Chapter 2

Theoretical Methods of Quantum Chemistry

2.1 Introduction

Quantum chemistry is (naturally) based on the principles of quantum physics first developed in the 1920's by such pioneers of modern physics as Heisenberg, Bohr, Sommerfeld, Born, Pauli, Schrödinger and Dirac. At its heart quantum chemistry is concerned with finding the eigenfunctions and eigenvalues of the time independent Schrödinger equation[1-3]:

$$\hat{H}\Psi_i = E_i\Psi_i \tag{2.1.1}$$

where $\hat{H}$ is the molecular Hamiltonian operator, Ψ_i is the total wavefunction of the *i*-th electronic state and E_i is the corresponding energy eigenvalue of the system of interest. Evaluation of the total energy of a system is, of course, of great value; in addition, knowledge of the wavefunction enables one to predict many other important properties of the atom, molecule or solid.

In this work, as in the majority of quantum chemical calculations to date, the non-relativistic Hamiltonian operator has been used:

$$\hat{H} = \hat{T}_N + \hat{T}_e + \hat{V}_{NN} + \hat{V}_{ee} + \hat{V}_{Ne} \tag{2.1.2}$$

where $\hat{T}_N$ and $\hat{T}_e$ are the kinetic energy operators for nuclei and electrons respectively:

$$\hat{T}_N = -\frac{1}{2}\sum_{I=1}^{N}\frac{1}{M_I}\nabla_I^2 \tag{2.1.3}$$

$$\hat{T}_e = -\frac{1}{2}\sum_{i=1}^{n}\nabla_i^2 \tag{2.1.4}$$

and $\hat{V}_{NN}$, $\hat{V}_{ee}$ and $\hat{V}_{Ne}$ are the Coulombic potential energy operators representing the inter-nuclear and inter-electron repulsions and the attraction between nuclei and electrons:

$$\hat{V}_{NN} = \sum_{I<J}^{N}\frac{Z_I Z_J}{|\boldsymbol{R}_I - \boldsymbol{R}_J|} \tag{2.1.5}$$

$$\hat{V}_{ee} = \sum_{i<j}^{n} \frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} \tag{2.1.6}$$

$$\hat{V}_{Ne} = -\sum_{I=1}^{N} \sum_{i=1}^{n} \frac{Z_I}{|\boldsymbol{R}_I - \boldsymbol{r}_i|} \tag{2.1.7}$$

In the above equations (and throughout this thesis unless otherwise noted) uppercase letters have been used to denote coordinates and indices relating to nuclei and lowercase for those relating to electrons. Thus N is the total number of nuclei, n is the total number of electrons, M_I, Z_I and $\boldsymbol{R}_I$ are the mass, charge and position vector of the I-th nucleus and $\boldsymbol{r}_i$ is the position vector of the i-th electron. Atomic units have been used here and throughout this work unless indicated otherwise.

Unfortunately, analytic solutions of the Schrödinger equation exist only for the simplest systems which contain no more than two interacting particles. Real systems, that is, atoms, molecules and solids, contain many interacting electrons and nuclei and thus approximations must be made to allow solutions to be found. A basic aspect of quantum chemistry involves the development of approximate yet accurate and efficient methods for calculating wavefunctions and energy eigenvalues. The following sections describe in detail the necessary approximations and the various resulting quantum chemical methodologies.

2.1.1 The Born-Oppenheimer Approximation

The first of these simplifications (for molecules and solids) is the Born-Oppenheimer approximation[4,5]. It is based upon the understanding that, as electrons have much lower masses than nuclei (by at least three orders of magnitude), they move much more quickly and as such, to a good approximation, the electrons can be regarded as being able to respond instantaneously to a change in nuclear geometry. The nuclear and electronic motions are thus said to be "decoupled". The total wavefunction of a given electronic state can therefore be separated into two components: one which describes the nuclear motion, $\{\Theta_K(\boldsymbol{R})\}$ (where each $\Theta_K(\boldsymbol{R})$ represent a ro-vibrational state of the molecule), and one which describes the motion of the electrons, $\psi_R(\boldsymbol{r})$, for a given nuclear configuration, $\boldsymbol{R}$:

$$\Psi(\boldsymbol{R},\boldsymbol{r}) = \Theta(\boldsymbol{R}) \times \psi_R(\boldsymbol{r}) \tag{2.1.8}$$

The electronic Schrödinger equation is thus constructed and solved for a fixed nuclear configuration using the Born-Oppenheimer (clamped nuclei) Hamiltonian:

$$\hat{H}_{BO}\psi_R(\boldsymbol{r}) = E_R\psi_R(\boldsymbol{r}) \tag{2.1.9}$$

$$\left[\hat{T}_e + \hat{V}_{NN}(\boldsymbol{R}) + \hat{V}_{Ne}(\boldsymbol{R}) + \hat{V}_{ee}\right]\psi_R(\boldsymbol{r}) = E_R\psi_R(\boldsymbol{r}) \tag{2.1.10}$$

resulting in the total electronic wavefunction, $\psi_R(\boldsymbol{r})$, and the energy, E_R, of the system for a given nuclear configuration. The energies, $\{E_R\}$, for all possible nuclear configurations form a potential energy surface for the molecule. The nuclear (ro-vibrational) wavefunctions, $\{\Theta_K(\boldsymbol{R})\}$, can in turn be obtained by solving the nuclear Schrödinger equation:

$$\left[\hat{T}_N + E_R\right]\Theta_K(\boldsymbol{R}) = \varepsilon_K\Theta_K(\boldsymbol{R}) \tag{2.1.11}$$

Errors due to the Born-Oppenheimer approximation are generally small and relatively unimportant in chemical applications except in systems where the electronic states are degenerate or near degenerate. In such cases the electronic states are coupled by the nuclear motion and the wavefunction needs to be expressed as

$$\Psi(\boldsymbol{R},\boldsymbol{r}) = \sum_{m,K} c_{mK}\psi_m(\boldsymbol{R},\boldsymbol{r}) \times \Theta_K(\boldsymbol{R}) \tag{2.1.12}$$

where the summation is over the ro-vibrational states and the electronic states which are (near) degenerate. Such situations were not encountered in this work.

2.2 Ab Initio Quantum Chemistry

2.2.1 Many-Electron Wavefunctions

The electronic wavefunction, $\psi_R(\boldsymbol{r})$, introduced above must describe the motion of all of the electrons in the system simultaneously; it is therefore a many-electron wavefunction. In general many-electron, viz. *n*-electron, wavefunctions are constructed as linear superpositions of *n*-electron basis functions (called configuration state functions or CSF's)[6]:

$$\psi_i(\boldsymbol{r}) = \sum_k a_{ki}\phi_k(\boldsymbol{r}) \tag{2.2.1}$$

where $\psi_i(\boldsymbol{r})$ is the electronic wavefunction of *i*-th electronic state of the system (at a particular geometry), $\{\phi_k(\boldsymbol{r})\}$ are the configuration state functions and $\{a_{ki}\}$ are numerical coefficients which can be optimised, as will be described below, so as to obtain as accurate a description of the electronic wavefunctions of the system as possible (within the confines of the finite basis expansion approach).

In the majority of applications the *n*-electron CSF's are constructed as antisymmetrised products of one-electron wavefunctions; these are generally atomic or molecular orbitals. CSF's are often defined as linear combinations of these products, such that a given CSF is spin and symmetry adapted.

The atomic or molecular orbitals are, in turn, constructed from sets of linearly independent one-electron basis functions:

$$\varphi_i = \sum_{p=1}^{m} c_{pi}\chi_p \tag{2.2.2}$$

In most modern applications, these basis functions, $\{\chi_p\}$, are atom-centred Gaussian type functions. The coefficients of the basis functions are also optimised in order to give the best possible description of the atomic or molecular orbitals.

More detailed descriptions of the formulation and optimisation of one- and many-electron wavefunctions are presented in later sections.

2.2.1.1 The Independent Particle Model

Just as the nuclear and electronic motions are separated using the Born-Oppenheimer approximation, the motions of the different electrons in a many-electron wavefunction can also be separated. Thus, to a first approximation, an *n*-electron CSF, $\phi_R\left(\boldsymbol{r}_1,\boldsymbol{r}_2,\boldsymbol{r}_3,...,\boldsymbol{r}_n\right)$, is expressed as a product of one electron spin orbitals:

$$\begin{aligned}\phi_R\left(\boldsymbol{r}_1,\boldsymbol{r}_2,\boldsymbol{r}_3...\boldsymbol{r}_n\right) &= \varphi_1\left(\boldsymbol{r}_1\right)\varphi_2\left(\boldsymbol{r}_2\right)\varphi_3\left(\boldsymbol{r}_3\right)...\varphi_n\left(\boldsymbol{r}_n\right) \\ &= \prod_{i=1}^{n}\varphi_i\left(\boldsymbol{r}_i\right)\end{aligned} \tag{2.2.3}$$

where $\varphi_i\left(\boldsymbol{r}_i\right)$ is the spin orbital of the *i*-th electron with position vector $\boldsymbol{r}_i$.

This is called the independent particle model. It is the original model used by Hartree[7] in his pioneering work on atoms and is potentially exact for systems of non-interacting particles. Electronic wavefunctions formed as products of individual electron spin orbitals are therefore known as Hartree products.

Most systems of interest, however, contain particles (electrons and nuclei) which do interact with each other; in these cases the independent particle model assumes that each electron moves independently of every other in the field of the nuclei and the average field of all the other electrons. While it is immediately clear that this is a much more severe approximation than the Born-Oppenheimer one (neglecting, most significantly, the fact that the total wavefunction must be antisymmetric and also not accounting for the effects of dynamic electron correlation, that is, the fact that individual electrons avoid each other), it allows for significant simplification of the problem of interest. Errors introduced with this approximation can, however, be corrected for at a later stage as described in **Sections 2.2.1.3** and **2.2.3**.

In practice, as noted earlier, accurate spin orbitals, $\{\varphi_i\}$, are obtained by constructing linear combinations of *m* atom-centred Gaussian type basis functions, χ_p, with coefficients, c_{pi}:

$$\varphi_i = \sum_{p=1}^{m} c_{pi}\chi_p \tag{2.2.4}$$

In order to allow for adequate flexibility in the description of the orbitals, *m* must be significantly larger than the number of occupied orbitals in the system. This immediately introduces linearly independent virtual (unoccupied) orbitals (in addition to the occupied ones). Further details on the construction of basis sets are given in **Section 2.4**.

2.2.1.2 Antisymmetry

Electrons are indistinguishable particles and, as such, the properties of the system should be invariant to the interchange of the coordinates of any two electrons. In particular, the probability density, $|\phi(\boldsymbol{r})|^2$, must remain unchanged.

As electrons are fermions (and therefore obey Fermi-Dirac statistics), the many-electron wavefunctions must also be antisymmetric with respect to this interchange of electron coordinates. Applying the permutation operator, $\hat{P}_{ij}$, to an *n*-electron wavefunction, $\phi(\boldsymbol{r})$, should, therefore, result in a change in sign:

$$\begin{aligned}\hat{P}_{ij}\phi\left(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_i,\ldots,\boldsymbol{r}_j,\ldots,\boldsymbol{r}_n\right) &= \phi\left(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_j,\ldots,\boldsymbol{r}_i,\ldots,\boldsymbol{r}_n\right)\\ &= -\phi\left(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_i,\ldots,\boldsymbol{r}_j,\ldots,\boldsymbol{r}_n\right)\end{aligned} \tag{2.2.5}$$

The Hartree products described above are clearly not antisymmetric. They can be made so, however, by the application of an antisymmetriser, $\hat{A}$, defined by:

$$\hat{A} = \frac{1}{\sqrt{n!}}\sum_{P}(-1)^p\,\hat{P} \tag{2.2.6}$$

Here the sum is over all possible permutation operators, $\hat{P}$, for *n* identical particles (including the identity); *p* is the parity of the relevant permutation.

The application of the antisymmetriser to a Hartree product results in a determinant:

$$\begin{aligned}\phi(\boldsymbol{r}) &= \hat{A}\left(\varphi_1(\boldsymbol{r}_1)\varphi_2(\boldsymbol{r}_2)\varphi_3(\boldsymbol{r}_3)...\varphi_n(\boldsymbol{r}_n)\right) \\ &= \frac{1}{\sqrt{n!}}\begin{vmatrix} \varphi_1(\boldsymbol{r}_1) & \varphi_1(\boldsymbol{r}_2) & \varphi_1(\boldsymbol{r}_3) & \cdots & \varphi_1(\boldsymbol{r}_n) \\ \varphi_2(\boldsymbol{r}_1) & \varphi_2(\boldsymbol{r}_2) & \varphi_2(\boldsymbol{r}_3) & \cdots & \varphi_2(\boldsymbol{r}_n) \\ \varphi_3(\boldsymbol{r}_1) & \varphi_3(\boldsymbol{r}_2) & \varphi_3(\boldsymbol{r}_3) & \cdots & \varphi_3(\boldsymbol{r}_n) \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \varphi_n(\boldsymbol{r}_1) & \varphi_n(\boldsymbol{r}_2) & \varphi_n(\boldsymbol{r}_3) & \cdots & \varphi_n(\boldsymbol{r}_n) \end{vmatrix}\end{aligned} \tag{2.2.7}$$

If the orbitals, $\{\varphi_i\}$, are orthonormal, the factor $\frac{1}{\sqrt{n!}}$ ensures that such an antisymmetrised product will be normalised, thus forming an orthonormal set of basis functions.

Such antisymmetrised electronic wavefunctions are generally referred to as Slater determinants after J. C. Slater who was instrumental in their development.[8]

2.2.1.3 Configuration Interaction Wavefunctions

The configuration state functions introduced earlier are usually either single Slater determinants or linear combinations thereof. The set of all possible Slater determinants (constructed by considering all possible arrangements of the electrons amongst the available spin orbitals) therefore forms a set of *n*-electron basis functions for the total electronic wavefunction of the system of interest, $\psi(\boldsymbol{r})$. If the set of one-electron basis functions (and thus the set of atomic or molecular spin orbitals) is complete (that is, infinite), the resulting set of Slater determinants (CSF's) also forms a complete *n*-electron basis set for $\psi(\boldsymbol{r})$. The exact *n*-electron wavefunction can therefore be formulated as:

$$\psi_i(\boldsymbol{r}) = \sum_k a_{ki}\phi_k(\boldsymbol{r}) \tag{2.2.8}$$

This is called the Configuration Interaction (CI) expansion of the wavefunction.[6] In practice, of course, the set of one-electron basis functions is finite and incomplete and thus the configuration interaction expansion is also finite and can only yield an approximation to the true total wavefunction. Even with a finite one-electron basis set, however, the full set of CSF's for a molecular system may still contain far too many Slater determinants for such calculations to be computationally feasible. In most applications, therefore, only a subset of these configurations is used.

For most molecules, especially near their equilibrium geometries, the wavefunction is dominated by a single CSF. In such cases the Schrödinger equation is first solved subject to the approximation that the wavefunction consists of only this determinant. This gives both a reference state wavefunction and a convenient set of optimised one-electron orbitals, $\{\varphi_i\}$, which can be used in the construction of other CSF's. While such single determinant wavefunctions do not account for the effects of electron correlation (as the independent particle model has been applied), extending them by the inclusion of additional terms in the configuration interaction expansion can correct for this deficiency.

Finding solutions of the Schrödinger equation therefore involves finding both the best set of coefficients for the CSF's, $\{a_k\}$, and the optimal set of orbital coefficients, $\{c_{pi}\}$. These coefficients can be obtained by the use of the Variation Principle (described in the next section) or, specifically in the case of the CSF coefficients, by Perturbation Theory[9,10]. **Sections 2.2.2** and **2.2.3** describe in more detail a range of approaches to this problem.

2.2.1.4 The Variation Principle

Given an approximate wavefunction for a system, the corresponding total energy is, by definition, the expectation value of the Hamiltonian operator:

$$E[\psi] = \frac{\langle\psi|\hat{H}|\psi\rangle}{\langle\psi|\psi\rangle} \qquad (2.2.9)$$

The Variation Principle (theorem)[11] states that if the energy is stationary with respect to any arbitrary variation, $\delta\psi$, in the wavefunction, i.e.,

$$\delta E = 0 \tag{2.2.10}$$

then the wavefunction is an eigenfunction of the Hamiltonian:

$$\hat{H}\psi = E\psi \tag{2.2.11}$$

and the lowest eigenvalue, E_0, is an upper bound to the true ground state energy of the system, ε_0:

$$E_0 \geq \varepsilon_0 \tag{2.2.12}$$

Moreover, according to McDonald's theorem[12], the higher eigenvalues, $\{E_i\}$, are upper bounds to the corresponding excited state energies, $\{\varepsilon_i\}$.

