CHAPTER 1

Introduction
1.1 Introduction:

Computational method finds one of its most important application in the support of experimental efforts. Many types of data that are measured experimentally can be computed as well. Computational methods also produce data that are not generally available from experiments. Recent advances indicate the determination of charge densities, which can also be correlated with other observable like bond length, bond angle and vibrational frequencies.

The prediction of molecular properties from computer simulations is playing an increasingly important role in the chemical and pharmaceutical industry. After revolution of theoretical developments, algorithm design and software implementation it is possible for computational science to have a qualitative impact on molecular design or promise of solving the rational drug design problem in a quantitative way.

Semiemprical and abinitio molecular orbital approaches, are examples of Electronic Structure methods applying Quantum Mechanics. They implicitly consider the electron distribution in system as a function of nuclear position. Electronic structure theories vary greatly in complexity and accuracy.

At present, the best and most flexible models are derived from quantum mechanics and are based on the Schrodinger equation. The Schrodinger equation relates the properties of electrons to those of waves and permits a mathematical description of atomic, and by extension, molecular characteristics. The standard form of the Schrodinger equation can be solved exactly, however, for only the simplest case, the hydrogen atom. Significant approximations are required to apply the Schrodinger
wave function approach to problems of interest. A commonly used and essentially standard set of approximations and assumptions has come to be known as Hartree-Fock (HF) Theory and is the basis for the majority of work done in electronic structure method at present.

A rigorous execution of Hartree-Fock Theory is called an ab initio ("from first principles") approach. These calculations involve a near complete mathematical treatment of the theoretical model underlying Hartree-Fock theory. Comprehensive calculations of this type result in a potentially enormous number of integrations and differentiations of complex algebraic formulae. The sheer number of separate computations can easily become so vast that only a supercomputer has the requisite speed, memory, and disk storage space for even moderately sized systems (i.e.,<100 non-hydrogen atoms). Ab initio methods, by virtue of being derived from the Hartree-Fock assumptions and approximations, have theoretical inaccuracies that cause difficulties in certain cases. Perhaps the most important of these is the neglect of the dynamic electron correlation effects in the motion of electrons within the self-consistent field used in the iterative solution process. Ab initio corrections are available for correlation, (e.g. Moller-Plesset (MP) Perturbation Theory, configuration interaction (CI), or multi-configuration-SCF (MCSCF), but are very expensive in terms of computing time and disk space. It should be emphasized that in the great majority of cases where ab initio methods have been rigorously applied, the results have been very good. However, the constraints listed above strictly limit the size and complexity of the systems feasible for a full ab initio treatment.

A computational method which is similar to, yet still separate from, other HF molecular orbital techniques is density functional theory
(DFT).\textsuperscript{1,2,3} The basic principle behind DFT is that the electron density is a fundamental quantity that can be used to develop a rigorous many-body theory, applicable to any atomic, molecular, or solid state system. In the mid-1960s Hohenberg, Kohn and Sham derived a formal proof of this principle as well as a set of equations (the Kohn-Sham equations) which are similar in form and function to the Hartree-Fock equations of molecular orbital theory. This formalism is such that electron correlation is inherently included in the method at no extra cost in computational efficiency. The basic difference between HF theory and DFT can be summarized in the following way: for a given set of atomic positions, HF theory expresses the total energy of the system of nuclei and electrons as a function of the total wave function, whereas DFT expresses this total energy as a functional of the total electron density. Current DFT methods contain no empirical or adjustable parameters and are thereby acknowledged to be "ab initio" approaches.

Acceptance of DFT methods by scientists is growing and general purpose computational packages exist containing them. This acceptance is also based on literature reports of systematic comparisons of DFT methods with experiment as well as with HF and post-HF methods. Chemists are also quickly learning that DFT methods are slightly computationally more efficient than ab initio HF methods. HF calculations formally scale as $N^4$ for $N$ basis functions but, in reality, scale $N^{2.5}-N^3$, depending on the size of the molecular system. Post-HF methods, which include electron correlation in some manner, scale as $N^m$ where $m>4$. DFT methods, however scale as $N^2-N^3$, including some electron correlation. Therefore, DFT calculations are practical for molecular systems which may be too large and/or troublesome for ab initio HF techniques. For
example, DFT methods have been particularly successful in predicting the properties of transition metal systems which have been notoriously difficult for HF and post-HF techniques.

Semi empirical quantum mechanical methods are also based on Hartree-Fock Theory. Semi empirical calculations ignore some of the less important aspects of HF theory that full ab initio treatments explicitly compute, so that fewer actual operations are performed. Also, the semi empirical approach uses empirically determined parameters and parameterized functions to replace some sections of a more complete HF treatment. The approximations in semi empirical theory result in much more rapid single energy calculations than in either HF or DFT ab initio methodologies. The advantage gained in the energy calculations leads to semi empirical methods being some 100-1000 times faster overall than ab initio HF or DFT methods of comparable predictive quality. The most popular of the semi empirical methods are those developed by or derived from work by Michael J.S. Dewar\textsuperscript{4}. They include MINDO3\textsuperscript{5}, MNDO\textsuperscript{6}, PM3\textsuperscript{7,8}, AM1\textsuperscript{9} and SAM1\textsuperscript{10}. Some older semi empirical programs and methods are still used successfully for specific purposes (e.g. ZINDO for spectroscopy on a wide range of elements). In summary, semi empirical methods offer chemical accuracy as well as computational efficiency. As computational power increases, so will the size of systems to which semi empirical methods are applied.

