quite a bit of progress has been made in Magnetic Field Density Functional Theory. However, more must be done before it becomes a tool which experimentalists can routinely use. The work presented in a portion of this thesis is just a beginning, and there are many questions remaining to be answered within this theory.

The first practical concern that must be addressed is that of computation. The nonlocal functionals explicated in Chapter 6, or more local approximation to these functionals, must be implemented within an electronic structure package. Such computation implementation will provide for a rigorous test of these functionals. If the accuracy of these functionals is less than desired, than the next step will be to paramaterize these functionals as was done for the local functionals. The parametrization of these functionals along with localization approximations will probably be the most important practical problem within this theory. It will be interesting to see if some of the nonlocality present in these functionals can be neglected, as that would reduce the computational aspect of the problem. In particular, there are presently three integrals that must be performed. Hence, this step would have a high computational scaling. The high computational scaling is mitigated by the need to perform only a single pass through the functional. As the zeroth order electron density is all that is required, the basic electronic structure calculation can be performed and then the functional evaluated once. Still it would be useful to reduce the scaling and theoretically interesting to see what degree of nonlocality is really required. The first obvious place in which nonlocality can be reduced is in the integration within W_2^0 in which the integral could by replaced by the sum of the endpoints. Once such computational work has been performed than this theory can really be used to ask questions about how the magnetic responses are really sensitive to electronic structure. For example, one could easily imagine mapping out orbital contributions to shifts that may allow one to precisely examine the sensitivity of NMR to bonding. One could also imagine merely using this theory as a faster method of calculating magnetic responses without using any of the potential advantages this theory has for interpretation. Hence, computation investigation is the first challenge that should be addressed.

Another logical extension of the work would be to include the orbital portion of the J coupling in this theory. Formally, most of this thesis has focused on the functionals when there is either a uniform field or a uniform field plus the field from a nuclear dipole. These are the appropriate fields for the magnetic susceptibility and the chemical shielding, respectively. However, they are both limits of one field: that due to two nuclear dipoles. The latter field is what gives rise to the orbital portion of the J coupling. So if one determined the functionals for the latter field, by taking limits one would obtain functionals for the other fields. What is needed to be done in order to incorporate the J coupling more fully into this theory is to reverse the limit. A full treatment of the orbital portion of the J coupling would require the exact same treatments as has been done except rather than considering the current density induced by a uniform field, one needs to consider the current density induced by a nuclear dipole. However, as one takes a dipole and moves it to infinity than one obtains a uniform field, i.e. considering the energy,

$$E^{\mu}[\rho(\tilde{r})] \rightarrow E^{B}[\rho(\tilde{r})] \tag{10.1}$$

as the dipole is moved to infinity. This suggests that to first approximation we ignore terms which vanish in the limit, and hence, replace the $\tilde{r} \times \nabla$ which appears in the nonlocal functional for the chemical shielding by $\frac{\tilde{r}}{|\tilde{r}-\tilde{R}|^3}$ where $\tilde{R}$ is the nuclear position and generate an approximation to the orbital J coupling. This should be a first approximation in extending the theory to handle another response.

There are other issues that presently are of more theoretical concern. The first is how to reconcile local and the nonlocal functionals. There are in some sense small deviations from opposite limits; the locally uniform electron gas in one instance, and an atomic system in the other. The exact functional would incorporate both limits, but it is not obvious how to connect these two limits. Such a reconciliation is a fundamental unanswered question in this theory.

Another theoretical issue is the role of exchange-correlation. A form of the exchange functional was derived for a uniform magnetic field. A form for the full exchange-correlation functional was postulated. There are several natural extensions of this work. One would be to prove that the full exchange-correlation form is correct. Another would be to extend this work to fields from a nuclear dipole and a uniform field. This would allow one to consider the role of field dependent exchange-correlation in the chemical shielding. An issue of more practical concern would be to actually parametrize the functionals so that they could be used in the calculation of NMR parameters. This would be of interest other workers tend to ignore the effect of the field-dependent exchange-correlation. However, at present one cannot make any rigorous claims as to the importance of this effect as other density functional theories are either too inaccurate to study the effect, or have an ad hoc basis. So would be useful to actually test for the importance of the field-dependent exchange-correlation that could be done within this theory.

An area that should be explored is the development of energy functionals. In most of this thesis, the functionals are current density functionals and so explicit calculation of the energy functionals is avoided. However, a current density and an energy approach are both equally valid. In work prior to the development of the general theory, Grayce and Harris used an electron gas approach to obtain a local energy functional that looks considerably different from any in this work. In would be interesting to bring that work into the context of this theory and to reconcile the energy and current density approaches. Of particular interest is the use of a different dimensionless variable $(\tilde{r}\rho(\tilde{r}))^{1/3}$ in the work of Grayce and Harris. This incorporates $\tilde{r}$ into the theory is a manifestly different manner that presently done. An investigation into using functionals of this form, perhaps in conjunction with the insight gained from the nonlocal functionals, is warranted. Also notice that is this work $\tilde{r}$ has been brought back into density functional theory through the nonlocal functionals. Perhaps similar approaches would be useful in other areas of density functional theory.

Though before giving up on the local functionals further investigations are also warranted. Extending this theory to carbon so that carbon shifts can be done readily is the next logical step. Additionally, recall from Chapter 4 that the local functionals were constructed from an approximation to the single-electron propagator, hence, it may be profitable to investigate other propagators. As an approximation to the propagator generates an approximation to the functional, and so perhaps using different propagator approximations would lead to other useful functionals.

Considerable work has been accomplished on linking density functional theory and magnetic fields in this dissertation. This thesis has paved the way for further theoretical and computation development of Magnetic Field Density Functional theory. Additionally, small effects have been addressed which require cutting-edge experimental techniques, but which could be interesting and useful to examine further both theoretically and experimental. Thus, there are still many open questions and so this field should remain one full of challenges for a considerable time.

ERNEST ORLANDO LAWRENCE BERKELEY NATIONAL LABORATORY
ONE CYCLOTRON ROAD | BERKELEY, CALIFORNIA 94720

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