The variational flexibility of most approximate wavefunctions is provided by the orbital and CI coefficients $\{c_{pi}\}$ and $\{a_k\}$. Variation of these coefficients can be thought of as mixing or rotation between occupied and virtual orbitals (for c_{pi}'s) or among the CSF's (for a_k's). A "variational" wavefunction, giving the lowest possible energy, is therefore stable under such mixings or rotations.

2.2.2 Hartree-Fock Self Consistent Field Theory[13,14]

As noted earlier, in most typical applications the wavefunction is relatively well described by a single CSF; the first problem is, therefore, to find the energy and wavefunction of this single determinantal reference state. This is readily achieved by the application of the Variation Principle in order to determine the optimal one-electron occupied orbitals for this wavefunction. This leads to Hartree-Fock Self Consistent Field Theory (HF-SCF).

For a single determinantal wavefunction, ϕ, the expectation value of the Hamiltonian is given by:

$$E = \frac{\langle \phi | \hat{H} | \phi \rangle}{\langle \phi | \phi \rangle} \tag{2.2.13}$$

where the (Born-Oppenheimer) Hamiltonian, $\hat{H}$, is expressed in terms of one- and two-electron contributions, as well as nuclear repulsion:

$$\hat{H} = \hat{h}_0 + \sum_i \hat{h}_i + \sum_{i<j} \hat{g}_{ij} \tag{2.2.14}$$

Here $\hat{h}_0$ is the internuclear repulsion term:

$$\hat{h}_0 = V_{NN} = \sum_{I<J} \frac{Z_I Z_J}{|\boldsymbol{R}_I - \boldsymbol{R}_J|} = \sum_{I<J} \frac{Z_I Z_J}{\boldsymbol{R}_{IJ}} \tag{2.2.15}$$

$\hat{h}_i$ is a one-electron term which contains both the kinetic energy of electron i and its Coulombic potential energy in the field of the nuclei:

$$\hat{h}_i = -\frac{1}{2}\nabla_i^2 - \sum_I \frac{Z_I}{\boldsymbol{r}_{iI}} \tag{2.2.16}$$

and $\hat{g}_{ij}$ is a typical inter-electron repulsion term:

$$\hat{g}_{ij} = \frac{1}{\boldsymbol{r}_{ij}} \tag{2.2.17}$$

Thus, when expectation values are taken, the $\hat{h}_0$ term is simply a constant and, with the application of the Slater-Condon rules[15], the expectation value of the one-electron terms simplifies to:

$$E^{(1)} = \sum_{i=1}^{n} \langle \varphi_i | \hat{h} | \varphi_i \rangle \tag{2.2.18}$$

where $\{\varphi_i\}$ are the occupied spin orbitals and $\hat{h}$ is a typical one-electron Hamiltonian operator.

The expectation value of the two-electron terms is thus:

$$\begin{aligned} E^{(2)} &= \sum_{i<j}^{n} \left\{ \left\langle \varphi_i(\boldsymbol{r}_1)\varphi_j(\boldsymbol{r}_2) \right| \hat{g}_{12} \left| \varphi_i(\boldsymbol{r}_1)\varphi_j(\boldsymbol{r}_2) \right\rangle - \left\langle \varphi_i(\boldsymbol{r}_1)\varphi_j(\boldsymbol{r}_2) \right| \hat{g}_{12} \left| \varphi_j(\boldsymbol{r}_1)\varphi_i(\boldsymbol{r}_2) \right\rangle \right\} \\ &= \sum_{i<j}^{n} \left\langle \varphi_i\varphi_j \middle\| \varphi_i\varphi_j \right\rangle \end{aligned} \tag{2.2.19}$$

where the summations are over all occupied spin orbitals.

The two terms that make up $E^{(2)}$ are known as the Coulomb and exchange integrals respectively. Their joint contribution is conveniently written using the notation: $\langle ij \| ij \rangle$, where i stands for the spin orbitals φ_i, etc. The total electron-electron repulsion energy can also be rewritten in terms of one-electron Coulomb and exchange operators ($\hat{J}_i$ and $\hat{K}_i$ for each occupied spin orbital, φ_i). These operators are defined through their action on an arbitrary one-electron function $f(\boldsymbol{r}_1)$:

$$\hat{J}_i f(\boldsymbol{r}_1) = \left[\int \frac{\varphi_i^*(\boldsymbol{r}_2)\varphi_i(\boldsymbol{r}_2)}{r_{12}} d\tau_2 \right] f(\boldsymbol{r}_1) \tag{2.2.20}$$

$$\hat{K}_i f(\boldsymbol{r}_1) = \left[\int \frac{\varphi_i^*(\boldsymbol{r}_2) f(\boldsymbol{r}_2)}{r_{12}} d\tau_2 \right] \varphi_i(\boldsymbol{r}_1) \tag{2.2.21}$$

Thus $E^{(2)}$ can be rewritten as:

$$\begin{aligned} E^{(2)} &= \frac{1}{2} \sum_{i,j}^{n} \langle \varphi_i | \hat{J}_j - \hat{K}_j | \varphi_i \rangle \\ &= \frac{1}{2} \sum_{i}^{n} \langle \varphi_i | \hat{J} - \hat{K} | \varphi_i \rangle \end{aligned} \tag{2.2.22}$$

where $\hat{J}$ and $\hat{K}$ are the total (*n*-electron) Coulomb and exchange operators:

$$\hat{J} = \sum_{i}^{n} \hat{J}_i \tag{2.2.23}$$

$$\hat{K} = \sum_{i}^{n} \hat{K}_i \tag{2.2.24}$$

The total energy can therefore be written as:

$$E = \sum_{i}^{n} \langle \varphi_i | \hat{h} | \varphi_i \rangle + \frac{1}{2} \sum_{i}^{n} \langle \varphi_i | \hat{J} - \hat{K} | \varphi_i \rangle + V_{NN} \tag{2.2.25}$$

As noted in **Section 2.2.1.4**, when the occupied orbitals are fully optimised for a particular system the energy is stationary with respect to mixing between the occupied orbitals, $\{\phi_i\}$, and the unoccupied (virtual) orbitals, $\{\phi_a\}$. The derivative of the energy with respect to this mixing is given by the Brillouin matrix elements[16]:

$$\frac{\partial E}{\partial X_{ai}} = \left\langle \phi \middle| \hat{H} \middle| \phi_i^a \right\rangle \tag{2.2.26}$$

where ϕ_i^a represents a singly substituted determinant obtained by the replacement of an occupied spin orbital, ϕ_i, by an unoccupied orbital, ϕ_a.

Application of the Slater-Condon rules leads to:

$$\begin{aligned}\frac{\partial E}{\partial X_{ai}} &= \langle \varphi_i | \hat{h} | \varphi_a \rangle + \langle \varphi_i | \hat{J} - \hat{K} | \varphi_a \rangle \\ &= \langle \varphi_i | \hat{F} | \varphi_a \rangle\end{aligned} \tag{2.2.27}$$

Thus the condition for stationary energy is

$$\langle \varphi_i | \hat{F} | \varphi_a \rangle = 0 \qquad \forall\, i, a \tag{2.2.28}$$

where the (one-electron) Fock operator, $\hat{F}$, is defined as

$$\hat{F} = \hat{h} + \hat{J} - \hat{K} \tag{2.2.29}$$

Thus the Brillouin matrix elements vanish for self consistent solutions of the Fock eigenvalue equations:

$$\hat{F}\varphi_i = \varepsilon_i \varphi_i \qquad \forall i \tag{2.2.30}$$

where $\{\varepsilon_i\}$ represents the individual orbital energies. The orbitals which satisfy these equations (and thus give a stationary energy for the system) are called the canonical Hartree-Fock SCF orbitals.

It should be noted that the total (*n*-electron) Fock operator is not equivalent to the Hamiltonian operator:

$$\begin{aligned}\hat{F}_{Tot} &= \sum_i \hat{F}(\boldsymbol{r}_i) \\ &= \sum_i \left[\hat{h}(\boldsymbol{r}_i) + \hat{J}(\boldsymbol{r}_i) - \hat{K}(\boldsymbol{r}_i) \right]\end{aligned} \tag{2.2.31}$$

while

$$\begin{aligned}\hat{H} &= \hat{h} + \frac{1}{2}\left(\hat{J} - \hat{K}\right) \\ &= \hat{F}_{Tot} - \frac{1}{2}\left(\hat{J} - \hat{K}\right)\end{aligned} \qquad (2.2.32)$$

Thus the sum of occupied orbital energies, $\sum_i \varepsilon_i$, differs from the total electronic energy, *E*, since the electron-electron repulsion terms are counted twice in the former.

In practice the Hartree-Fock SCF orbitals are found by solving the matrix eigenvalue equations:

$$\boldsymbol{Fc} = \boldsymbol{Sc\varepsilon} \qquad (2.2.33)$$

where ***F*** is the Fock matrix with elements:

$$F_{ij} = \left\langle \chi_i \middle| \hat{F} \middle| \chi_j \right\rangle \qquad (2.2.34)$$

c is the matrix of eigenvectors which determine the SCF orbitals:

$$\boldsymbol{\varphi} = \boldsymbol{\chi c} \qquad (2.2.35)$$

and ***S*** is the overlap matrix with elements:

$$S_{ij} = \left\langle \chi_i \middle| \chi_j \right\rangle \qquad (2.2.36)$$

The matrix eigenvalue equations (2.2.33) are generally known as the Roothaan-Hall[17,18] equations.

2.2.2.1 The Self Consistent Field (SCF) Procedure

Since the Fock operator actually depends on its eigenvectors, $\{\varphi_i\}$ (through the construction of the Coulomb and exchange operators), the Roothaan-Hall equations must be solved using an iterative procedure.

In most implementations of HF-SCF theory this firstly involves making a guess of the coefficient matrix, $\boldsymbol{c}$. This is done by either simply orthogonalising the atomic orbital basis, by diagonalising the one-electron part of the Hamiltonian:

$$\boldsymbol{hc} = \boldsymbol{Sc\varepsilon} \tag{2.2.37}$$

or by utilising a semi-empirical method such as INDO[19] or extended Hückel theory[20].

Secondly the Fock matrix is constructed and then diagonalised by solving the Roothaan-Hall equations. This is most easily done if a unitary transformation is performed in order to orthonormalise the original basis set (so that the overlap matrix becomes the identity). The standard approach is to use the Löwdin orthogonalisation method[21] where the transformation is made using the $\boldsymbol{S}^{-1/2}$ matrix:

$$\boldsymbol{S}^{-1/2}\boldsymbol{F}\boldsymbol{S}^{-1/2}\boldsymbol{S}^{1/2}\boldsymbol{c} = \boldsymbol{S}^{-1/2}\boldsymbol{S}\boldsymbol{S}^{-1/2}\boldsymbol{S}^{1/2}\boldsymbol{c\varepsilon} \tag{2.2.38}$$

which yields:

$$\tilde{\boldsymbol{F}}\tilde{\boldsymbol{c}} = \tilde{\boldsymbol{c}}\boldsymbol{\varepsilon} \tag{2.2.39}$$

where:

$$\tilde{\boldsymbol{F}} = \boldsymbol{S}^{-1/2}\boldsymbol{F}\boldsymbol{S}^{-1/2} \tag{2.2.40}$$

$$\tilde{\boldsymbol{c}} = \boldsymbol{S}^{1/2}\boldsymbol{c} \tag{2.2.41}$$

and the eigenvalues, $\boldsymbol{\varepsilon}$, are (hopefully) a more accurate estimate of the true orbital energies. In the simplest implementation of SCF optimisation the orbitals obtained in a given diagonalisation step are used to construct a new Fock matrix, thus allowing a new set of orbitals to be generated. This process can be iterated until the coefficient matrix is unchanged from one iteration to the next (to within a specified threshold). The orbitals are then said to be "self consistent". In most applications damping and convergence accelerating techniques must be used to ensure reasonably rapid convergence to the final optimised orbitals.[22-24]

The choice of occupied orbitals (for the construction of $\hat{F}$) is a key aspect of the SCF procedure. The application of the Aufbau Principle is often adequate, but in more complex situations a predetermined occupancy may need to be enforced so that the calculations converge to the state of interest.[22]

At convergence the total energy of the system is thus given by:

$$E = E_{orb} - \frac{1}{2}\sum_{i \neq j} \langle ij || ij \rangle \quad (2.2.42)$$

where E_{orb} is the total orbital energy:

$$E_{orb} = \sum_{i} \varepsilon_i \quad (2.2.43)$$

2.2.2.2 Spin Unrestricted Hartree-Fock Theory[25]

SCF theory formulated in terms of atomic or molecular spin orbitals as described above is known as (Spin) Unrestricted Hartree-Fock Theory. In practice this gives a Fock matrix, ***F***, which is block diagonal with respect to the α and β spin orbitals (φ^{α} and φ^{β} or φ and $\overline{\varphi}$ respectively). The Fock operator, $\hat{F}$, can therefore be split into α and β components:

$$\hat{F}^{(\alpha)} = \hat{h} + \hat{J} - \hat{K}^{(\alpha)} \quad (2.2.44)$$

$$\hat{F}^{(\beta)} = \hat{h} + \hat{J} - \hat{K}^{(\beta)} \quad (2.2.45)$$

The non-zero matrix elements of $\hat{J}$, $\hat{K}^{(\alpha)}$ and $\hat{K}^{(\beta)}$ are:

$$\left\langle \varphi_i \left| \hat{J} \right| \varphi_j \right\rangle = \sum_{k^{(\alpha)}} \left\langle \varphi_i \varphi_k^\alpha \left| \varphi_j \varphi_k^\alpha \right.\right\rangle + \sum_{k^{(\beta)}} \left\langle \varphi_i \varphi_k^\beta \left| \varphi_j \varphi_k^\beta \right.\right\rangle \tag{2.2.46}$$

where φ_i and φ_j are (spin) orbitals of the same spin (that is, both α or both β),

$$\left\langle \varphi_i^\alpha \left| \hat{K}^{(\alpha)} \right| \varphi_j^\alpha \right\rangle = \sum_{k^{(\alpha)}} \left\langle \varphi_i^\alpha \varphi_k^\alpha \left| \varphi_k^\alpha \varphi_j^\alpha \right.\right\rangle \tag{2.2.47}$$

$$\left\langle \varphi_i^\beta \left| \hat{K}^{(\beta)} \right| \varphi_j^\beta \right\rangle = \sum_{k^{(\beta)}} \left\langle \varphi_i^\beta \varphi_k^\beta \left| \varphi_k^\beta \varphi_j^\beta \right.\right\rangle \tag{2.2.48}$$

Given that each spin orbital is a product of spatial and spin components; that is,

$$\varphi_i^\alpha = \varphi_i(\boldsymbol{r})\alpha(\boldsymbol{\sigma}) \tag{2.2.49}$$

$$\varphi_i^\beta = \varphi_i(\boldsymbol{r})\beta(\boldsymbol{\sigma}) \tag{2.2.50}$$

where $\varphi_i(\boldsymbol{r})$ is now a spatial orbital and $\alpha(\boldsymbol{\sigma})$ and $\beta(\boldsymbol{\sigma})$ are spin functions with $\boldsymbol{\sigma}$ representing the "spin coordinate", the total wavefunction can be written as an antisymmetrised product of an *n*-electron spatial function, θ, and an *n*-electron spin function, Θ:

$$\begin{aligned} \psi &= \hat{A}\left(\varphi_1\bar{\varphi}_2\varphi_3\bar{\varphi}_4\varphi_5\ldots\right) \\ &= \hat{A}\left[\left(\varphi_1\varphi_2\varphi_3\varphi_4\varphi_5\ldots\right)\left(\alpha\beta\alpha\beta\alpha\ldots\right)\right] \\ &= \hat{A}\left[\theta\left(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots\right)\Theta\left(\boldsymbol{\sigma}_1,\boldsymbol{\sigma}_2,\ldots\right)\right] \end{aligned} \tag{2.2.51}$$

Such a wavefunction will always be an eigenfunction of the $\hat{S}_z$ spin operator as each spin function is itself an eigenfunction, by definition. The wavefunction may not, however, be an eigenfunction of the $\hat{S}^2$ total spin operator; this is because the total spin function, Θ, is not an eigenfunction of $\hat{S}^2$ but rather a linear combination of several spin eigenfunctions which have different eigenvalues.