1.2 Hartree-Fock Theory

Hartree-Fock theory is fundamental to much of electronic structure theory. It is the basis of molecular orbital (MO) theory, which posits that
each electron's motion can be described by a single-particle function (orbital) which does not depend explicitly on the instantaneous motions of the other electrons. Huckel MO theory takes Hartree-Fock MO theory as an implicit foundation and throws away most of the terms to make it tractable for simple calculations. The ubiquity of orbital concepts in Physics is a testimony to the predictive power and intuitive appeal of Hartree-Fock MO theory. Hartree-Fock theory often provides a good starting point for more elaborate theoretical methods which are better approximations to the electronic Schrödinger equation (e.g., many-body perturbation theory, single-reference configuration interaction).

Hartree-Fock theory was developed to solve the electronic Schrödinger equation that results from the time-independent Schrödinger equation after invoking the Born-Oppenheimer approximation. In atomic units, the electronic Schrödinger equation is

\[
-\frac{1}{2} \sum_i V_i^2 - \sum_{\alpha} \frac{Z_{\alpha}}{r_{\alpha}} + \sum_{\alpha,\beta} \frac{Z_{\alpha} Z_{\beta}}{R_{\alpha \beta}} + \sum_{\alpha,\beta} \frac{1}{r_{\alpha \beta}} \right] \Psi(r; R) = E_\sigma \Psi(r; R),
\]

or, in our previous more compact notation,

\[
\left[ \hat{T}_e(r) + \hat{V}_{\text{NN}}(r; R) + \hat{V}_{\text{NN}}(r) + \hat{V}_{\text{el}}(r) \right] \Psi(r; R) = E_\sigma \Psi(r; R),
\]

The term \( V_{\text{NN}}(R) \), will give us the potential energy experienced by the nuclei. In other words, it gives the potential energy surface (from which we can get, for example, the equilibrium geometry and vibrational frequencies). That's one good reason why it is desirable to solve the electronic Schrödinger equation. The electronic wavefunction \( \psi(r; R) \) contains lots of useful information about molecular properties such as dipole (and multipole) moments, polarizability, etc.
1.2.1 Concept of the Hartree Fock Theory

The basic idea of Hartree-Fock theory is as follows. We know how to solve the electronic problem for the simplest atom, hydrogen, which has only one electron. We imagine that perhaps if we added another electron to hydrogen, to obtain H\(^-\), then maybe it might be reasonable to start off pretending that the electrons don't interact with each other (i.e., that \(V_\alpha = 0\)). If that was true, then the Hamiltonian would be separable, and the total electronic wavefunction \(\psi(r_1, r_2)\) describing the motions of the two electrons would just be the product of two hydrogen atom wavefunctions (orbitals), \(\psi(r_1) \psi(r_2)\). For a \(N\)-electronic system the wave function is given as:

\[
\Psi_{HF}(r_1, r_2 \ldots \ldots r_N) = \Phi_1(r_1) \Phi_2(r_2) \ldots \ldots \Phi_N(r_N)
\]  

which is known as a Hartree Product.

While this functional form is fairly convenient, it has at least one major shortcoming: it fails to satisfy the antisymmetry principle, which states that a wavefunction describing fermions should be antisymmetric with respect to the interchange of any set of space-spin coordinates. By space-spin coordinates, we mean that fermions have not only three spatial degrees of freedom, but also an intrinsic spin coordinate, \(\alpha\) or \(\beta\). We call a generic (either \(\alpha\) or \(\beta\)) spin coordinate \(\omega\), and the set of space-spin coordinates \(x=\{r, \omega\}\). We will also change our notation for orbitals from \(\phi(r)\), a spatial orbital, to \(X(x)\), a spin orbital. Then, with the full set of coordinates, the Hartree Product becomes:

\[
\Psi_{HF}(x_1, x_2 \ldots \ldots x_N) = X_1(x_1)X_2(x_2) \ldots \ldots X_N(x_N)
\]

This wavefunction does not satisfy the antisymmetry principle!
1.2.2 Slater Determinants

For a two-electron system we can satisfy the antisymmetry principle by a wavefunction like:

\[ \Psi(x_1, x_2) = \frac{1}{\sqrt{2}} \left[ X_1(x_1)X_2(x_2) - X_1(x_2)X_2(x_1) \right] \quad (5) \]

This satisfies the antisymmetry requirement for any choice of orbitals \( X_1(x) \) and \( X_2(x) \).