Nevertheless, because of its simplicity, the UHF procedure is widely used, especially for open shell systems. It is capable of providing a qualitatively correct description of bond dissociation; UHF potential energy surfaces may, however, contain unphysical bifurcation regions. In the region of equilibrium geometries UHF generally performs well, however attention must be paid to the expectation value of $\hat{S}^2$. In this work it was found that in most cases $\langle \hat{S}^2 \rangle$ is close to the desired eigenvalue of $S(S+1)$ (S = ½, 1, 1½ … for open shell doublet, triplet, quartet, etc. systems) but occasionally the deviation is significant due to mixing with states with higher spin (spin contamination). It is possible to obtain a more pure spin state by projection whereby the most serious contaminants are annihilated to give a Projected Unrestricted Hartree-Fock (PUHF) wavefunction[26] which is an (approximate) eigenfunction of $\hat{S}^2$. Unfortunately in some cases this method is inadequate and the resulting wavefunction is still significantly contaminated. A better (although more computationally expensive) alternative is to use a Restricted Hartree-Fock formalism (**Section 2.2.2.4**) or Multiconfigurational SCF theory (**Section 2.2.3.1**).

2.2.2.3 Spin Restricted Closed Shell Hartree-Fock Theory (RHF)

Most stable molecules have singlet ground states, corresponding to closed shell configurations; that is, each spatial orbital is occupied by a pair of electrons with opposite spins. The Hartree-Fock wavefunction can thus be written as:

$$\phi = \hat{A}\left(\varphi_1\bar{\varphi}_1\varphi_2\bar{\varphi}_2 \ldots \varphi_{n/2}\bar{\varphi}_{n/2}\right) \tag{2.2.52}$$

Such wavefunctions are automatically eigenfunctions of $\hat{S}^2$. In addition, the alpha and beta Fock matrices are identical (as the wavefunction and energy are clearly invariant under spin interchange). This means that only one of $\hat{F}^{(\alpha)}$ and $\hat{F}^{(\beta)}$ needs to be evaluated and thus the computational effort involved is approximately halved. Moreover, closed shell RHF calculations generally converge faster than their UHF counterparts. For most singlet state molecules in the neighbourhood of their equilibrium geometries there is, in fact, no distinct UHF solution; that is, UHF calculations converge to the RHF wave function.

2.2.2.4 Spin Restricted Open Shell Hartree-Fock Theory[27]

As noted earlier, UHF theory can sometimes yield wavefunctions with considerable spin contamination. In order to avoid this, Restricted Open Shell Hartree-Fock Theory (ROHF) can be applied; this method has been developed so as to ensure that the resulting wavefunction is an eigenfunction of $\hat{S}^2$.

ROHF theory involves partitioning the orbital space into a subset, *D*, which contains doubly occupied orbitals, a subset, *P*, which contains orbitals which are allowed to be partially occupied and a subset, *V*, which are unoccupied (virtual). When the orbitals are optimised under the SCF procedure, mixing between all three subsets needs to be considered. These three types of mixing (*D/P*, *D/V* and *P/V*) give rise to three different Fock operators between orbitals of different subsets; when the orbitals are fully optimised the energy will be stable with respect to all possible mixings between the subsets. This condition is known as the generalised Brillouin theorem[22]; it corresponds to the appropriate off-diagonal matrix elements of the Fock operators being zero.

Computationally this method is significantly more expensive than the UHF or RHF procedures, largely because ROHF wavefunctions are often difficult to converge. In this work, therefore, it is generally only applied when an earlier UHF calculation has indicated the need for a restricted formalism. While ROHF theory is most readily applied to high spin open shell states, it can be generalised to cover more complex situations such as open shell singlet or state averaged systems.

2.2.3 Electron Correlation

The term "electron correlation" is generally used to describe all effects which are not accounted for by Hartree-Fock theory. This definition was originally proposed by Löwdin[28], who also introduced the concept of the correlation energy, E_{corr}, defined by the equation:

$$E_{corr} = E_{exact} - E_{HF} \tag{2.2.53}$$

Here E_{exact} is the exact non-relativistic energy of the system of interest and E_{HF} is the Hartree-Fock energy. In practice E_{exact} is not known and must be approximated as described below.

There are two major phenomena that contribute to the correlation energy. Non-dynamical correlation is the term used for near-degeneracy effects which are not resolved at the Hartree-Fock level. This usually only occurs in systems for which the highest energy (formally) occupied orbitals are close in energy to the (formally) unoccupied orbitals, resulting in several near-degenerate configurations. In such situations the wavefunction will not be dominated by a single configuration (determinant), and multiconfigurational methods such as MCSCF (see below) must be applied to obtain a good reference state.

While non-dynamical correlation only occurs in special situations, dynamical correlation needs to be considered for all systems. As mentioned earlier, dynamical correlation describes the fact that individual electrons avoid each other. Although the use of a single determinant wavefunction in conjunction with the independent particle model (as for Hartree-Fock SCF Theory) has neglected this effect, it can be corrected for by the inclusion of additional determinants in the wavefunction. Several methods of varying complexity and accuracy have been proposed in order to account for the dynamical correlation effects; these include the configuration interaction method, Møller-Plesset perturbation theory and coupled cluster theory.

Accounting for the correlation of each pair of electrons is naturally quite expensive computationally. In many practical applications, therefore, it is only the correlation of the valence electrons which is explicitly considered while the core electrons are left uncorrelated or "frozen" (the frozen core approximation). The effects of the correlation of the core electrons do need to be considered, however, when high accuracy is required.

2.2.3.1 Multiconfigurational SCF Theory (MCSCF)[29-31]

In Hartree-Fock theory the wavefunction is defined as a single Slater determinant, ϕ. While in many situations such a wavefunction provides an acceptable reference state for more extensive (correlated) calculations, it is inadequate when there are degeneracies or near degeneracies in the valence molecular orbitals. This situation arises particularly for bond breaking reactions, where the occupied and unoccupied orbitals converge in energy as the bond is stretched. In such situations there is a corresponding near-degeneracy amongst the configurations and therefore all near-degenerate Slater determinants, $\{\phi_k\}$, need to be included in the wavefunction in order to properly describe the system:

$$\psi = \sum_k a_k \phi_k \tag{2.2.54}$$

where $\{a_k\}$ are the variational coefficients and the summation is over the subset of configurations which are expected to make a significant contribution to the wavefunction. Thus in MCSCF theory both the configuration interaction coefficients, $\{a_k\}$, and the molecular orbital coefficients, $\{c_{pi}\}$, are simultaneously optimised.

The complete active space SCF (CASSCF) method[30,32] provides a well defined procedure for choosing n-electron configurations in a MCSCF wavefunction. As in ROHF, the orbitals are split into three subsets (spaces):

$$\underbrace{\varphi_1 \cdots \varphi_i}_{\text{inactive}}\ \underbrace{\varphi_{i+1} \cdots \varphi_{i+a}}_{\text{active}}\ \underbrace{\varphi_{i+a+1} \cdots \varphi_{i+a+v}}_{\text{virtual}}$$

where the i inactive orbitals are defined as being doubly occupied, the v virtual orbitals as unoccupied while the a active orbitals have partial occupancy. The relevant configurations are then constructed by considering every possible way (with correct spin and spatial symmetry) of distributing the $n-2i$ active electrons amongst the a active orbitals.

A second order Newton-Raphson type procedure[33] (or an approximate version thereof) is then applied to determine the CI and orbital coefficients such that the generalised Brillouin theorem is satisfied. In other words, on convergence the energy is invariant to rotations between the inactive, active and virtual orbitals.

2.2.3.2 Configuration Interaction (CI)[6]

As outlined in **Section 2.2.1** the full many-electron wavefunction for a system can be expressed in terms of the configuration interaction expansion (Equation (2.2.1)). This CI expansion involves all possible determinants which can be constructed by considering every possible arrangement of the available electrons amongst all the linearly independent molecular orbitals that can be formed from the one particle basis set. For many systems, however, the many-electron wavefunction, ψ, is dominated by a single determinant, ψ_0; in such cases all other configurations can be thought of as a correction, χ, to this reference wavefunction. This correction then accounts for electron correlation.

$$\psi = \psi_0 + \chi \tag{2.2.55}$$

Application of the Hamiltonian operator followed by projection onto the Hartree-Fock reference state gives:

$$E = E_0 + \langle \psi_0 | \hat{H} | \chi \rangle \tag{2.2.56}$$

where E is the total non-relativistic energy of the system and E_0 is the Hartree-Fock reference energy. Thus, according to the definition in Equation (2.2.53), the correlation energy is simply given by:

$$E_{corr} = \langle \psi_0 | \hat{H} | \chi \rangle \tag{2.2.57}$$

This is known as the correlation energy formula.

The correction, χ, can be constructed in a systematic way by generating configurations which correspond to the substitution of 1, 2, …, *n* occupied spin orbitals in the reference determinant by unoccupied spin orbitals:

$$\psi = \psi_0 + \sum_{i,a} a_i^a \phi_i^a + \sum_{\substack{i<j, \\ a<b}} a_{ij}^{ab} \phi_{ij}^{ab} + \ldots \tag{2.2.58}$$

where ϕ_i^a indicates a determinant obtained by single substitutions (*i* substituted by *a*), etc. and $\{a_i^a\}$, $\{a_{ij}^{ab}\}$, ... are the CI coefficients which will be determined either variationally or by perturbation theory. The orbitals ϕ_i^a, ϕ_{ij}^{ab}, … are often referred to as singly, doubly, etc. excited configurations (that is, the electron in orbital *i* has been excited into orbital *a*, etc.). As the one-electron, viz. molecular orbital (MO), basis has already been optimised in the SCF determination of the Hartree-Fock reference state, the CI coefficients might be expected to show rapid convergence. Unfortunately this is not the case in practice; while the individual coefficients of higher than double excitations do systematically decrease in magnitude, their collective energetic contributions converge slowly with the order of the excitation. This is associated with the difficult problem of resolving the electron cusp using wavefunctions that do not explicitly depend on inter-electron coordinates.[34]

Although the full CI expansion formally has up to *n*-fold excitation terms (where *n* is the number of electrons in the system), it can be shown that when E_{corr} is evaluated by the correlation energy formula it is only the double excitation terms which contribute. This is because in the orthonormal SCF MO basis the Brillouin condition (Equation (2.2.28)) applies and, according to the Slater-Condon rules, terms with higher than double excitations have zero Hamiltonian matrix elements with the reference state, ψ_0. Thus

$$\begin{aligned} E_{corr} &= \sum_{\substack{i<j, \\ a<b}} \langle \psi_0 | \hat{H} | \phi_{ij}^{ab} \rangle a_{ij}^{ab} \\ &= \sum_{\substack{i<j, \\ a<b}} \langle ij || ab \rangle a_{ij}^{ab} \end{aligned} \tag{2.2.59}$$

Unfortunately, before E_{corr} can be calculated via this method the coefficients $\{a_{ij}^{ab}\}$ must be known. In the Full Configuration Interaction (full-CI) method the calculation of $\{a_{ij}^{ab}\}$

involves the application of the variational principle to solve the appropriate matrix eigenvalue equations (Equation (2.1.9)) for the full configuration interaction expansion of the wavefunction. This is straightforward in principle but in practice the number of configurations, and thus the computational cost of calculations, rises rapidly with the number of electrons and the size of the MO basis. The computations can be made more efficient by the consideration of spatial and spin symmetry and the application of the Direct CI approach[35,36] (with the Davidson diagonalisation method[37]). Nevertheless, full-CI calculations are still only feasible for small molecules with up to ~ 10 electrons and modest basis sets (up to about double zeta plus polarisation functions quality).

It is therefore common practice to truncate the CI expansion at the double excitation terms, neglecting triple and higher excitations. While this reduces the size of the problem so that it becomes computationally feasible, the resulting solutions are not size extensive, that is, they do not scale correctly with the number of electrons in the system. This is a serious problem, especially in the context of computing molecular binding energies and intermolecular forces. A useful, although very approximate, way to correct for size extensivity is via the Davidson correction:[38]

$$E_{Dav} = E_{corr}\left(1 - a_0^{\ 2}\right) \tag{2.2.60}$$

or via[39]

$$E_{Dav} = E_{corr}\frac{\left(1 - a_0^{\ 2}\right)}{a_0^{\ 2}} \tag{2.2.61}$$

where a_0 is the coefficient of the reference state in the normalised CI expansion. While the variational CI method is important as background theory for other methods such as Møller-Plesset perturbation theory and Coupled Cluster theory, it has not been used extensively in this thesis due to the lack of size extensivity.

CI can also be extended to multireference wavefunctions, where the reference state is typically a CASSCF wave function. This results in a method of very high accuracy but also high cost. While the multireference CI (MRCI) method[40-45] is one of the most accurate pure ab initio techniques it has not been employed in this work.

2.2.3.3 Møller-Plesset Perturbation Theory (MPPT)[9,10]

MPPT involves the use of perturbation theory to determine the coefficients in the CI expansion. It is based upon the assumption that the effects of dynamical correlation can be regarded as a perturbation, $\hat{V}$, to the all-electron Fock operator, $\hat{F}$, (described in **Section 2.2.2**). The Hamiltonian is formally partitioned:

$$\hat{H} = \hat{F} + \hat{V} \tag{2.2.62}$$

where $\hat{V}$ is known as the fluctuation operator.

Starting with the Hartree-Fock wave function as the unperturbed state, the application of Rayleigh-Schrödinger perturbation theory yields the perturbative corrections to the wavefunction $\psi^{(1)}$, $\psi^{(2)}$, $\psi^{(3)}$, etc.; these are constructed from the single, double, triple, etc. excitations as specified in the configuration interaction expansion of the wavefunction (Equation (2.2.58)). The perturbation corrections to the energy, $E_{(1)}$, $E_{(2)}$, $E_{(3)}$ … (to first, second, third, ... order) and the corresponding contributions to the coefficients ($\{a_i^a\}$, $\{a_{ij}^{ab}\}$, etc.) in the CI expansion can thus be determined.

As the first order energy correction is simply the expectation value of the perturbing fluctuation operator with respect to the Hartree-Fock reference state, perturbation theory to first order in the energy yields the original Hartree-Fock energy.

The second order energy correction, $E_{(2)}$, in the basis of the occupied (*i*, *j*, …) and unoccupied (*a*, *b*, …) spin orbitals is found to be:

$$E_{(2)} = \frac{1}{4}\sum_{\substack{i,j\\a,b}} \frac{\langle ij||ab\rangle^2}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} \tag{2.2.63}$$

where ε_i, ε_j, … are the Hartree-Fock orbital energies.

$E_{(2)}$ is known as the MP2 correlation energy. Møller-Plesset perturbation theory to second order (in the energy) is widely used as it is computationally inexpensive and thus allows correlated calculations to be performed for relatively large molecules.

Perturbation theory up to fourth order in the energy (MP4) is also commonly used; this requires knowledge of the second order correction to the wavefunction, $\psi^{(2)}$, which has contributions from single, double, triple and quadruple excitations. Accounting for triple excitations has been found to be more difficult (and expensive) than accounting for the quadruples so they are often neglected, giving MP4(SDQ) theory. (MP4 theory with triple excitations included is denoted MP4(SDTQ).) It has been observed that the additional accuracy obtainable by including higher order terms in the perturbation expansion comes at a high additional computational expense; it is therefore more practical to use configuration interaction or coupled cluster methods when higher accuracy is required.

Møller-Plesset perturbation theory can be applied within the framework of both single- and multi-determinant reference states. The most successful implementation of the latter is the complete active space second order perturbation theory (CASPT2) method of Andersson et al.[46,47] Being based on a CASSCF reference state, CASPT2 accounts for both dynamical and non-dynamical correlation. As the formalism is significantly more complex than for single determinant perturbation theory (due to the more complex form of the reference state) the computational effort and cost are also greater.

2.2.3.4 Coupled Cluster Theory (CC)[48-52]

Coupled cluster theory represents a seemingly different approach to the electron correlation problem from that of configuration interaction; much of this difference is, however, semantic. A coupled cluster wavefunction is formulated in terms of the cluster operator, $\hat{T}$:

$$\psi = \mathrm{e}^{\hat{T}}\psi_0 \tag{2.2.64}$$

where $\hat{T}$ is constructed from one body, two body, three body, etc. cluster terms, $\hat{T}_1$, $\hat{T}_2$, $\hat{T}_3$, … which represent single, double, triple, etc. excitation operators:

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + ... \tag{2.2.65}$$

where

$$\hat{T}_1 = \sum_{i,a} t_i^a \hat{a}_a^+ \hat{a}_i \tag{2.2.66}$$

$$\hat{T}_2 = \sum_{\substack{i<j \\ a<b}} t_{ij}^{ab} \hat{a}_b^+ \hat{a}_j \hat{a}_a^+ \hat{a}_i \tag{2.2.67}$$

etc.

These equations have been written using the formalism of second quantisation[53] where $\{\hat{a}_a^+\}$ are creation operators which generate an electron in spin orbital *a* and $\{\hat{a}_i\}$ are annihilation operators which remove an electron from orbital *i*. Together they represent the excitation of an electron from orbital *i* to orbital *a*.

The cluster amplitudes, $\{t_i^a\}$, $\{t_{ij}^{ab}\}$, etc., are simply numerical coefficients for each term.

The asymptotic expansion of the $\mathrm{e}^{\hat{T}}$ operator yields:

$$\begin{aligned} \mathrm{e}^{\hat{T}} &= 1 + \hat{T} + \frac{1}{2}\hat{T}^2 + \frac{1}{6}\hat{T}^3 + ... \\ &= 1 + \hat{T}_1 + \left[\hat{T}_2 + \frac{1}{2}\hat{T}_1^2\right] + \left[\hat{T}_3 + \hat{T}_1\hat{T}_2 + \frac{1}{6}\hat{T}_1^3\right] + ... \\ &= 1 + \hat{c}_1 + \hat{c}_2 + \hat{c}_3 + ... \end{aligned} \tag{2.2.68}$$

where $\hat{c}_1$, $\hat{c}_2$, $\hat{c}_3$, etc. are one-, two-, three-, … body clusters each representing the excitation of 1, 2, 3, … electrons from occupied to virtual spin orbitals.

This means that the coefficients for the double, triple, etc. excitations of CI are now expressed in terms of one-, two-, three-, … body cluster amplitudes:

$$a_{ij}^{ab} = t_{ij}^{ab} + t_i^a t_j^b \tag{2.2.69}$$

$$a_{ijk}^{abc} = t_{ijk}^{abc} + t_i^a t_{jk}^{bc} + \frac{1}{6} t_i^a t_j^b t_k^c \tag{2.2.70}$$

As in CI, implementation of the coupled cluster method with up to *n*-fold excitation operators is not feasible computationally and in practice the cluster operator is truncated after double excitations. Thus

$$\begin{aligned} \psi &= \mathrm{e}^{\hat{T}_1+\hat{T}_2}\psi_0 \\ &= \begin{pmatrix} 1+\hat{T}_1+\hat{T}_2+\frac{1}{2}\hat{T}_1^2+\hat{T}_1\hat{T}_2+\frac{1}{2}\hat{T}_1^2\hat{T}_2 \\ +\frac{1}{6}\hat{T}_1^3+\frac{1}{2}\hat{T}_2^2+\frac{1}{24}\hat{T}_1^4+\ldots \end{pmatrix}\psi_0 \end{aligned} \tag{2.2.71}$$

As this expansion shows, triple, quadruple and higher excitations are accounted for as products of single and double excitations, or, in the language of many body perturbation theory, all connected diagrams are implicitly present.

The coupled cluster wavefunction cannot be calculated using standard eigenvalue methods because the function is not linear in the cluster amplitudes, $\{t_i^a\}$, $\{t_{ij}^{ab}\}$, etc. Instead the wavefunctions are obtained iteratively by solving the Schrödinger equation in the subspace of the configurations used, that is, the reference state and the single and double excitations. The equations which need to be solved are therefore:

$$\left\langle \psi_0 \middle| \hat{H} \middle| \mathrm{e}^{\hat{T}}\psi_0 \right\rangle = E \tag{2.2.72}$$

$$\left\langle \phi_i^a \middle| \hat{H} \middle| \mathrm{e}^{\hat{T}}\psi_0 \right\rangle = t_i^a E \tag{2.2.73}$$

$$\left\langle \phi_{ij}^{ab} \middle| \hat{H} \middle| \mathrm{e}^{\hat{T}}\psi_0 \right\rangle = t_{ij}^{ab} E \tag{2.2.74}$$

where *E* is the coupled cluster energy.

This approach is known as the coupled cluster with singles and doubles method, CCSD. Although the coupled cluster wavefunction is size extensive, the solution of Equations (2.2.72) - (2.2.74) does not yield an upper bound to the true energy.

It is also possible to truncate the cluster expansion after the $\hat{T}_3$ term, thus including the three body clusters (that is, connected components of the triple excitations) and resulting in the CCSDT method. The added computational cost, however, is at present too high to allow this method to be used routinely. An alternative is to use perturbation theory to approximate the contribution of the connected triple excitations using the coupled cluster wavefunction as the unperturbed reference state:[54]

$$\Delta E_{triples} = \sum_{\substack{i<j<k \\ a<b<c}} \frac{\left\langle \left(1+\hat{T}_1+\hat{T}_2\right)\psi_0 \middle| \hat{H} \middle| \phi_{ijk}^{abc} \right\rangle \left\langle \left(1+\hat{T}_2\right)\psi_0 \middle| \hat{H} \middle| \phi_{ijk}^{abc} \right\rangle}{\left(\varepsilon_i+\varepsilon_j+\varepsilon_k\right)-\left(\varepsilon_a+\varepsilon_b+\varepsilon_c\right)} \qquad (2.2.75)$$

where ε_i, ε_j, … are the Hartree-Fock orbital energies.

CCSD with perturbative triples is denoted CCSD(T); it is currently the most commonly used method for generating highly accurate molecular energies and has been used extensively in this thesis.

Coupled cluster theory as described above is based on a single reference determinant. The accuracy and reliability of the results are strongly dependant on the validity of the assumption that the reference state is dominant in the coupled cluster expansion. To determine if this condition is satisfied the τ_1 diagnostic has been introduced.[55] The quantity τ_1 is defined by:

$$\tau_1 = \frac{\left\| \boldsymbol{t}_1 \right\|}{\sqrt{n}} \qquad (2.2.76)$$

where $\boldsymbol{t}_1$ is the vector of single excitation amplitudes and n is the number of correlated electrons. Based on extensive computational experience it has been suggested that if τ_1 is larger than 0.02 then non-dynamical correlation effects are potentially important and CCSD may be unreliable. The inclusion of the perturbative triples correction has been shown to reduce these problems, however, with reliable energies having been obtained when τ_1 is as large as 0.04.[56]

2.2.3.5 Quadratic Configuration Interaction (QCI)[57]

QCI can be viewed either as an extension of the configuration interaction methods or an approximation to coupled cluster theory where only the terms which are required to ensure size extensivity are retained. For quadratic configuration interaction theory with single and double excitations (QCISD) the equations which need to be solved are:

$$\left\langle \psi_0 \middle| \hat{H} \middle| \left(1+\hat{T}_1+\hat{T}_2\right)\psi_0 \right\rangle = E \tag{2.2.77}$$

$$\left\langle \phi_i^a \middle| \hat{H} \middle| \left(1+\hat{T}_1+\hat{T}_2+\hat{T}_1\hat{T}_2\right)\psi_0 \right\rangle = t_i^a E \tag{2.2.78}$$

$$\left\langle \phi_{ij}^{ab} \middle| \hat{H} \middle| \left(1+\hat{T}_1+\hat{T}_2+\frac{1}{2}\hat{T}_2^2\right)\psi_0 \right\rangle = t_{ij}^{ab} E \tag{2.2.79}$$

The effects of perturbative triples can also be included for QCISD theory:

$$\Delta E_{triples} = \sum_{\substack{i<j<k \\ a<b<c}} \frac{\left\langle \left(1+2\hat{T}_1+\hat{T}_2\right)\psi_0 \middle| \hat{H} \middle| \phi_{ijk}^{abc} \right\rangle \left\langle \left(1+\hat{T}_2\right)\psi_0 \middle| \hat{H} \middle| \phi_{ijk}^{abc} \right\rangle}{\left(\varepsilon_i+\varepsilon_j+\varepsilon_k\right)-\left(\varepsilon_a+\varepsilon_b+\varepsilon_c\right)} \tag{2.2.80}$$

where ε_i, ε_j, … are the Hartree-Fock orbital energies.

The resulting QCISD(T) theory is significantly more accurate than MP4 and is, in general, a good approximation to CCSD(T). Like standard coupled cluster theory, QCI is based on a single reference expansion; a Q_1 diagnostic (analogous to the τ_1 diagnostic) has been introduced to test the dominance of this reference state.[58]

2.3 Density Functional Theory

Density functional theory (DFT) is an entirely different approach to computational quantum chemistry from the wavefunction methods described in **Section 2.2**. It involves expressing the energy of a system as a functional of the electron density, ρ, rather than of a wavefunction, ψ. This is based on the proof of Hohenberg and Kohn[59] that "There exists a universal functional of the density, $F[\rho(\boldsymbol{r})]$, independent of $v(\boldsymbol{r})$ [the external potential due to the nuclei], such that the expression $E = \int v(\boldsymbol{r})\rho(\boldsymbol{r})d\boldsymbol{r} + F[\rho(\boldsymbol{r})]$ has as its minimum the correct ground state energy associated with $v(\boldsymbol{r})$." Density Functional Theory is thus formally an exact theory given that the mathematical form of this universal functional is known. Unfortunately, in practice it is not known, nor can it be precisely determined or systematically improved. Approximate functionals have therefore been proposed, often on the basis of fits which give the correct results for certain well characterised systems. Density functional theory is, therefore, a semi-empirical theory. It is important to note, however, that as DFT is based upon the actual electron density, both dynamical and non-dynamical correlation are implicitly accounted for in DFT calculations.

2.3.1 The Kohn-Sham Equations[60]

The density functional energy can be written as:

$$E[\rho] = T[\rho] + V_{Ne}[\rho] + V_{ee}[\rho] \tag{2.3.1}$$

where $T[\rho]$ is the kinetic energy and $V_{Ne}[\rho]$ and $V_{ee}[\rho]$ are the nucleus-electron and electron-electron interaction energies.

While $V_{Ne}[\rho]$ (as indicated above) is simply given by:

$$V_{Ne}[\rho] = \int \rho(\boldsymbol{r}) v(\boldsymbol{r}) d\boldsymbol{r} \tag{2.3.2}$$

the forms of $T[\rho]$ and $V_{ee}[\rho]$ for systems containing interacting electrons are unknown; these functionals must therefore be approximated. A starting point for this is found in Hartree-Fock theory where it is recognised that the electron-electron interaction contains Coulomb and exchange terms and that the Coulomb component is given by:

$$J[\rho]=\frac{1}{2}\int\int\frac{1}{r_{12}}\rho(\boldsymbol{r}_1)\rho(\boldsymbol{r}_2)d\boldsymbol{r}_1 d\boldsymbol{r}_2 \tag{2.3.3}$$

In addition, while the form of the kinetic energy functional is unknown for systems with interacting electrons, when the electrons do not interact the kinetic energy, $T_s[\rho]$, and the density $\rho(\boldsymbol{r})$ are given by:

$$T_s[\rho]=\sum_i^n\left\langle\phi_i\left|-\frac{1}{2}\nabla^2\right|\phi_i\right\rangle \tag{2.3.4}$$

$$\rho(\boldsymbol{r})=\sum_i^n\left|\phi_i(\boldsymbol{r})\right|^2 \tag{2.3.5}$$

Kohn and Sham therefore proposed that the exact density for a system of interacting particles should also be specified in terms of the spin orbitals, $\{\phi_i(\boldsymbol{r})\}$, (as in Equation (2.3.5)) and that the energy should be partitioned as:

$$\begin{aligned}E[\rho]&=T_s[\rho]+V_{Ne}[\rho]+J[\rho]+(T[\rho]-T_s[\rho])+(V_{ee}[\rho]-J[\rho])\\&=T_s[\rho]+V_{Ne}[\rho]+J[\rho]+E_{xc}[\rho]\end{aligned} \tag{2.3.6}$$

where $E_{xc}[\rho]$ is the exchange-correlation energy which accounts for all the effects in the molecule neglected by the earlier Hartree type approximations. It has an associated exchange-correlation potential, $v_{xc}(\boldsymbol{r})$:

$$v_{xc}(\boldsymbol{r})=\frac{\delta E_{xc}[\rho(\boldsymbol{r})]}{\delta\rho(\boldsymbol{r})} \tag{2.3.7}$$

The Kohn-Sham equations are therefore formulated in terms of the Kohn-Sham orbitals, $\{\phi_i(\boldsymbol{r})\}$:

$$\left[-\frac{1}{2}\nabla^2 + v(\boldsymbol{r}) + \int \frac{\rho(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} d\boldsymbol{r}' + v_{xc}(\boldsymbol{r})\right]\phi_i(\boldsymbol{r}) = \varepsilon_i \phi_i(\boldsymbol{r}) \tag{2.3.8}$$

These equations are analogous to the Fock equations (2.2.30) where the exchange operator, $\hat{K}$, has been replaced by the exchange correlation potential, $v_{xc}(\boldsymbol{r})$. The accuracy and reliability of density functional theory as formulated above depends, therefore, on the accuracy of the exchange-correlation functional, $E_{xc}[\rho]$.

2.3.2 The Local Density Approximation (LDA)

A simple formulation of this exchange-correlation functional is obtained by the study of a convenient model system, namely the uniform electron gas in the presence of a uniform continuum of positive charge. Here $V_{Ne}[\rho]$ and $J[\rho]$ sum to zero and the total energy is simply:

$$E[\rho] = T_s[\rho] + E_{xc}[\rho] \tag{2.3.9}$$

$$= T_s[\rho] + E_x[\rho] + E_c[\rho] \tag{2.3.10}$$

where $E_{xc}[\rho]$ has been separated into an exchange part, $E_x[\rho]$, and a correlation part, $E_c[\rho]$.

By using a plane wave basis set with periodic boundary conditions it has been shown that[60-62]

$$T_s[\rho] = C_F \int \rho(\boldsymbol{r})^{5/3}\, d\boldsymbol{r} \tag{2.3.11}$$

$$E_x[\rho] = -C_x \int \rho(\boldsymbol{r})^{4/3}\, d\boldsymbol{r} \tag{2.3.12}$$

where the constants are:

$$C_F = \frac{3}{10}\left(3\pi^2\right)^{2/3} = 2.8712$$
$$C_x = \frac{3}{4}\left(3\pi^{-1}\right)^{1/3} = 0.7386$$

When the α and β spin densities are different, the following more general results are obtained:

$$T_s\left[\rho^\alpha,\rho^\beta\right] = 2^{2/3}C_F\int\left[\rho^\alpha\left(\boldsymbol{r}\right)^{5/3} + \rho^\beta\left(\boldsymbol{r}\right)^{5/3}\right]d\boldsymbol{r} \tag{2.3.13}$$

$$E_x\left[\rho^\alpha,\rho^\beta\right] = -2^{1/3}C_x\int\left[\rho^\alpha\left(\boldsymbol{r}\right)^{4/3} + \rho^\beta\left(\boldsymbol{r}\right)^{4/3}\right]d\boldsymbol{r} \tag{2.3.14}$$

The exchange energy generated via this approach is called the Dirac-Slater[62] exchange although it was, in fact, first developed by Bloch[63].

Finally, the correlation functional, $E_c[\rho]$, has been formulated by Vosko, Wilk and Nusair[64]. This work was based on quantum Monte-Carlo simulations of the uniform electron gas performed by Ceperley and Alder[65] for a range of electron densities. The functional is designed to ensure that $E[\rho]$ as defined in Equation (2.3.10) reproduces the quantum Monte-Carlo results; it is known as the VWN correlation functional.

This formulation of the exchange and correlation functionals is called the Local Density Approximation. When applied to atoms and molecules via the Kohn-Sham equations it has been found that the LDA approach is not particularly useful for quantum chemical applications, having an accuracy which is comparable with that of Hartree-Fock SCF theory. To improve this situation various corrections to the LDA have been introduced.

2.3.3 Corrections to the LDA

The most significant of these is a correction to the exchange energy (or more specifically to its potential) introduced by Becke[66] in 1988. This correction term introduces non-locality (shell structure) to the description of the system via a dependence on the gradient, $\nabla\rho$. The correction is given as

$$\begin{aligned}\varepsilon_x^B &= -\beta\rho^{1/3}\frac{x^2}{\left(1+6\beta x\sinh^{-1}x\right)} \\ x &= \frac{|\nabla\rho|}{\rho^{4/3}}\end{aligned} \qquad (2.3.15)$$

where β is an adjustable parameter determined so that $\varepsilon_x^{Dirac}+\varepsilon_x^B$ correctly reproduces the exchange energy for six noble gas atoms; the resulting value for β is 0.0042.