We can generalize the above solution to \( N \) electrons by using determinants. In the two electron case, we can rewrite the above functional form as :

\[ \Psi(x_1, x_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} X_1(x_1) & X_2(x_1) \\ X_1(x_2) & X_2(x_2) \end{vmatrix} \quad (6) \]

Now the generalization to \( N \) electrons is then easy to see, it is

\[ \Psi = \frac{1}{\sqrt{N}} \begin{vmatrix} X_1(x_1) & X_2(x_1) & \ldots & X_N(x_1) \\ X_1(x_2) & X_2(x_2) & \ldots & X_N(x_2) \\ \vdots & \vdots & \ddots & \vdots \\ X_1(x_N) & X_2(x_N) & \ldots & X_N(x_N) \end{vmatrix} \quad (7) \]

A determinant of spin orbitals is called a Slater determinant after John Slater. An interesting consequence of this functional form is that the electrons are all indistinguishable.
1.2.3 Simplified Notation for the Hamiltonian

We define a one-electron operator as follows

$$h(i) = \frac{1}{2} \nabla_i^2 - \sum_{\A} \frac{Z_{\A}}{r_{i\A}}$$  \hspace{1cm} (8)$$

and a two-electron operator $V(i, j)$ as

$$V(i, j) = \frac{1}{r_{ij}}$$ \hspace{1cm} (9)$$

Now we can write the electronic Hamiltonian much more simply, as

$$\hat{H}_{el} = \sum_i h(i) + \sum_{i<j} V(i, j) + V_{NN}$$  \hspace{1cm} (10)$$

Since $V_{NN}$ is just a constant for the fixed set of nuclear coordinates $\{R\}$, we will ignore it for now (it doesn't change the eigenfunctions, and only shifts the eigenvalues).

1.2.4 Energy Expression

Now we have a form for the wavefunction and a simplified notation for the Hamiltonian. Now the Hartree-Fock wavefunction will have the form of a Slater determinant, and that the energy will be given by the usual quantum mechanical expression (assuming the wavefunction is normalized):

$$E_{el} = (\Psi / \hat{H}_{el} / \Psi)$$ \hspace{1cm} (11)$$
Now, we can re-write the Hartree-Fock energy $E_{el}$ in terms of integrals of the one- and two-electron operators:

$$E_{HF} = \sum_i <i || h || i> + \frac{1}{2} \sum_{ij} [ii || jj - jj || ii]$$  \hspace{1cm} (12)

where the one electron integral is

$$<i || h || j> = \int dx_i X_i(x_i) h(r_i) X_j(x_j)$$  \hspace{1cm} (13)

and a two-electron integral (Chemists' notation) is

$$(ij || ki) = \int dx_1 dx_2 X_i^*(x_1) X_j(x_2) \frac{1}{r_{12}} X_k^*(x_2) X_j(x_2)$$  \hspace{1cm} (14)

There exist efficient computer algorithms for computing such one- and two-electron integrals.

1.2.5 The Hartree-Fock Equations

Again, the Hartree-Fock method seeks to approximately solve the electronic Schrödinger equation, and it assumes that the wavefunction can be approximated by a single Slater determinant made up of one spin orbital per electron. Since the energy expression is symmetric, the variational theorem holds, and the Slater determinant. We can accomplish this by Lagrange's method of undetermined multipliers, where we employ a functional defined as:

$$\mathcal{F} \left[ \{X_i\} \right] = E_{HF} \left[ \{X_i\} \right] - \sum_{ij} \epsilon_{ij} \left( <i || j> - \delta_{ij} \right)$$  \hspace{1cm} (15)

where $\epsilon_{ij}$ are the undetermined Lagrange multipliers and $<i||j>$ is the overlap between spin orbitals i and j, i.e.,
\[ <i/f> = \int x_i^*(x) x_j(x) \, dx \]  \hspace{1cm} (16)

Setting the first variation \( \delta \mathcal{L} = 0 \), we eventually arrive at the Hartree-Fock equations defining the orbitals:

\[
h(x_i) X_i(x_i) + \sum_{j \neq i} \left[ \int dx_2 \left| X_j(x_2) \right|^2 r_{12}^{-1} \right] X_i(x_1) - \sum_{j \neq i} \left[ \int dy_2 \right. \left. X_j^*(y_2) x_2(x_2) r_{12}^{-1} \right] X_j(x_i) = \varepsilon_i X_i(x_i) \]  \hspace{1cm} (17)

where \( \varepsilon \) is the energy eigenvalue associated with orbital \( X_i \).

The Hartree-Fock equations can be solved numerically (exact Hartree-Fock), or they can be solved in the space spanned by a set of basis functions (Hartree-Fock-Roothan equations). In either case, the solutions depend on the orbitals. Hence, we need to guess some initial orbitals and then refine our guesses iteratively. For this reason, Hartree-Fock is called a self-consistent-field (SCF)\(^{11,12}\) approach.

The first term above in square brackets,

\[
\sum_{j \neq i} \left[ \int dx_2 \left| X_j(x_2) \right|^2 r_{12}^{-1} \right] X_i(x_1) \]  \hspace{1cm} (18)

gives the Coulomb interaction of an electron in spin orbital \( X_i \) with the average charge distribution of the other electrons. This is called the Coulomb term, and it is convenient to define a Coulomb operator as

\[
J_i(x_1) = \int dx_2 \left| X_j(x_2) \right|^2 r_{12}^{-2} \]  \hspace{1cm} (19)

which gives the average local potential at point \( x_1 \) due to the charge distribution from the electron in orbital \( X_i \).

The other term in brackets in Eq. (17) is harder to explain and does not have a simple classical analog. It arises from the antisymmetry requirement of the wavefunction. It looks much like the Coulomb term,
except that it switches or exchanges spin orbitals $X_i$ and $X_i$. Hence, it is called the *exchange term*:

$$\sum_{j \neq i} \int dx_2 X_j^*(x_2)X_j(x_2) r_{ij}^{-2} X_i(x_1)$$  \hspace{1cm} (20)$$

We can define an exchange operator in terms of its action on an arbitrary spin orbital $X_i$:

$$X_j(x_1)X_j(x_1)=\left[ \int dx_2 X_j^*(x_2) r_{ij}^{-1} X_j(x_2) \right] X_j(x_1)$$  \hspace{1cm} (21)$$

In terms of these Coulomb and exchange operators, the Hartree-Fock equations become considerably more compact.

$$\left[ h(x_1) + \sum_{j \neq i} J_{j}(x_1) - \sum_{j \neq i} X_j(x_1) \right] X_i(x_1) = \varepsilon_i X_i(x_1)$$  \hspace{1cm} (22)$$

It is clear that the Hartree-Fock equations are eigenvalue equations. If we realize that

$$\left[ J_{j}(x_1) - X_j(x_1) \right] X_i(x_1) = 0$$  \hspace{1cm} (23)$$

We remove the restrictions $j \neq i$ in the summations, and we can introduce a new operator, the *Fock operator*, as

$$f_j(x_1) = h_j(x_1) + \sum_{j} J_{j}(x_1) - K_j(x_1)$$  \hspace{1cm} (24)$$

And now the Hartree-Fock equations are just

$$f_j(x_1) X_j(x_1) = \varepsilon_i X_i(x_1)$$  \hspace{1cm} (25)$$
Introducing a basis set that transforms the Hartree-Fock equations into the Roothaan equations. Denoting the atomic orbital basis functions as $X$, we have the expansion

$$X_i = \sum_{\mu=1}^{K} C_{\mu i} \overline{X}_{\mu}$$  \hspace{1cm} (26)$$

for each spin orbital $i$. This leads to

$$f(x_i) \sum_v C_{vi} X_v(x_i) = \varepsilon_i X_i(x_i) \sum_v C_{vi} \overline{X}_v(x_i)$$  \hspace{1cm} (27)$$

This can be simplified by introducing the matrix element

$$S_{\mu v} = \int dx_1 \overline{X}_{\mu}(x_1) \overline{X}_v(x_1)$$  \hspace{1cm} (28)$$

$$F_{\mu v} = \int dx_1 \overline{X}_{\mu}(x_1) F(x_1) \overline{X}_v(x_1)$$  \hspace{1cm} (29)$$

Now the Hartree-Fock-Roothaan equations can be written in matrix form as:

$$\sum_v F_{\mu v} C_v = \varepsilon_i \sum_v S_{\mu v} C_v$$  \hspace{1cm} (30)$$

or even more simply as matrices

$$F C = \varepsilon S C$$  \hspace{1cm} (31)$$

where $\varepsilon$ is a diagonal matrix of the orbital energies $\varepsilon$. This is like an eigenvalue equation except for the overlap matrix $S$. One performs a transformation of basis to go to an orthogonal basis to make $S$ vanish. Since $F$ depends on it's own solution (through the orbitals), the process is done iteratively. This is why the solution of the Hartree-Fock-Roothaan equations are often called the self-consistent-field procedure.
1.3 Density-functional theory

This section describes the remarkable theorems of density-functional theory (DFT)\(^{(13)}\), which allow us to find ground-state properties of a system without dealing directly with the many-electron state \(\psi\). We deal with a system of \(N\) electrons moving in a static potential, and adopt a conventional normalisation in which \((\psi/\psi) = N\).

1.3.1 The Hohenberg-Kohn theorems

As a result of the Born-Oppenheimer approximation, the Coulomb potential arising from the nuclei is treated as a static external potential \(V_{\text{ext}}(r)\)

\[
V_{\text{ext}}(r) = -\sum_{a} \frac{Z_{a}}{|r-r_{a}|}
\]  

(32)

We define the remainder of the electronic Hamiltonian as \(F\):

\[
F = -\frac{1}{2} \sum_{i} \nabla_{i}^{2} + \frac{1}{2} \sum_{i \neq j} \frac{1}{|r_{i}-r_{j}|}
\]  

(33)

such that \(H = F + V_{\text{ext}}\) where

\[
V_{\text{ext}} = \sum_{i} V_{\text{ext}}(r_{i})
\]  

(34)

\(F\) is the same for all \(N\)-electron systems, so that the Hamiltonian, and hence the ground-state \((\psi_{0})\), are completely determined by \(N\) and \(V_{\text{ext}}(r)\). The ground-state \((\psi_{0})\) for this Hamiltonian gives rise to a ground-state electronic density \(n_{0}(r)\)

\[
n_{0}(r) = (\Psi_{0}|n|\Psi_{0}) = \int \prod_{i=2}^{N} dr_{i} |\Psi_{0}(r, r_{2}, r_{3}, \ldots, r_{N})|^{2}
\]  

(35)
Thus the ground-state ($\psi_0$) and density $n_0(r)$ are both functionals of the number of electrons $N$ and the external potential $V_{\text{ext}}(r)$. Density-functional theory, introduced in 1964 by Hohenberg and Kohn,$^{(14)}$ makes two remarkable statements.

- The external potential $V_{\text{ext}}(r)$ is uniquely determined by the corresponding ground-state electronic density, to within an additive constant.
- For all $v$-representable densities $n(r) \rightarrow E_v[N] > E_0$ where $E_0$ is now the ground-state energy for $N$ electrons in the external potential $V(r)$.