The correlation functional as determined for the uniform electron gas is similarly inadequate for an accurate description of real molecules. Utilising the Colle and Salvetti[67] formula for the correlation energy for the helium atom, Lee, Yang and Parr[68] (with further contributions by Miehlich, Savin, Stoll and Preuss[69]) derived a functional for the correlation energy of closed shell systems:

$$\begin{aligned}E_c[\rho] &= -a\int\frac{\rho}{1+d\rho^{-1/3}}d\mathbf{r} - ab\int\omega\rho^2\left[C_F\rho^{8/3}+|\nabla\rho|^2\left(\frac{5}{12}-\delta\frac{7}{72}\right)-\frac{11}{24}\rho^2|\nabla\rho|^2\right]d\mathbf{r} \\ \omega &= \frac{\exp\left(-c\rho^{-1/3}\right)}{1+d\rho^{-1/3}}\rho^{-11/3} \\ \delta &= c\rho^{-1/3}+\frac{d\rho^{-1/3}}{1+d\rho^{-1/3}}\end{aligned} \qquad (2.3.16)$$

where a = 0.04918, b = 0.132, c = 0.2533 and d = 0.349 are the empirical parameters which were determined by Colle and Salvetti for the helium atom. The presence of these parameters along with the β in the Becke exchange correction implies that density functional theory is a semi-empirical computational method. $E_c[\rho]$ as defined in Equation (2.3.16) is known as the LYP correlation functional. The presence of gradient terms in this functional, in addition to it being derived on the basis of a two-electron wavefunction, means that LYP, like the Becke exchange correction, is non-local. Consequently, it is much more realistic than the VWN correlation functional.

In general, functionals (such as the Becke correction and LYP) which can be expressed in terms of ρ and $|\nabla\rho|$:

$$E_{xc}[\rho] = \int F\left(\rho_\alpha, \rho_\beta, \zeta_{\alpha\alpha}, \zeta_{\beta\beta}, \zeta_{\alpha\beta}\right) d\boldsymbol{r}$$
$$\zeta_{\sigma\sigma'} = \nabla\rho_\sigma \cdot \nabla\rho_{\sigma'} \tag{2.3.17}$$

are referred to as Generalised Gradient Approximation (GGA) functionals.

While many other functionals have also been developed[70-72], the LYP correlation functional along with Becke's correction to the exchange are currently the most commonly used.

Further improvements to $E_{xc}[\rho]$ have come with the introduction of adiabatic connection functionals[73]. Instead of simply using the exchange functional given by $E_x^{Dirac} + E_x^B$, Becke[74] proposed that some "exact exchange" as obtained by a Hartree-Fock calculation (E_x^{HF}) should be included. His three parameter B3LYP functional[75] is defined as:

$$E_{xc} = AE_x^{Dirac} + (1-A)E_x^{HF} + B\Delta E_x^B + (1-C)E_c^{VWN} + CE_c^{LYP} \tag{2.3.18}$$

where A, B and C are semi-empirical parameters chosen to reproduce the exchange-correlation energy of the 31 species in the G1 molecule set. The optimum values are A = 0.80, B = 0.72, C = 0.81. Functionals which include both Hartree-Fock and density functional exchange are called hybrid functionals. Of these, B3LYP is currently regarded to be the most reliable for routine use; all DFT calculations in this thesis have used the B3LYP functional.

2.3.4 Implementation of DFT

While the exchange and correlation functionals described above (such as B3LYP) allow DFT to give good descriptions of molecular energies, geometries and related properties, their forms, in particular the presence of fractional powers of the density, mean that the integrals involved cannot be calculated analytically. This necessitates the use of numerical quadrature with a three dimensional grid of points spanning the space of the molecule. Full details of the implementation of such schemes can be found in References 70-73. It is important to note that when such numerical procedures are employed for quantum chemical calculations of energies and their gradients the grids used must be sufficiently fine grained to guarantee adequate precision in the quantities of interest.

2.4 Basis Sets

As noted earlier, the one-particle bases used for the construction of many-electron molecular wavefunctions consist of atomic spin orbital functions. Since the formation of a molecule results in relatively small changes in the atomic wavefunctions, these atom centred functions provide a suitable (and easy to obtain) basis for the description of molecular wavefunctions.

Atomic orbitals are generally expressed as products of radial $R(r)$ and angular $Y_{lm}(\theta,\phi)$ functions:

$$\chi(r,\theta,\phi) = R(r)Y_{lm}(\theta,\phi) \tag{2.4.1}$$

where r, θ and ϕ are the radial and angular coordinates (in a spherical polar coordinate representation).

The angular functions, Y_{lm}, are normalised spherical harmonics given by

$$Y_{lm}(\theta,\phi) = (-1)^{(m-|m|)/2}\left[\frac{2l+1}{4\pi}\frac{(l-|m|)!}{(l+|m|)!}\right]^{\frac{1}{2}} P_l^{|m|}(\cos\theta)\mathrm{e}^{\mathrm{i}m\phi} \tag{2.4.2}$$

where l and m are the angular momentum and magnetic quantum numbers and $P_l^{|m|}(\cos\theta)$ are associated Legendre polynomials[80].

The radial nature of the one-electron atomic orbitals is, naturally, critically dependant on the Coulombic forces between the electron and the nucleus. This means that a wavefunction would be expected to have a singularity (cusp) at the nucleus and to decay exponentially at large values of r. It therefore seems natural to choose radial functions of the form:

$$R(r) = Cr^n \mathrm{e}^{-\alpha r} \tag{2.4.3}$$

where n is an integer and C and α are constants. Atomic orbitals of this form are called Slater type orbitals (STO's).[81] While such orbitals give the best physical description of the wavefunction, difficulties associated with the calculation of multicentre electron repulsion integrals using STO's make them impractical for use for anything other than small linear molecules.

2.4.1 Gaussian Type Orbitals[82]

A significant simplification is made by the introduction of Gaussian type orbitals (GTO's) of the form:

$$R(r) = Cr^n \, \mathrm{e}^{-\alpha r^2} \tag{2.4.4}$$

The advantage of GTO's is that the evaluation of the necessary integrals is so much simpler and faster than for STO's that it is rarely the limiting step in any practical computational study. This is a direct consequence of the Gaussian product theorem[83] which states that a product of two Gaussian functions on different centres gives a new Gaussian centred at a new position in space. This property allows the "difficult" 3 and 4 centre repulsion integrals to be simplified to integrals involving only two centres.

The use of Gaussian functions does have disadvantages, however. In particular, they no longer have a cusp at $r = 0$ and decay too quickly as $r \to \infty$. This problem can be corrected for by the formation of contracted Gaussian type orbitals (CGTO's); that is, by defining orbitals as combinations (sums) of several "primitive" Gaussians (Equation (2.4.4)) with a range of exponents, α. Thus, tighter (higher exponent) functions are employed to describe the nuclear regions while more diffuse (lower exponent) functions will describe the valence and outer regions as $r \to \infty$. CGTO's can be expressed in the form:

$$\chi_q^{CGTO} = \sum_p C_{qp} \chi_p^{GTO} \left(\alpha_p \right) \tag{2.4.5}$$

where the exponents, α_p, and the contraction coefficients, C_{qp}, are usually determined on the basis of atomic SCF or CI calculations.

2.4.2 Construction of Contracted Gaussian Basis Sets

In order for a set of basis functions for a particular element to be applicable to calculations involving molecules, solids and ions as well as free atoms it is necessary for it to be sufficiently flexible to be able to both describe the changes in electron density involved with formation of more complex systems and resolve the effects of dynamical electron correlation.

A minimal basis set for an element contains one CGTO for each atomic orbital in every fully or partially occupied shell. Although this should in principle give a good description of the atom (or a more complex system of which it is a part), it cannot, in fact, adequately describe the changes in the orbitals due to bonding (such as contraction and polarisation), nor can it account for electron correlation. The orbital contraction effects can be corrected for by using two or more CGTO's (rather than just one) to describe each atomic orbital; this leads to double-ζ (DZ), triple-ζ (TZ), etc. basis sets. In order to obtain a perfect description of a system ideally an infinite-ζ basis set would be needed, however in reality a compromise must be made between the accuracy required and the time and computational resources available. Currently sextuple-ζ (6Z) are the largest basis sets in common usage and then only for small molecules, such as first row di- and tri-atomics. As the orbital contraction effects occur largely in the valence orbitals, it is often the case that for second or higher row elements only the minimal number of CGTO's are used for the core orbitals while the valence orbitals are augmented to double-, triple- and higher-ζ quality; such basis sets are called split valence.

The formation of bonds between two or more atoms is, of course, accompanied by a polarisation of the atomic orbitals. It is therefore necessary to include polarisation functions in the basis sets to account for these effects. This involves augmenting the basis set with functions of successively higher angular momentum (l); for example, p and d functions are added to polarise s functions; d and f functions are added to polarise p functions, etc.

Diffuse functions, that is, functions with lower exponents than those found in the standard set, may also be added to a basis in order to account for longer range electronic effects. They are necessary for obtaining satisfactory descriptions of anions and Rydberg states and in situations where the outer regions of the density are of importance, for example in studies of polarisabilities and weak interactions such as hydrogen bonding and van der Waals forces.

The basis sets used in this thesis fall into two categories: (1) the Gaussian type basis functions of Pople and coworkers[84-90]; and (2) the correlation consistent basis sets developed by Dunning et al.[91-95] Both are split valence basis sets.

2.4.3 Pople's Gaussian Basis Sets

The standard nomenclature for these basis sets is typified by, for example:

$$6\text{-}31{+}G(2df,p)$$

This notation indicates that the core orbitals have a minimal description, each being constructed from 6 primitive GTO's, while the valence orbitals are double zeta, one CGTO being constructed from 3 primitives and the other being uncontracted (1). The "+" indicates that diffuse functions have been included while "2*df*,*p*" specifies that two *d* and one *f* polarisation functions have been added to the non-hydrogen (or He) atoms and one *p* polarisation function has been included for hydrogen (and helium).

2.4.4 Correlation Consistent Basis Sets

The correlation consistent (cc) basis sets, cc-pV*x*Z,[91,94] have been constructed to form a sequence in which, as the cardinal number of the basis set, *x*, (and hence the basis set size) increases, the improvement in the description of electron correlation is systematic and predictable. This intention was inspired by the work of Almlöf, Taylor and co-workers[96,97] who observed that, when constructing atomic natural orbital (ANO) basis sets, the introduction of functions corresponding to the same principal quantum number made similar contributions to the correlation energy.

The application of this principle is most readily understood by an example. The smallest basis sets in the correlation consistent sequence, cc-pVDZ, are of double-ζ (DZ) quality; for first row atoms they have the composition [3*s*, 2*p*, 1*d*]. In order to improve these basis sets to triple-ζ (TZ) quality all functions corresponding to $n = 4$ must be included, that is, an additional *s*, *p* and *d* function as well as an *f* function, [1*s*, 1*p*, 1*d*, 1*f*]. The cc-pVTZ basis sets therefore have the composition [4*s*, 3*p*, 2*d*, 1*f*]. Similarly, a further [1*s*, 1*p*, 1*d*, 1*f*, 1*g*] must be added to give the cc-pVQZ basis sets, resulting in [5*s*, 4*p*, 3*d*, 2*f*, 1*g*].

The additional functions are chosen so as to maximise their contribution to the electron correlation. This means that significant improvements in the description of the correlation energy are seen as the basis set increases from DZ to TZ to QZ to 5Z and so on. In addition, the exponents have been carefully chosen so as to minimise the number of primitives in the basis sets (in comparison with ANO's) while still achieving the same correlation energy.

The major advantage of such systematic improvements in the treatment of electron correlation is that the energies from a sequence of correlation consistent calculations can be fitted to smooth monotonic functions and hence extrapolated to a hypothetical complete basis set limit. In conjunction with accurate theories such as CCSD(T), this extrapolation allows for the calculation of highly accurate atomisation energies and heats of formation at relatively low computational cost.

The inclusion of diffuse functions in correlation consistent basis sets is indicated by the prefix "aug-" (or even "d-aug-" or "t-aug-" to indicate two or three sets of diffuse functions).[93] The cc-pCV*x*Z basis sets[98] (correlation consistent polarised core-valence *x* zeta) have also been used in this thesis; these basis sets are based on their cc-pV*x*Z analogues but have additional tight correlating functions added in order to describe the correlation of core electrons and between core and valence electrons.

2.4.5 Basis Set Superposition Error

A consequence of using finite (and hence incomplete) atom-centred basis sets in calculations of interaction energies (including covalent bonding, hydrogen bonding and van der Waals interactions) is the presence of basis set superposition error. Briefly stated, this is the phenomenon whereby, given an interacting system *AB*, the moiety *A* can be stabilised by the nearby presence of the basis functions belonging to moiety *B* (in addition to any true interaction between *A* and *B*) and vice versa. This is because these additional basis functions compensate for the incompleteness of *A*'s own basis, thus improving the description of *A* and lowering its energy. Thus the system is not only stabilised by any true interaction between *A* and *B* but also by this superposition effect.

An estimate of the magnitude of this effect (and hence a possible correction for it) can be obtained via the counterpoise method of Boys and Bernardi.[99] This involves calculating the energy of each moiety (atom or fragment) both with its own basis functions, E_A, E_B, and in the presence of the basis functions of the entire system $E_{A[B]}$, $E_{[A]B}$. The counterpoise corrections for A and B then given by:

$$\Delta E_A^{CP} = E_{A[B]} - E_A \qquad (2.4.6)$$

$$\Delta E_B^{CP} = E_{[A]B} - E_B \qquad (2.4.7)$$

The sum of these counterpoise corrections, $\Delta E_A^{CP} + \Delta E_B^{CP}$, therefore represents the total correction to the interaction energy and thus the counterpoise corrected interaction energy is given by:

$$\Delta E_{AB}^{corrected} = E_A + E_B - E_{AB} + \Delta E_A^{CP} + \Delta E_B^{CP} \qquad (2.4.8)$$

It should be noted that $E_{A[B]}$ and $E_{[A]B}$ are evaluated at the geometry optimised for *AB*, that is, the geometry used to calculate E_{AB}. If *A* and/or *B* are molecular fragments, these geometries may be different from their equilibrium geometries (those used to calculate E_A and E_B); this may be a potential source of inaccuracy in $\Delta E_A^{CP} + \Delta E_B^{CP}$. This further highlights the approximate nature of the counterpoise correction.

2.5 Derivatives of the Energy[100]

The calculation of derivatives of the energy of a molecular system with respect to perturbations of the system is essential for determining molecular properties. For instance, first derivatives with respect to nuclear displacements yield the forces on the nuclei and allow the identification of stationary points on the molecular potential energy surface, such as minimum energy structures. Derivatives with respect to an applied electrostatic field yield the dipole moment, polarisability and hyperpolarisability of the molecule and derivatives with respect to an applied magnetic field give the magnetisability and the magnetic shielding tensors which, along with spin-spin coupling tensors, are essential for the quantitative prediction of NMR spectra.

Derivatives can be calculated numerically or analytically. While numerical derivatives are conceptually simpler (simply involving the calculation of energies at different values of the perturbation parameter followed by polynomial fitting to obtain derivatives), they are generally more resource intensive and less accurate than analytic methods for all but the simplest systems. This discussion will therefore focus on the calculation of analytic derivatives.

2.5.1 Analytic Energy Derivatives

The first derivative of the energy with respect to an arbitrary perturbation parameter, λ, is given by:

$$\frac{dE}{d\lambda} = \left\langle \psi \left| \frac{\partial \hat{H}}{\partial \lambda} \right| \psi \right\rangle + 2 \left\langle \frac{\partial \psi}{\partial \lambda} \right| \hat{H} \left| \psi \right\rangle \tag{2.5.1}$$

where it is assumed that $\hat{H}$ is Hermitian and ψ is real.

Now, the wavefunction can be affected by the perturbation through both the CI and MO coefficients, $\{a_k\}$ and $\{c_{pi}\}$, collectively labelled $\boldsymbol{C}$, and through the basis functions, $\{\chi_p\}$.