Thus the problem of solving the Schrödinger equation for non-degenerate ground-states can be recast into a variational problem of minimising the functional $E_v[n]$ with respect to $v$-representable densities. It should be noted that simple counter-examples of $v$-representable densities have been found$^{(15,16,17)}$, but this restriction and the non-degeneracy requirement are overcome by the constrained search formulation.

1.3.2 The constrained search formulation

Following Levy$^{(18,19)}$ a functional of the density $n(r)$ for the operator $F$ is defines as:

$$F[n]=\min_{\Psi \rightarrow n} \langle \Psi | F | \Psi \rangle$$

(36)

i.e. the functional takes the minimum value of the expectation value with respect to all states ($\psi$) which give the density $n(r)$. For a system with external potential $V(r)$ and ground-state ($\psi$) with energy $E_0$, consider a
state \( \langle \psi_{\text{in}} \rangle \), an N-electron state which yields density \( n(r) \) and minimises \( F[n] \). Define \( E_v[n] \) as:

\[
E_v[n] = F[n] + \int dr \, n(r) V(r) = \langle \Psi_{\text{in}} | (F + V) | \Psi_{\text{in}} \rangle
\]

but since \( H = F + V \), by the variational principle one can obtain

\[
E_v[n] \geq E_0
\]

with equality only if \( \langle \psi_{\text{in}} \rangle = \langle \psi_0 \rangle \). This holds for all densities which can be obtained from an N-electron wave-function (N-representable). But from the definition of \( F[n] \) Eq. (36) we must also have

\[
F[n_0] \leq \langle \psi_0 | F | \psi_0 \rangle
\]

since \( \langle \psi_0 \rangle \) must be one of states which yields \( n_0(r) \). Adding \( \int dr \, n_0(r) V(r) \) gives

\[
E_v[n_0] \leq E_0
\]

which when combined with Eq. (38) gives the desired result that

\[
E_v[n] \geq E_v[n_0] = E_0
\]

Thus the ground-state density \( n_0(r) \) minimises the functional \( E_v[n] \) and the minimum value is the ground-state electronic energy. The requirements of N-representability are much weaker and satisfied by any well-behaved density, indeed the only condition is proper differentiability i.e. that the quantity \( \int dr |\nabla n^2(r)|^2 \) is real and finite.
1.3.3 Exchange and correlation

The remarkable results of density-functional theory are the existence of the universal functional $F[n]$, which is independent of the external potential, and that instead of dealing with a function of $3N$ variables (the many-electron wave-function) we can instead deal with a function of only three variables (the density). The complexity of the problem has thus been much reduced, and we note here that this complexity now scales linearly with system-size $N$, so that quantum-mechanical calculations based on density-functional theory can in principle be performed with an effort which scales linearly with system-size.

The exact form of the universal functional $F[n]$ is unknown. The Thomas-Fermi functional\textsuperscript{(20,21)},

$$F_{TF}[n]=\frac{3}{10}(3\pi^2)^{\frac{2}{3}}\int dr\frac{5}{n^3}(r)+\int dr\,dr'\frac{n(r)n(r')}{|r-r'|}$$

(42)

can, be viewed as a tentative approximation to this universal functional, but fails to provide even qualitatively correct predictions for systems other than isolated atoms although recent, more accurate developments have led to the implementation of linear-scaling orbital-free methods for nearly-free electron metals.

The failure to find accurate expressions for the density-functional is a result of the complexity of the many-body problem which is at the heart of the definition of the universal functional. For the electron gas, a system of many interacting particles, the effects of exchange and correlation are crucial to an accurate description of its behavior. In a non-interacting system, the antisymmetry of the wave-function requires that particles
with the same spin occupy distinct orthogonal orbital, and this results in the particles becoming spatially separated. In an interacting system such as the electron gas in which all the particles repel each other, exchange will thus lead to a lowering of the energy. Moreover, the interactions cause the motion of the particles to become correlated to further reduce the energy of interaction. Thus it is impossible to treat the electrons as independent particles. These effects are completely neglected by the Thomas-Fermi model, and must in part account for its failure, the other source of error being the local approximation for the kinetic energy.

1.3.4 The Kohn-Sham equations

In order to take advantage of the power of DFT without sacrificing accuracy (i.e. including exchange and correlation effects) we follow the method of Kohn and Sham\(^{22}\) to map the problem of the system of interacting electrons onto a fictitious system of non-interacting "electrons". The variational problem for the Hohenberg-Kohn density-functional, introducing a Lagrange multiplier \(\mu\) to constrain the number of electrons to be \(N\) is given as:

\[
\delta[F[n]] + \int dr V_{ext}(r)n(r) - \mu \left( \int dr n(r) - N \right) = 0
\]  

(43)

Kohn and Sham separated \(F[n]\) into three parts

\[
F[n] = T_B[n] = \frac{1}{2} \int dr dr' \frac{n(r)n(r')}{|r-r'|} + E_{xc}[n]
\]  