Thus,

$$\frac{\partial \psi}{\partial \lambda} = \frac{\partial \psi}{\partial \boldsymbol{C}}\frac{\partial \boldsymbol{C}}{\partial \lambda} + \frac{\partial \psi}{\partial \boldsymbol{\chi}}\frac{\partial \boldsymbol{\chi}}{\partial \lambda} \tag{2.5.2}$$

For all perturbations apart from those which change the nuclear configuration itself the basis functions are independent of the perturbation:

$$\frac{\partial \boldsymbol{\chi}}{\partial \lambda} = 0 \tag{2.5.3}$$

Perturbations of the molecular geometry therefore form a special case which will be dealt with separately in **Section 2.5.2**. For all other perturbations, however, Equation (2.5.1) simplifies to:

$$\frac{dE}{d\lambda} = \left\langle \psi \left| \frac{\partial \hat{H}}{\partial \lambda} \right| \psi \right\rangle + 2\left\langle \frac{\partial \psi}{\partial \boldsymbol{C}} \left| \hat{H} \right| \psi \right\rangle \frac{\partial \boldsymbol{C}}{\partial \lambda} \tag{2.5.4}$$

Clearly for fully variational wavefunctions, such as HF, MCSCF and full-CI, the second term (known as the first order response of the wavefunction to the perturbation) vanishes, as the wavefunction has been fully optimised with respect to all coefficients, ***C***. Such a wavefunction therefore obeys the Hellmann-Feynmann theorem:

$$\frac{dE}{d\lambda} = \left\langle \psi \left| \frac{\partial \hat{H}}{\partial \lambda} \right| \psi \right\rangle \tag{2.5.5}$$

that is, the derivative is given by the expectation value of the perturbation to the Hamiltonian, $\hat{V}$:

$$\frac{dE}{d\lambda} = \left\langle \psi \left| \hat{V} \right| \psi \right\rangle \tag{2.5.6}$$

where $\hat{H} = \hat{H}_0 + \lambda \hat{V}$.

Most wavefunctions in common use, such as Møller-Plessett, (truncated) CI or coupled cluster wavefunctions, are not fully variational, however, and the non-Hellmann-Feynman term (the second term in Equation (2.5.4)) must also be considered. The calculation of the response of the coefficient matrix to the perturbation, $\frac{\partial \boldsymbol{C}}{\partial \lambda}$, is a demanding task, however it can be avoided using Lagrange's method of undetermined multipliers[101-103].

For example: for a CI wavefunction, which is non-variational with respect to the MO coefficients, the Lagrange function is

$$L_{CI} = E_{CI} + \boldsymbol{\kappa} \frac{\partial E_{HF}}{\partial \boldsymbol{c}} \tag{2.5.7}$$

Choosing the Lagrange multipliers, $\boldsymbol{\kappa}$, so that:

$$\frac{\partial L_{CI}}{\partial \boldsymbol{c}} = 2\left\langle \frac{\partial \psi_{CI}}{\partial \boldsymbol{c}} \middle| \hat{H} \middle| \psi_{CI} \right\rangle + 2\boldsymbol{\kappa}\left[\left\langle \frac{\partial^2 \psi_{HF}}{\partial \boldsymbol{c}^2} \middle| \hat{H} \middle| \psi_{HF} \right\rangle + \left\langle \frac{\partial \psi_{HF}}{\partial \boldsymbol{c}} \middle| \hat{H} \middle| \frac{\partial \psi_{HF}}{\partial \boldsymbol{c}} \right\rangle \right] = 0 \tag{2.5.8}$$

allows the derivative in Equation (2.5.4) to be simplified to

$$\frac{\partial E_{CI}}{\partial \lambda} = \frac{\partial L_{CI}}{\partial \lambda} = \left\langle \psi_{CI} \middle| \frac{\partial \hat{H}}{\partial \lambda} \middle| \psi_{CI} \right\rangle + \boldsymbol{\kappa} \left\langle \frac{\partial \psi_{HF}}{\partial \boldsymbol{c}} \middle| \frac{\partial \hat{H}}{\partial \lambda} \middle| \psi_{HF} \right\rangle \tag{2.5.9}$$

where the dependence of the coefficients on the perturbation is no longer required. This treatment is readily generalised for the calculation of analytic second derivatives.

2.5.2 Geometric Derivatives[104]

As noted above, when derivatives are taken with respect to geometric parameters the wavefunction depends on the perturbation through both the coefficients, $\boldsymbol{C}$, and the basis functions, $\boldsymbol{\chi}$. This is because, as the nuclei move, the atom-centred basis functions move with them. It is thus easiest to derive the equations for the derivatives when the energy is expressed in terms of these basis functions; for example, for a Hartree-Fock wavefunction:

$$E = \sum_{p,q} \langle \chi_p | h | \chi_q \rangle D_{pq} + \frac{1}{2} \sum_{p,q,r,s} \langle \chi_p \chi_r \| \chi_q \chi_s \rangle D_{pq} D_{rs} + V_{NN} \tag{2.5.10}$$

where $\{D_{pq}\}$ are the elements of the density matrix

$$D_{pq} = \sum_{i}^{n_{occ}} c_{pi} c_{qi} \tag{2.5.11}$$

The first derivative of the Hartree-Fock energy is thus given by

$$E' = \sum_{p,q} \langle \chi_p | h | \chi_q \rangle' D_{pq} + \frac{1}{2} \sum_{p,q,r,s} \langle \chi_p \chi_r \| \chi_q \chi_s \rangle' D_{pq} D_{rs} - \sum_{pq} W_{pq} \langle \chi_p | \chi_q \rangle' + V'_{NN} \tag{2.5.12}$$

where the primed notation is used to denote the derivative with respect to the change in geometry and

$$W_{pq} = \sum_{i=1}^{n_{occ}} c_{pi} \varepsilon_i c_{qi} \tag{2.5.13}$$

where $\{\varepsilon_i\}$ are the orbital energies.

Thus, as for derivatives with respect to other parameters, geometric first derivatives do not require the calculation of derivatives of the density (coefficient) matrix. It is, however, now necessary to calculate the derivatives of the one- and two-electron integrals, $\langle \chi_p | \chi_q \rangle'$ and $\langle \chi_p \chi_r \| \chi_q \chi_s \rangle'$; the calculation of the derivatives of these two-electron integrals represents the most resource intensive aspect of the calculation of gradients.

Second as well as some higher geometric derivatives have also been derived. The second derivative of the SCF energy is given by:

$$\begin{aligned} E'' = &\sum_{p,q} \langle \chi_p | h | \chi_q \rangle'' D_{pq} + \frac{1}{2} \sum_{p,q,r,s} \langle \chi_p \chi_r || \chi_q \chi_s \rangle'' D_{pq} D_{rs} \\ &- \sum_{pq} W_{pq} \langle \chi_p | \chi_q \rangle'' - \sum_{pq} W_{pq}' \langle \chi_p | \chi_q \rangle' \\ &+ \sum_{p,q} \langle \chi_p | h | \chi_q \rangle' D_{pq}' + \sum_{p,q,r,s} \langle \chi_p \chi_r || \chi_q \chi_s \rangle' D_{pq}' D_{rs} + V_{NN}'' \end{aligned} \quad (2.5.14)$$

where now the first derivative of the density matrix is required. This can be calculated using the Coupled Perturbed Hartree-Fock (CPHF) method[105]. The theory and implementation of this method will not be described here, however an excellent summary can be found in Jensen's book[106].

2.6 Molecular Properties

2.6.1 Geometry Optimisation[107]

A molecule with N atoms has $3N$–6 internal degrees of freedom ($3N$–5 if linear) in a Cartesian coordinate system. These correspond to three degrees of freedom for each of the N atoms less the three degrees of freedom associated with translations of the (rigid) molecule and the three (or two) degrees of freedom corresponding to molecular rotation. The potential energy surface (PES) of the molecule, $E(\boldsymbol{R})$, is therefore a function of these $3N$–6 ($3N$–5) internal distortions of the molecule.

In most chemical applications one is interested in energies and other properties of molecules at their equilibrium geometries, which represent minima on this PES, and at transition state geometries, which correspond to first order saddle points. A local minimum on the PES is characterised by the energy gradient, $\boldsymbol{F}$, being zero with respect to all geometric parameters:

$$F_i = \frac{\partial E(\boldsymbol{R})}{\partial R_i} = 0 \quad \forall i \tag{2.6.1}$$

Furthermore, it is also required that the Hessian, $\boldsymbol{H}$, be positive definite; that is, have all its eigenvalues greater than zero. $\boldsymbol{H}$ is the second derivative matrix with matrix elements:

$$H_{ij} = \frac{\partial^2 E(\boldsymbol{R})}{\partial R_i \partial R_j} \tag{2.6.2}$$

For a transition state (a first order saddle point) the gradient is also zero, while the Hessian has one negative eigenvalue. This corresponds to a geometry where the energy is a minimum with respect to all geometric parameters except one, the reaction coordinate, for which it is at a maximum.

In order to successfully find an equilibrium structure or transition state on the potential energy surface it is necessary to start with a molecular configuration, $\boldsymbol{R}_0$, which is in the neighbourhood of the appropriate local minimum or saddle point geometry, $\boldsymbol{R}_e$. The PES, $E(\boldsymbol{R})$, can then be expanded as a Taylor series around $\boldsymbol{R}_0$:

$$E(\boldsymbol{R}) = E(\boldsymbol{R}_0) + \sum_i \frac{\partial E(\boldsymbol{R})}{\partial R_i}\left(R_i - R_i^0\right) + \frac{1}{2}\sum_{i,j}\frac{\partial^2 E(\boldsymbol{R})}{\partial R_i \partial R_j}\left(R_i - R_i^0\right)\left(R_j - R_j^0\right) + \ldots \quad (2.6.3)$$

$$= E(\boldsymbol{R}_0) + \Delta\boldsymbol{R}^+ \boldsymbol{F} + \frac{1}{2}\Delta\boldsymbol{R}^+ \boldsymbol{H}\Delta\boldsymbol{R} + \ldots \quad (2.6.4)$$

where $\Delta R_i = R_i - R_i^0$.

The geometry corresponding to the minimum of the above quadratic expression (Equation (2.6.3)) is obtained by solving

$$\frac{\partial E(\boldsymbol{R})}{\partial R_i} = \left.\frac{\partial E(\boldsymbol{R})}{\partial R_i}\right|_{\boldsymbol{R}=\boldsymbol{R}_0} + \sum_j \left.\frac{\partial^2 E(\boldsymbol{R})}{\partial R_i \partial R_j}\right|_{\boldsymbol{R}=\boldsymbol{R}_0}\left(R_i - R_i^0\right) = 0 \quad (2.6.5)$$

that is,

$$\boldsymbol{F} + \boldsymbol{H}\Delta\boldsymbol{R} = \boldsymbol{0} \quad (2.6.6)$$

where the gradient vector, $\boldsymbol{F}$, and Hessian, $\boldsymbol{H}$, are evaluated at $\boldsymbol{R}_0$.

The solution for the required change in geometry is therefore given by

$$\Delta\boldsymbol{R} = -\boldsymbol{H}^{-1}\boldsymbol{F} \quad (2.6.7)$$

The truncation of the Taylor expansion at second order means that the PES has been approximated by a parabolic surface with the same gradient and curvature as the PES at $\boldsymbol{R}_0$ (see **Figure 2.6.1**). Correcting $\boldsymbol{R}_0$ by $\Delta\boldsymbol{R}$ moves the geometry to the stationary point of this quadratic surface, $\boldsymbol{R}_1$, which, if the starting geometry is within the "local" region of the stationary point sought, will be closer to $\boldsymbol{R}_e$. This process is repeated at the new geometry thus found until the elements of the gradient vector are below some preset convergence threshold, at which point the geometry is said to be converged and the equilibrium geometry has been found. This iterative process is known as the Newton-Raphson method; it represents a second order local model, since in a given search it aims to find the closest stationary point.

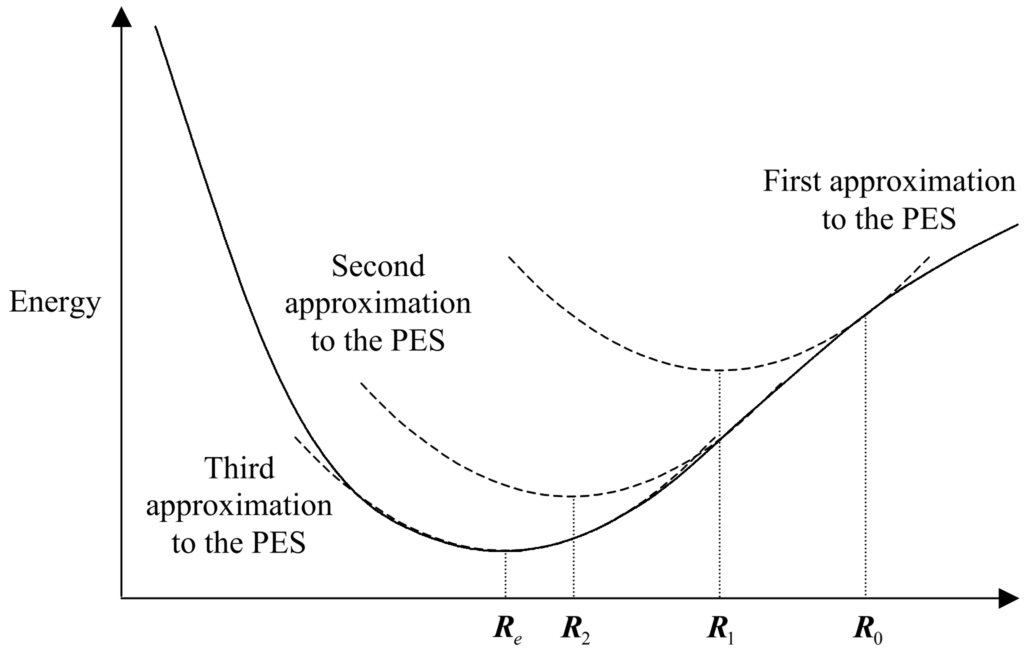

Figure 2.6.1 Newton-Raphson steps (in one dimension) for optimising geometries.

In practice calculating the Hessian in each step is quite expensive and, if possible, it is avoided. This can be done by making a reasonable initial guess of the diagonal elements on the basis of computed force constants and using the gradient information to improve the approximate Hessian during the optimisation procedure. While this process works well for equilibrium geometries, the "local" region is generally much smaller for transition state structures and thus much more accurate Hessians are required. If the starting geometry is close enough to $\boldsymbol{R}_e$ it is sufficient to only calculate the Hessian fully in the first Newton-Raphson step; for more difficult cases, however, it may be necessary to recompute it at every step.

While gradients and Hessians are initially calculated with respect to the Cartesian coordinates of the atoms, it is usually more convenient for the purposes of geometry optimisation to perform a conversion such that they are expressed in terms of the $3N$–6 (or $3N$–5) internal coordinates of the molecule. This approach also allows experimental or empirical force constants to be more readily utilised for the construction of approximate Hessians.

2.6.1.1 Partial Geometry Optimisation

Sometimes it is desirable to perform a geometry optimisation where various constraints have been applied. These constraints are particularly useful when mapping potential energy surfaces where one geometric parameter is systematically varied while the others are allowed to relax in response. In such situations the Hessian needs to be calculated with respect to the molecular internal coordinates. The Lagrange method described earlier (**Section 2.5.1**) can be applied in order to obtain derivatives with the constraints embedded in them; these can then be used to aid in the location of critical points as described above.

2.6.2 Normal Mode Analysis

By definition the Hessian matrix is the matrix of force constants. When expressed in terms of internal coordinates, its elements are the harmonic force constants for the $3N–6$ ($3N–5$) internal degrees of freedom of the molecule of interest. These determine the molecule's harmonic vibrational frequencies. The latter, by definition, correspond to the normal vibrational modes; these can be determined by a unitary transformation of the Hessian such that the classical potential (V) and kinetic (T) energies of the system are in a diagonal representation. In the Cartesian representation V and T are given by:

$$V = \boldsymbol{X}^{+}\boldsymbol{H}\boldsymbol{X} \tag{2.6.8}$$

$$T = \frac{1}{2}\dot{\boldsymbol{X}}^{+}\boldsymbol{M}\dot{\boldsymbol{X}} \tag{2.6.9}$$

where $\boldsymbol{H}$ is the Hessian matrix, $\boldsymbol{M}$ is the (diagonal) matrix of atomic masses and $\boldsymbol{X}$ is the vector of Cartesian displacements of the atoms with time derivative, $\dot{\boldsymbol{X}}$.