(44)

in which \(T_B[n]\) is defined as the kinetic energy of a non-interacting gas with density \(n(r)\) (not the same as that of the interacting system, although we might hope that the two quantities were of the same order of
magnitude), the second term is the classical electrostatic (Hartree) energy and the final term is an implicit definition of the exchange-correlation energy which contains the non-classical electrostatic interaction energy and the difference between the kinetic energies of the interacting and non-interacting systems. The aim of this separation is that the first two terms can be dealt with simply, and the last term, which contains the effects of the complex behaviour, is a small fraction of the total energy and can be approximated well. Using this separation, Eq. (43) can be rewritten:

$$\frac{\delta T_{v}^{[n]}}{\delta \rho(r)} + V_{KS}(r) = \mu$$

(45)

in which the Kohn-Sham potential $V_{KS}(r)$ is given by

$$V_{KS}(r) = \int dr' \frac{n(r')}{|r-r'|} + V_{u}(r) + V_{aw}(r)$$

(46)

and the exchange-correlation potential $V_{XC}(r)$ is

$$V_{XC}(r) = \frac{\delta E_{xc}^{[n]}}{\delta \rho(r)}$$

(47)

The crucial point to note here is that Eq. (45) is precisely the same equation which would be obtained for a non-interacting system of particles moving in an external potential $V_{KS}(r)$. To find the ground-state density $n_{0}(r)$ for this non-interacting system we simply solve the one-electron Schrödinger equations:

$$\left[ -\frac{1}{2} \nabla^{2} + V_{KS}(r) \right] \Psi_{i}(r) = \varepsilon_{i} \Psi_{i}(r)$$

(48)
for 1/2N single-particle states \( \psi_i \) with energies \( \epsilon_i \), constructing the density from

\[
n(r) = 2 \sum_{i=1}^{N/2} |\Psi_i(r)|^2
\]

(49)

(the factor 2 is for spin degeneracy, assuming the orbitals are singly-occupied) and the non-interacting kinetic energy \( T_B[n] \) from

\[
T_B[n] = -\sum_{i=1}^{N/2} \int dr \nabla \psi_i(r) \nabla^2 \psi_i(r)
\]

(50)

Since the Kohn-Sham potential \( V_{KS}(r) \) depends upon the density \( n(r) \) it is necessary to solve these equations self-consistently i.e. having made a guess for the form of the density, the Schrödinger equation is solved to obtain a set of orbitals \( \{ \psi_i(r) \} \) from which a new density is constructed, and the process repeated until the input and output densities are the same. In practice there is no problem converging to the ground-state minimum because of the convex nature of the density-functional.

The energy of the non-interacting system, the sum of one-electron eigenvalues, is

\[
2 \sum_{i=1}^{N/2} \epsilon_i = T_B[n] + \int dr \ n(r) V_{KS}(r)
\]

\[
= T_B[n] + \int dr \ dr' \frac{n(r) n(r')}{|r-r'|} + \int dr \ n(r) V_{KS}(r) + \int dr \ n(r) V_{EXT}(r)
\]

(51)

which, compared to the interacting system, double-counts the Hartree energy and over-counts the exchange-correlation energy so that the interacting energy is
\[ E = 2 \sum_{\alpha \beta} \epsilon_{\alpha} - \frac{1}{2} \text{tr} \left[ \frac{n(r)n(r')}{|r-r'|} \right] - \int dr n(r) V_{\text{xc}}(r) + E_{\text{xc}}[n] \]  \hspace{1cm} (52)

Direct solution of the Schrödinger equation for the extended non-interacting orbitals \( \psi_i(r) \) requires a computational effort which scales as the cube of the system-size, due to the cost of diagonalising the Hamiltonian or orthogonalising the orbitals, whereas the original complexity of finding a minimum of the Hohenberg-Kohn functional only required an effort which scaled linearly with. Thus a linear-scaling method must modify this Kohn-Sham scheme.

1.3.5 The local density approximation

The results so far are exact, provided that the functional form of \( \text{Exc}[n] \) is known. The problem of determining the functional form of the universal Hohenberg-Kohn density functional has now been transferred to this one term, and therefore this term is not known exactly. Remarkably, it is possible to make simple approximations for the exchange-correlation energy which work extremely well, and the simplest of these, which is the approximation adopted in this work, is the local density approximation (LDA).\(^{23}\)

In the LDA, the contribution to the exchange-correlation energy from each infinitesimal volume in space, \( dr \), is taken to be the value it would have if the whole of space were filled with a homogeneous electron gas with the same density as is found in \( dr \) i.e.

\[ E_{\text{xc}}[n] = \int dr \epsilon_{\text{xc}}(n(r)) n(r) \]  \hspace{1cm} (53)
where $\varepsilon_{XC}(n(r))$ is the exchange-correlation energy per electron in a homogeneous electron gas of density $n(r)$. The exchange-correlation potential $V_{XC}(r)$ then takes the form

$$V_{XC}(r) = \frac{\delta E_{xc}[n]}{\delta n(r)} = \varepsilon_{xc}^{W}(n(r)) + n(r) \frac{d \varepsilon_{xc}^{W}(n)}{dn} \bigg|_{n=n(r)} \quad (54)$$