The normal modes, $\boldsymbol{Q}$, are related to $\boldsymbol{X}$ via a linear transformation:

$$\boldsymbol{X} = \boldsymbol{A}\boldsymbol{Q} \tag{2.6.10}$$

In the normal mode representation V and T are therefore given as:

$$V = \boldsymbol{Q}^{+}\boldsymbol{A}^{+}\boldsymbol{HAQ} \tag{2.6.11}$$

$$T = \frac{1}{2}\dot{\boldsymbol{Q}}^{+}\boldsymbol{A}^{+}\boldsymbol{MA}\dot{\boldsymbol{Q}} \tag{2.6.12}$$

Thus, if $\boldsymbol{A}$ satisfies the generalised eigenvalue equations

$$\boldsymbol{HA} = \boldsymbol{MA\Lambda} \tag{2.6.13}$$

where $\boldsymbol{\Lambda}$ is the diagonal matrix of eigenvalues, one obtains:

$$V = \boldsymbol{Q}^{+}\boldsymbol{\Lambda Q} \tag{2.6.14}$$

$$T = \frac{1}{2}\dot{\boldsymbol{Q}}^{+}\dot{\boldsymbol{Q}} \tag{2.6.15}$$

The normal mode frequencies are simply proportional to the square roots of the elements of $\boldsymbol{\Lambda}$.

If the geometry of interest corresponds to a minimum on the PES, $\boldsymbol{H}$ is positive definite and thus all diagonal elements of $\boldsymbol{\Lambda}$ will be positive and all frequencies will be real. If the geometry is a transition state or higher order saddle point, one or several of the elements of $\boldsymbol{\Lambda}$ will be negative and will thus return imaginary frequencies.

The total zero-point energy (ZPE) of the molecular system in the harmonic approximation can be readily obtained from the vibrational frequencies by summing over the zero-point energies of all modes:

$$ZPE = \frac{1}{2}\sum_{i} h\nu_{i} \tag{2.6.16}$$

where h is Planck's constant.

In reality the harmonic approximation does not provide a true representation of the vibrational modes since bond stretches are much better represented by Morse type potentials and bending / torsional modes are periodic. Nevertheless, so long as the vibrational amplitudes are small, the harmonic approximation can be demonstrated to be valid for at least the lowest energy vibrations. An anharmonic treatment or at least anharmonic corrections need to be applied in situations where this harmonic approximation fails, such as in the computation of vibrational overtones. No such treatments were, however, needed in this work.

2.7 Computational Strategies for Chemical Accuracy

Ideally all calculations of molecular and atomic energies would be performed using full-CI with an infinitely large (complete) basis set. In reality this is, of course, not possible and a trade off must be made between the desired accuracy and the time and computational resources available for the job.

Much of the work in this thesis involves calculating energies (and thus heats of formation) for the determination of the thermochemistry and kinetics of reactions. For this purpose reaction energies are needed which are accurate to within ± 1 kcal mol^{-1} (chemical accuracy). With current algorithms and the levels of processing power available it is not presently possible to achieve this accuracy for most systems of interest (particularly those involving heavy atoms such as phosphorus) from a single set of calculations (at one particular level of theory with one chosen basis set).

Various approximation schemes have, however, been proposed in order to attempt to quantify the effects associated with potential improvements in the level of theory and increases in the basis set size. Such procedures, including isodesmic / isogyric reaction schemes, Gaussian-*n* methods and complete basis set (CBS) schemes, can be used to obtain reaction energies of chemical accuracy at a reasonable computational cost.

2.7.1 Isodesmic and Isogyric Reaction Schemes

Isodesmic and isogyric reaction schemes provide a method for obtaining heats of formation of reasonably high accuracy from relatively low level calculations. They rely on the principle that for a given reaction a particular computational approach can be expected to have similar deficiencies for both reactants and products (when these are chemically similar). The deficiencies are therefore expected to cancel to an appreciable degree when the energy (or enthalpy) of a reaction is calculated. If reliable experimental (or high level theoretical) atomisation energies (ΣD_0) or heats of formation ($\Delta_f H^0$) are available for all the species in the reaction other than the molecule of interest, these can be used in conjunction with the computed reaction energy at relatively low levels of theory to obtain much better estimates of ΣD_0 (or $\Delta_f H^0$) than from the calculated atomisation energy alone. Usually several such reactions are constructed so as to give a range of estimates of the atomisation energy which can then be averaged.

In an isodesmic reaction scheme the number of each type of chemical bond is conserved throughout the reaction. For example, a reasonable isodesmic reaction for the calculation of the ΣD_0 of $CHClBr_2$ would be

$$CHClBr_2 + 2CH_4 \rightarrow CH_3Cl + 2CH_3Br$$

where both reactants and products have one C-Cl bond, two C-Br bonds and nine C-H bonds. Since the atomisation energies of CH_4, CH_3Cl and CH_3Br are well known, an accurate calculation of the energy of this reaction allows the prediction of the atomisation energy of $CHClBr_2$ with similar accuracy.

In an isogyric reaction scheme only the number of electron pairs are conserved, for example:

$$2HF \rightarrow H_2 + F_2$$

Isodesmic schemes are expected to provide more reliable error cancellation than isogyric ones and this is usually borne out by experience. Often, however, it is not possible to find suitable isodesmic schemes, particularly when dealing with inorganic systems, and in such cases isogyric reactions become an attractive alternative. In many of the systems studied in this thesis, however, there were insufficient experimental data for the construction of either isodesmic or isogyric schemes. This necessitated the use of more complicated schemes requiring the application of higher levels of theory and larger basis sets in order to obtain reliable predictions of atomisation energies.

2.7.2 Gaussian-*n* (Gn) Methods

The Gaussian-*n* methods were first introduced by Pople et al.[108] in 1989 with the aim of generating atomisation energies for molecules containing first and second row elements to within ± 2 kcal mol^{-1}. Since then the Gaussian methods have been further refined so that the most recent modification has resulted in a mean absolute deviation of less than 1 kcal mol^{-1} for the G3/99 test set of molecules.[109] The general principle is to perform a calculation at a high level of theory (QCISD(T)) with a relatively small basis set and then correct this value for deficiencies in the basis set using less expensive, lower level theories such as MP4 and/or MP2. Geometries and vibrational frequencies are obtained at even lower levels of theory, with the assumption that these properties are relatively insensitive to the level of theory and basis set size; that is to say, small inaccuracies in the geometry or frequencies will cause negligible errors in the molecular energies in comparison with the overall accuracy of the methods. Spin restricted (RHF) based formalisms are used for all singlet state molecules while unrestricted Hartree-Fock methods (UHF) are employed for open shell systems. While the Gn type methods were originally developed within a single reference formulation, Sølling et al.[110] have recently formulated a multireference equivalent of G2(MP2) and G3(MP2) using MRCI+Q and CASPT2 calculations in place of QCISD(T) and MP2. These methods have not, however, been utilised in this thesis.

2.7.2.1 Gaussian-1 (G1) Theory

Gaussian-1 theory[108] was the first of the Gaussian methods to be developed. Geometries are optimised using MP2(Full) theory, that is, with all electrons correlated, in conjunction with the 6-31G(*d*) basis set[87,89]. Harmonic vibrational frequencies (for the calculations of zero-point energies and thermal corrections to the enthalpies and entropies) are generated using HF/6-31G(*d*) and scaled by a factor of 0.8929 to account for known deficiencies in this method for the calculation of frequencies.[111] The effects of anharmonicity on the zero-point energies are assumed to be accounted for by the scaling.

The determination of the G1 energy is based upon a QCISD(T) calculation using the 6-311G(*d*,*p*) basis set. Corrections are then made for the inclusion of diffuse functions, $\Delta E(+)$, and additional polarisation functions, $\Delta E(2df, p)$, using MP4.

$$\Delta E(+) = E\left[\text{MP4/6-311+G}(d,p)\right] - E\left[\text{MP4/6-311G}(d,p)\right] \tag{2.7.1}$$

$$\Delta E(2df,p) = E\left[\text{MP4/6-311G}(2df,p)\right] - E\left[\text{MP4/6-311G}(d,p)\right] \tag{2.7.2}$$

The assumption is that these corrections are additive although it was recognised that this is a potential weakness of the theory. The addition of these two corrections to the QCISD(T)/6-311G(*d*,*p*) energy effectively approximates a QCISD(T)/6-311+G(2*df*,*p*) calculation. As even QCISD(T)/6-311+G(2*df*,*p*) does not adequately reproduce experimental atomisation energies, a further empirical higher level correction (hlc) is introduced to correct for deficiencies in the QCISD(T)/6-311+G(2*df*,*p*) calculation. This correction is based on the number of alpha and beta electrons in the molecule and was constructed so that the correct absolute energies would be obtained for H and H_2. The hlc (in milli-Hartrees) is

$$\Delta E(\text{hlc}) = -0.19 n_\alpha - 5.95 n_\beta \tag{2.7.3}$$

The G1 molecular energy is thus defined as:

$$\begin{aligned} E_0(\text{G1}) = {} & E\left[\text{QCISD(T)/6-311G}(d,p)\right] + \Delta E(+) + \Delta E(2df,p) \\ & + \Delta E(\text{hlc}) + \text{ZPE} \end{aligned} \tag{2.7.4}$$

G1 has been shown to be capable of an accuracy (when compared with experiment) of ± 2 kcal mol^{-1} or better for most molecules containing first row atoms and ± 3 kcal mol^{-1} for molecules with second row elements.

2.7.2.2 Gaussian-2 (G2) Theory

Gaussian-2 theory was introduced by Curtiss et al.[112] in 1991 to compensate for some of the deficiencies in G1. There are three major improvements in G2 over G1: firstly a correction is made for the assumption that the $\Delta E(+)$ and $\Delta E(2df,p)$ corrections are additive; a correction is also made for the extension of the basis to 6-311+G(3*df*,2*p*); finally the higher level correction is also refined. The first two corrections are both made at the MP2 level of theory, resulting in the following expression for the G2 energy correction:

$$\begin{aligned}\Delta E(\text{G2}) = {} & E\left[\text{MP2/6-311+G}(3df,2p)\right] - E\left[\text{MP2/6-311G}(2df,p)\right] \\ & - E\left[\text{MP2/6-311+G}(d,p)\right] + E\left[\text{MP2/6-311G}(d,p)\right]\end{aligned} \qquad (2.7.5)$$

G2 can therefore be regarded as an approximation to QCISD(T)/6-311+G(3*df*,2*p*).

The G1 higher level correction is modified so as to minimise the deviation of the G2 atomisation energy from experimental values for a set of 55 molecules (where the experimental atomisation energies are well known). The modification is

$$\Delta E\left(\text{hlc}_{\text{corr}}\right) = 1.14 n_{pair} \qquad (2.7.6)$$

where n_{pair} is the number of valence electron pairs in the molecule and the units of $\Delta E\left(\text{hlc}_{\text{corr}}\right)$ are milli-Hartrees.

The resulting G2 energy is thus given by

$$\begin{aligned}E_0(\text{G2}) = {} & E\left[\text{QCISD(T)/6-311G}(d,p)\right] \\ & + \Delta E(+) + \Delta E(2df,p) + \Delta E(\text{G2}) \\ & + \Delta E(\text{hlc}) + \Delta E\left(\text{hlc}_{\text{corr}}\right) + \text{ZPE}\end{aligned} \qquad (2.7.7)$$

The mean absolute deviations of G2 atomisation energies from experiment for the molecules in the test set was found to be 0.92 kcal mol^{-1} for species containing only first row elements and 1.08 kcal mol^{-1} for molecules which also contain second row atoms.

Several modifications to G2 theory have been introduced[113-120] with the aim of reducing the computational cost of the method while still providing reasonable accuracy. The most well known of these is G2(MP2) theory[115], where the corrections for basis set expansion are made using only MP2 rather than both MP2 and MP4. The G2(MP2) energy is therefore given by

$$\begin{aligned} E_0(\mathrm{G2}) = {} & E\left[\mathrm{QCISD(T)/6\text{-}311G}(d,p)\right] \\ & + E\left[\mathrm{MP2/6\text{-}311{+}G}(3df,2p)\right] - E\left[\mathrm{MP2/6\text{-}311G}(d,p)\right] \\ & + \Delta E(\mathrm{hlc}) + \Delta E(\mathrm{hlc_{corr}}) + \mathrm{ZPE} \end{aligned} \tag{2.7.8}$$

G2(MP2) theory has been found to yield an average deviation of 1.52 kcal mol^{-1} from experiment for the atomisation energies of the 125 molecules in the test set.

2.7.2.2.1 G2-RAD Theory

As noted earlier, sometimes the use of the UHF formalism can result in spin contamination of the reference state and thus the G2 method, as described above, cannot be reliably employed. A modification of the G2 procedure, called G2-RAD, has been developed by Parkinson, Mayer and Radom[121] to deal with such systems. In this method an RCCSD(T) reference energy is used rather than UQCISD(T) and all MPPT and HF-SCF calculations are performed using the restricted open-shell formalism.

2.7.2.3 Gaussian-3 (G3) Theory

In 1998 Curtiss et al.[122] proposed G3 theory as an improved Gaussian method for the computation of thermochemical data. The geometry and vibrational frequencies are obtained in the same way as for G1 and G2. The reference energy, however, is now calculated at the QCISD(T)/6-31G(*d*) level of theory rather than with QCISD(T)/6-311G(*d*,*p*). The basis set has been changed in response to criticism that the valence-triple zeta basis set is unbalanced.[123] Consequently in G3 theory the parent basis is 6-31G(*d*). The corrections due to the addition of diffuse and extra polarisation functions are therefore given by:

$$\Delta E(+) = E\left[\text{MP4/6-31+G}(d)\right] - E\left[MP4/6\text{-}31G(d)\right] \tag{2.7.9}$$

$$\Delta E(2df,p) = E\left[\text{MP4/6-31G}(2df,p)\right] - E\left[\text{MP4/6-31G}(d)\right] \tag{2.7.10}$$

The largest basis set used in G2 theory, namely 6-311+G(3*df*,2*p*), has also been modified, both to improve the uniformity of the set and to provide corrections for further basis set enlargement; core-polarisation functions were also included. The resulting basis set is termed G3Large[122]; its composition is [4*s*, 2*p*] for H and He, [5*s*, 5*p*, 3*d*, 1*f*] for first row atoms, [7*s*, 6*p*, 4*d*, 3*f*] for second row atoms and [9*s*, 8*p*, 7*d*, 3*f*] for atoms of the third row[124].

It must be noted that for third row non-transition elements G3 employs the new 6-31G(*d*) basis sets (and their extensions with diffuse and polarisation functions) of Rassolov et al.[125] (these differ from the 6-31G(*d*) sets in the basis set libraries of most computational chemistry packages).[126] In addition, the 3*d* electrons are included in the valence space of all frozen core calculations. G3 theory has not yet been extended to include transition block elements.

As a further improvement over G2, core-core and core-valence correlation effects are also accounted for by performing a MP2(Full)/G3Large calculation. $\Delta E(\text{G2})$ is thus replaced by the G3Large correction:

$$\begin{aligned}\Delta E(\text{G3Large}) = E&\left[\text{MP2(Full)/G3Large}\right] - E\left[\text{MP2/6-31G}(2df,p)\right] \\ &- E\left[\text{MP2/6-31+G}(d)\right] + E\left[\text{MP2/6-31G}(d)\right]\end{aligned} \tag{2.7.11}$$

G2 theory has been found to perform relatively poorly in the description of ionisation potentials and electron affinities. This has been largely corrected through modification of the higher level correction term, in particular by using different formulae for atoms and molecules. The hlc now takes the form:

$$\Delta E(\text{hlc}_{\text{atoms}}) = -6.219 n_\beta - 1.185(n_\alpha - n_\beta) \tag{2.7.12}$$

$$\Delta E(\text{hlc}_{\text{molecules}}) = -6.386 n_\beta - 2.977(n_\alpha - n_\beta) \tag{2.7.13}$$

In addition the effects of spin-orbit (SO) coupling corrections for the atoms are also included in G3 theory; thus the final G3 energy is given by:

$$\begin{aligned} E_0(\text{G3}) = E\left[\text{QCISD}(\text{T})/\text{6-31G}(d)\right] + \Delta E(+) + \Delta E(2df, p) + \Delta E(\text{G3Large}) \\ + \Delta E(\text{hlc}) + \Delta E(\text{SO}) + \text{ZPE} \end{aligned} \tag{2.7.14}$$

The test set for evaluating the performance of Gaussian-*n* theories was also extended to include 299 energies (atomisation energies, ionisation potentials, electron affinities and proton affinities).[109] With this new test set, G2 theory now has a mean absolute deviation (MAD) of 1.48 kcal mol^{-1} while for G3 theory the MAD is only 1.02 kcal mol^{-1}.