The exchange-correlation energy for the homogeneous electron gas has been calculated by Ceperley and Alder\cite{24} using Monte Carlo methods and in this work we use a parameterisation by Perdew and Zunger\cite{25}. The LDA is exact in the limit of slowly-varying densities, however, the density in systems of interest is generally rapidly varying, and the LDA would appear to be a crude approximation in these cases. Its use is justified \textit{a posteriori} by its surprising success at predicting physical properties in real systems. This success may be due in part to the fact that the sum rule for the exchange-correlation hole, which must be obeyed by the real functional, is reproduced by the LDA\cite{26}. We can connect the interacting and non-interacting systems using a variable coupling constant $\lambda$ which varies between 0 and 1. We replace the Coulomb interaction by

$$\frac{\lambda}{|r-r'|}$$

and vary $\lambda$ in the presence of an external potential $V_\lambda(r)$ so that the ground-state density for all values of $\lambda$ is the same\cite{28}. The Hamiltonian is therefore

$$H_\lambda = -\frac{1}{2} \sum_r V_i^2 + \frac{1}{2} \sum_{j\neq i} \frac{1}{|r_i-r_j|} + V_{\text{ext}} + V_\lambda \quad (55)$$
The exchange-correlation hole \( n_{\text{XC}}(r, r') \) is then defined in terms of a coupling-constant integration of the pair correlation function \( g(r, r'; \lambda) \) of the system with density \( n(r) \) and scaled Coulomb interaction:

\[
n_{\text{YY}}(r, r') = n(r') \int_0^1 d\lambda [g(r, r'; \lambda) - 1]
\]  

(56)

The exchange-correlation energy can then be expressed in the form of a classical electrostatic interaction between the density \( n(r) \) and the hole density \( n_{\text{XC}}(r, r') \):

\[
E_{\text{MC}}[n] = \frac{1}{2} \int dr \, dr' \frac{n(r)n_{\text{YY}}(r, r')}{|r - r'|}
\]

(57)

The sum rule follows from the definition of the pair correlation function

\[
\int dr' n_{\text{YY}}(r, r') = -1
\]

(58)

which is interpreted by saying that the exchange-correlation hole excludes one electron as expected. It can also be shown that the exchange-correlation energy depends only weakly on the detailed shape of the exchange-correlation hole\(^{[28]}\), and these two facts account, at least in part, for the success of the LDA. This view is supported by the fact that improvements to the LDA involving gradient expansions show no consistent improvement unless they enforce the sum rule obeyed by the LDA.

1.4 Density-functional theory and the Kohn-Sham equations

The calculation of the many-body wave function of a system of interacting electrons is a formidable task which can only be carried out and is only meaningful for systems with a few tens of electrons. If
observable for larger systems are to be determined, the calculation of the many-body wave function has to be avoided. One possibility is to write the desired quantities as functional of the electronic density, a function of just three variables, $r_x$, $r_y$, $r_z$. A very early attempt along these lines is the Thomas-Fermi theory\textsuperscript{[20]}, a modern and theoretically rigorous approach is density-functional theory (DFT). Within DFT usually the Kohn-Sham (KS) equations are utilized which describe independent particles moving in an effective potential. Thus DFT provides with the KS equations a theoretically sound procedure to map the real system of interacting electrons onto a fictitious system of non-interacting so-called Kohn-Sham electrons. In this way the KS equations provide a powerful tool for the numerical determination of the electronic ground state of many-electron systems.

Since the electron-electron interaction is known (Coulomb potential), the Hamilton operator of a quantum-mechanical many-electron system is completely determined once the external potential $V_{\text{ext}}(r)$ is specified in which the electrons move. From a very fundamental point of view the problem is therefore solved, leaving only the "technical detail" of actually computing the solution of the Schrodinger equation. The theorem of Hohenberg and Kohn (HK), which is the foundation of density-functional theory, focuses on the relationship between $V_{\text{ext}}(r)$ and the electronic density $n(r)$ of the ground state. The theorem states that there exists a one-to-one mapping between $V_{\text{ext}}(r)$ and $n(r)$. In order to fully specify an electronic system it is therefore equivalent to determine either $V_{\text{ext}}(r)$ or $n(r)$.

$V_{\text{ext}}(r)$ be an arbitrary external potential. It then holds:
(a) For a non-degenerate ground state \( \psi \) of the system the external potential \( V_{\text{ext}}(r) \) is determined, within a trivial additive constant, as a functional of the electronic density \( n(r) \).

(b) Given an external potential \( V_{\text{ext}}(r) \), the correct ground-state density \( n(r) \) minimizes the ground-state energy \( E_0 \), which is a functional uniquely determined by \( n(r) \). It holds.

\[
E_0 \leq E_V [n] \tag{59}
\]

where \( n(r) \) is any trial density fulfilling \( n(r) \geq 0 \) and \( \int d^3 r n(r) = N \), \( N \) being the number of electrons in the system.

The theorem which has a remarkable short proof guarantees the existence of an energy functional \( E[n] \) that reaches its minimum for the correct density \( n(r) \) yet, gives no explicit prescription for its construction. In order to determine \( E[n] \) it is useful to separate the various known contributions to the total energy, like \( T_8[n] \), the kinetic energy of a non-interacting electron gas, \( E_{\text{ext}}[n] \), the classical Coulomb energy of the electrons moving in the external potential \( V_{\text{ext}}(r) \), and \( E_{\text{Coul}}[n] \), the classical energy due to the mutual Coulomb interaction of the electrons:

\[
E[n(r)] = T_8[n(r)] + E_{\text{ext}} [n(r)] + E_{\text{Coul}} [n(r)] + E_{\text{xc}}[n(r)] \tag{60}
\]

The last term \( E_{\text{xc}} [n] \) contains the quantum-mechanical exchange and correlation energy and in principle the difference between the true kinetic energy, \( T[n] \), and \( T_8[n] \), the kinetic energy of the gas of non-interacting KS-electrons. But since this difference is very small it is typically neglected.

Due to the second part of the HK theorem, namely that the total energy is minimized by the true ground-state density, the variational
principle can now be utilized. With the standard functional derivatives and the additional definition of the so-called exchange correlation potential.

\[ V_{xc}(r) = \frac{\delta E_{xc}[n(r)]}{\delta n(r)} \bigg|_{n(r)=n(r)} \]  

(61)

the following set of equations

\[ \left[ -\frac{\hbar^2}{2m} \nabla^2 + V_{\text{eff}}(r) \right] \Psi_i(r) = \varepsilon_i \Psi_i(r) \]  

(62)

where the effective potential as a functional of the electronic density is given by

\[ V_{\text{eff}}(r) = V_{\text{eff}}[n(r)] = V_{\text{cv}}(r) + e^2 \int d^3r' \frac{n(r')}{|r - r'|} + V_{xc}[n(r)] \]  

(63)

and the electronic density as

\[ n(r) = 2 \sum_{i=1}^{N} |\Psi_i(r)|^2 \]  

(64)

Formally the KS equations describe a system of non-interacting particles. This makes the KS equations so easy to solve. However, since the KS electrons move in an effective potential which is set up by the other electrons, many-body correlation effects are considered within the KS equation. In fact, the KS equations give an exact description of the many-electron system since up to this point no approximations have been made.

The approximations enter in the expression for the unknown exchange-correlation functional \( E_{\text{xc}} \). A widely used approach is the local-density approximation (LDA). It is assumed that the density of an
inhomogeneous system can be locally described by a homogeneous electron gas. A homogeneous electron gas is fully specified by its electronic particle density \( n \) which is often expressed in terms of the corresponding Wigner-Seitz radius \( r_s \).

\[
T_s = \left( \frac{3}{4\pi n} \right)^{\frac{1}{3}}
\]  

(65)

Within the LDA the functional for the exchange-correlation energy, \( E_{xc} \) can be written as

\[
F_{xc} [n] = \int d^3 r \{ n(r) \in \mathcal{W} \} \{ n(r) \} \]

(66)

where \( \epsilon_{xc} \) is the exchange-correlation energy per particle of a homogeneous electron gas of density \( n \). From the last equation the exchange-correlation potential can be further evaluated. The functional derivative can be simplified to an ordinary derivative.

\[
\frac{V_{xc}}{\operatorname{d}n} = \frac{\delta F_{xc}}{\operatorname{d}n} = \frac{d}{dn} \{ n(r) \in \mathcal{W} \} \{ n(r) \}
\]

(67)

In the next step, the exchange-correlation potential is split into its exchange part \( V_x \) and a correlation part \( V_c \).

\[
V_{xc}(T_s) = n_x(r_s) + v_c(r_s)
\]

(68)

Wigner and Seitz showed within the Thomas-Fermi model that \( v_x \) can be approximated by (here and in the following Hartree atomic units are used)

\[
n_x(r_s) = -\left( \frac{9}{4\pi^2} \right)^{\frac{1}{3}} \left( \frac{1}{T_s} \right)^{\frac{1}{3}} \Rightarrow n_x(n) = -\left( \frac{3}{\pi} \right)^{\frac{1}{3}}
\]

(69)
The situation is more difficult for the correlation part. However, there are accurate values for $\varepsilon_c(n)$ available which stem from quantum Monte Carlo calculations by Ceperley and Alder\cite{24}; a widely used parametrization of these data is due to Perdew and Zunger\cite{25}. Finally, the resulting $v_c$ is

$$V_c(r_s) = A \ln r_s + \left( \frac{B}{3} - \frac{A}{3} \right) \frac{2}{3} C r_s \ln r_s + \frac{1}{3} (2D - C) r_s, \quad r_s < 1 \quad (70)$$

and

$$V_c(r_s) = \frac{\gamma}{1 + \sqrt{\beta_1 T_s + \beta_2 r_s}} \frac{1 + \frac{7}{6} \beta_1 \sqrt{T_s} + \frac{4}{3} \beta_2 r_s}{1 + \sqrt{\beta_1 T_s + \beta_2 r_s}}, \quad r_s \geq 1 \quad (71)$$

with numerical parameters $\gamma = -0.1423$, $\beta_1 = 1.0529$, $\beta_2 = 0.3334$, $A = 0.0311$, $B = -0.048$, $C = 0.0020$ and $D = -0.0116$.

With the best functionals available today which are much more complicated than the one presented above the total energy can be calculated to within 2 kcal/mol ($\approx 0.09$eV/atom). This value is about a factor of 2 worse than the accuracy achieved with quantum chemical calculations (configuration interaction, CI) and it is assumed that it will not be improved essentially in the future. However, geometries determined within DFT achieve an accuracy which is comparable to those of CI calculations.
Reference:

4. Most of this work was accomplished at the University of Texas at Austin.