Modifications of G3 in the spirit of G2(MP2), and some other modifications such as scaling of energies, changes in geometries and the use of coupled cluster theory rather than QCISD(T), have also been introduced.[127-132]

2.7.2.3.1 G3-RAD Theory

As for G2, a G3-RAD procedure has been developed (by Henry, Parkinson and Radom[133]) to describe open shell systems, particularly those which suffer from spin contamination. As for its G2 counterpart, the G3-RAD procedure employs an RCCSD(T) reference energy and ROMP*n* corrections. It uses B3LYP/6-31G(*d*), however, to generate geometries and vibrational frequencies (the latter scaled by 0.9806) and the MPPT calculations are performed using all Cartesian components of the *d* and *f* polarisation functions (6 and 10 respectively). The higher level correction has also been reoptimised for this method and now takes the form:

$$\Delta E(\text{hlc}_{\text{atoms}}) = -6.561 n_\beta - 1.341(n_\alpha - n_\beta) \tag{2.7.15}$$

$$\Delta E(\text{hlc}_{\text{molecules}}) = -6.884 n_\beta - 2.747(n_\alpha - n_\beta) \tag{2.7.16}$$

2.7.2.4 Gaussian-3X (G3X) Theory

The most recent addition to the Gaussian-*n* family of theories is G3X (due to Curtiss, Redfern, Raghavachari and Pople[134]). This was introduced specifically to correct for deficiencies in G3 theory when describing molecules containing second row elements. In G3X theory the geometries and vibrational frequencies are determined using density functional theory, specifically the B3LYP functional, and the larger 6-31G(2*df*,*p*) basis set. (Frequencies are scaled by 0.9854.) The effects of adding *g* functions to the basis sets for the second row elements are also included through the introduction of the G3XLarge basis set (formed by simply adding a *g* function to G3Large). This correction is applied at the SCF level:

$$\Delta E(\text{G3XLarge}) = E[\text{HF/G3XLarge}] - E[\text{HF/G3Large}] \qquad (2.7.17)$$

Thus the correlation effects of the *g* functions are not taken into account. Finally, the higher level correction has also been reoptimised, giving A = 6.783 mE_h, B = 3.083 mE_h, C = 6.877 mE_h and D = 1.152 mE_h.

The test set of molecules has also been increased, now including 376 reaction energies (including atomisation energies, ionisation energies and proton affinities). For this set G3 has a MAD of 1.07 kcal mol^{-1} while G3X shows a small improvement with a MAD of 0.95 kcal mol^{-1}. While most first row molecules are hardly affected by the replacement of G3 by G3X theory, the description of second row molecules is appreciably improved.

2.7.2.5 G3X2 Theory

Finally, Haworth and Bacskay[135] have observed that G3X theory still shows systematic deficiencies in the description of molecules containing second row atoms, particularly phosphorus. We have therefore proposed an extension to G3X, denoted G3X2, in which the G3XLarge correction (Equation (2.7.17)) is applied at the MP2(Full) level, thus recovering additional correlation energy. This is equivalent to performing a G3 calculation using the G3XLarge basis set rather than G3Large (using the B3LYP/6-31G(2*df*,*p*) geometry and vibrational frequencies). Counterpoise corrections for BSSE in the core-valence correlation of second row atoms are also included at the MP2/G3XLarge level of theory. While G3X2 shows improvement over G3X for a small set of phosphorus containing species, further testing, particularly for molecules containing other second row atoms, is required before this method can be recommended for general use.

2.7.3 Complete Basis Set Methods

The complete basis set methods currently represent the highest level of theoretical treatment available for the reliable calculation of heats of formation and related properties. They employ coupled cluster theory in conjunction with the correlation consistent basis sets.

As noted earlier, the cc-pV*x*Z basis sets have been constructed so that the incremental energy lowering due to the addition of correlating functions follows well defined trends. This means that the energies obtained in a sequence of correlation consistent calculations can be fitted to a smooth function of x and extrapolated to a theoretical complete basis set (CBS) limit, that is, $x = \infty$.

A number of extrapolation schemes have been proposed for this purpose over the last 10 years; the most commonly used are the mixed exponential/Gaussian extrapolation of Feller[136] ("*mix*", Equation (2.7.18)), the Schwartz type extrapolations[137] ("$l_{\max}$", Equation (2.7.19) and "$n^{-4} + n^{-6}$", Equation (2.7.20)) and the "x^{-3}" scheme of Helgaker et al.[138] (Equation (2.7.21)).

$$E(x) = A + B\exp(1-x) + C\exp\left(-(1-x)^2\right) \tag{2.7.18}$$

$$E(x) = A + B\left(l_{\max} + 1/2\right)^{-4} \tag{2.7.19}$$

$$E(x) = A + B\left(l_{\max} + 1/2\right)^{-4} + C\left(l_{\max} + 1/2\right)^{-6} \tag{2.7.20}$$

$$E(x) = A + Bx^{-3} \tag{2.7.21}$$

In these equations x is the cardinal number of the basis set (that is, 3 for TZ, 4 for QZ and 5 for 5Z), l_{max} is the highest angular momentum quantum number in the basis, and A, B and C are fitted parameters. As a result of recent work by several groups, the x^{-3} scheme is emerging as the most reliable and trusted of these extrapolations.[138,139] This follows from the observation that the error in the description of the correlation energy is roughly inversely proportional to the number of basis functions, and the number of basis functions in the correlation consistent sets scales as x^3.[139]

Usually calculations using up to (at least) the cc-pV5Z basis sets are used for the extrapolations. Diffuse functions are also often included for electronegative atoms such as oxygen. Furthermore, it has been found that the x^{-3} extrapolation scheme gives the best results when only the energies corresponding to the largest and second largest values of x are used in the fit.[140]

As CCSD(T) has emerged as the most accurate and reliable correlated method, giving an excellent approximation to full-CI, it is the theory of choice for the CBS methods. Furthermore, since SCF energies converge more rapidly than correlation energies, in order to achieve the highest level of accuracy the SCF and correlation energies can be extrapolated separately (although this is not, as a rule, part of the standard procedure).

The effects of correlation of core electrons and between core and valence electrons are usually computed using significantly smaller basis sets than those used for the extrapolations; the cc-pCVTZ basis sets (with augmentation if required) are often the largest which can be employed for this purpose, although for very small molecules cc-pCVQZ may also be used. The core-valence (CV) correlation correction is calculated as the difference in molecular energies when all electrons are correlated and when only valence correlation is accounted for. It is assumed that CV and valence only correlation energies are additive, so a computed CV correction is simply added to the extrapolated valence correlated energy. While it is preferable to compute the CV correlation correction using CCSD(T), lower levels of theory such as MP2 may also be used.

Although relativistic effects tend to be small for molecules which can be treated by CBS methods (usually only first row elements), they are often large enough to be significant.

Scalar relativistic effects are usually included via the computation of the Darwin and mass-velocity terms[141,142]; in our work these have been calculated using Finite Perturbation Theory at the CASPT2 or CASSCF levels of theory. Spin orbit effects are also included in the calculation of thermochemistry where appropriate (usually only for atoms).

As noted above, CBS methods are currently the most accurate methods available for quantum chemical calculations of thermochemistry. Due to the use of the highly correlated CCSD(T) method along with large basis sets, CBS methods are significantly more computationally expensive than the Gaussian-*n* schemes; they are, however, also capable of delivering significantly higher accuracy[143-145], to within ± 0.2 to 2.0 kcal mol^{-1} for heats of formation from atomisation energies, depending on the size of the molecule. CBS theory has therefore successfully achieved an aim that has been a holy grail of computational chemistry, that is, the reliable prediction of reaction energies to chemical accuracy.

2.8 Thermochemistry

The calculation of theoretical heats of formation is essential for many of the applications of quantum chemistry, in particular for aiding in the interpretation of experimental results and for the prediction of reaction kinetics. Unfortunately, however, this requires the computation of the reaction enthalpy for the formation of a molecule relative to the standard states of its constituent elements; in many cases these standard states are liquids or solids for which direct calculation of the energy is not feasible. Given that accurate experimental values are available for the enthalpies of formation of free atoms, a practical alternative is to use these in conjunction with a theoretical prediction of the atomisation energy, ΣD_0, to predict the heat of formation for the molecule of interest. Thus, given an atomisation energy at 0K,

$$\sum D_0 = \sum_{atoms} E_{atom} - E_{molecule} \tag{2.8.1}$$

(where the total molecular energy includes the zero-point vibrational energy), Hess' law can be applied to obtain the $\Delta_f H_0^0$:

$$\Delta_f H_0^0(molecule) = \sum_{atoms} \Delta_f H_0^0(atom) - \sum D_0 \tag{2.8.2}$$

Heats of formation at other temperatures ($\Delta_f H_T^0$) as well as entropies (S_T^0) and Gibbs free energies of formation ($\Delta_f G_T^0$) can then be calculated using the standard methods of statistical mechanics.

2.8.1 Partition Functions[146,147]

The first step in determining the thermal contributions to the enthalpies and entropies of a molecule is to determine its partition function, q; this is a measure of the number of states accessible to the molecule (translational, rotational, vibrational and electronic) at a particular temperature.

Given the energies, E_i, of the available quantum states of a molecule, q is defined as:

$$q = \sum_{i=1}^{\infty} g_i \, \mathrm{e}^{-\beta E_i} \tag{2.8.3}$$

where g_i is the degeneracy of the *i*-th state and

$$\beta = \frac{1}{k_B T} \tag{2.8.4}$$

where k_B is Boltzmann's constant and T is the temperature of interest. The summation in Equation (2.8.3) is over all possible quantum states of the system.

It is assumed that the translational (T), rotational (R), vibrational (V) and electronic (E) modes of the system can be separated, thus allowing the energy of each level, E_i, to be separated into T, R, V and E contributions:

$$E_i = E_i^T + E_i^R + E_i^V + E_i^E \tag{2.8.5}$$

While the translational modes are truly independent from the rest, the separations of the other modes are based on approximations, in particular the Born-Oppenheimer approximation[4] described in **Section 2.1.1** for electronic and (ro-)vibrational motion and the Rigid Rotor Approximation[148] (which assumes that the geometry of the molecule does not change as it rotates) for vibrational and rotational modes. Within these approximations, the total molecular partition function can therefore be factorised into translational, rotational, vibrational and electronic contributions:

$$q = q^T q^R q^V q^E \tag{2.8.6}$$

The translational partition function is given by:

$$\begin{aligned} q^T &= \frac{V}{\Lambda^3} \\ \Lambda &= h\left(\frac{\beta}{2\pi m}\right)^{1/2} \end{aligned} \tag{2.8.7}$$

where h is Planck's constant, m is the mass of the molecule, and V is the volume available to it; for a gas phase system this is the molar volume at the specified temperature and pressure (usually determined by the ideal gas equation).

The formulation for rotational partition functions depends on whether or not the molecule is linear. For linear molecules

$$q^R = \frac{k_B T}{\sigma hcB} \tag{2.8.8}$$

and for non-linear molecules

$$q^R = \frac{1}{\sigma}\left(\frac{k_B T}{hc}\right)^{\frac{3}{2}}\left(\frac{\pi}{ABC}\right)^{\frac{1}{2}} \tag{2.8.9}$$

where σ is the rotational symmetry number of the molecule, c is the speed of light and A, B and C are the rotational constants.

The vibrational partition function in the harmonic approximation is

$$q^V = \prod_i \frac{1}{1 - \mathrm{e}^{-\beta hc\tilde{\nu}_i}} \tag{2.8.10}$$

where $\tilde{\nu}_i$ are the harmonic vibrational frequencies (expressed as wavenumbers) and the product is taken over all (3N–6 or 3N–5) vibrational modes (excluding the reaction coordinate for transition states).

For the electronic partition function it is usually assumed that there will be no thermal excitation into higher electronic states so that the partition function, q^E, is simply given by the degeneracy of the appropriate electronic state.

2.8.2 Thermodynamic Properties[149]

The thermal contributions to thermodynamic properties such as enthalpy, entropy, free energy, heat capacity, etc. are all derived from the molecular partition functions.

For a system of N molecules the internal energy (relative to internal energy at 0K) is given by

$$U_T^0 - U_0^0 = -N\left(\frac{\partial \ln q}{\partial \beta}\right)_V \tag{2.8.11}$$

where the derivative is taken at constant volume.

The enthalpy is therefore

$$\begin{aligned} H_T^0 - H_0^0 &= \left(U_T^0 - U_0^0\right) + p\Delta V \\ &= \left(U_T^0 - U_0^0\right) + Nk_B T \end{aligned} \tag{2.8.12}$$

The entropy of the system is given by

$$S^0 = \frac{\left(U_T^0 - U_0^0\right)}{T} + Nk_B \ln q \tag{2.8.13}$$

so that the change in Gibbs free energy is

$$\begin{aligned} \left(G_T^0 - G_0^0\right) &= \left(H_T^0 - H_0^0\right) - TS^0 \\ &= Nk_B T - Nk_B T \ln q \end{aligned} \tag{2.8.14}$$

The Gibbs free energy change for a reaction is, of course, related to the equilibrium constant for the reaction:

$$\Delta_r G^0 = -Nk_B T \ln K_{eq} \tag{2.8.15}$$

2.9 Kinetics

2.9.1 Transition State Theory (TST)[150-152]

The construction of partition functions is also essential for the calculation of kinetic rate parameters. The central principle of transition state theory (TST), or activated complex theory, is that there is a critical point on the reaction path that connects reactants and products called the transition state, $TS^{\ddagger}$. Once this point has been reached the formation of products is inevitable, that is, the molecule can no longer relax to reform the reactants. For most molecular potential energy surfaces this transition state is identified as a first order saddle point corresponding to a maximum with respect to the reaction coordinate; that is, the minimum energy pathway between reactants and products. This is shown schematically in **Figure 2.9.1**, where the barrier height (with zero point energy included) is defined as the critical energy, $\Delta E^{\ddagger}$, of the reaction.

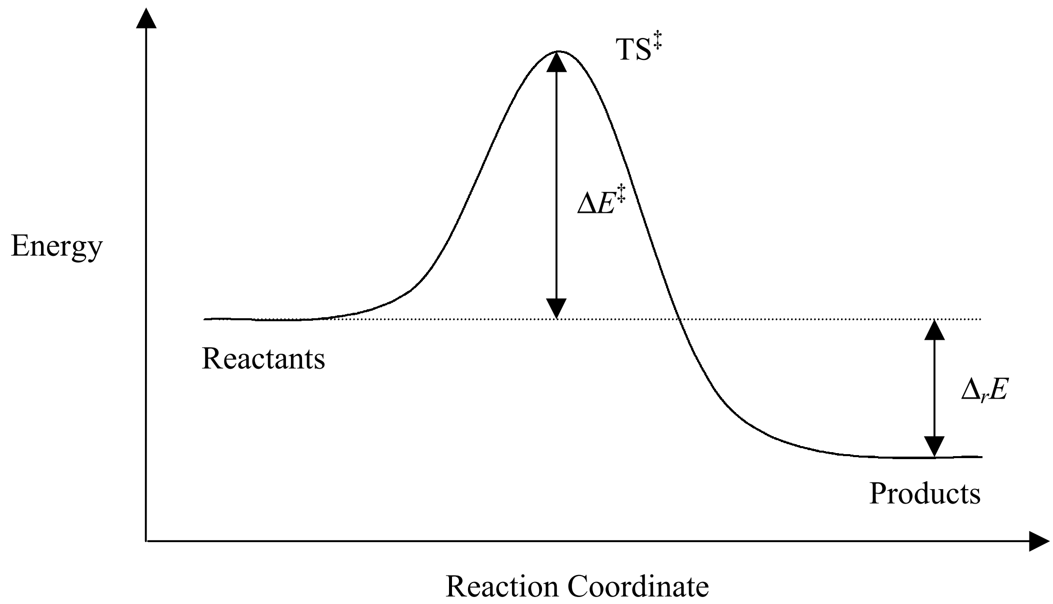

Figure 2.9.1 A schematic potential energy surface.

The statistical derivation of rate coefficients is based upon several assumptions. In addition to the condition that all molecules which reach the transition state must go on to form products (as noted above), it is also necessary to assume that the Born-Oppenheimer approximation[4] is valid and that both reactants and molecules at the transition state geometry are distributed among their states according to the Maxwell-Boltzmann law (even in the absence of an equilibrium between reactants and products). It is also assumed that motion along the reaction coordinate in the transition state can be regarded as a translation rather than a vibration (hence it is also left out of the calculation of the vibrational partition function as noted earlier).

The rate coefficient of a given reaction (in the high pressure limit) at a particular temperature, $k_\infty(T)$, has thus been derived as

$$k_\infty(T) = \frac{k_B T}{h} \frac{q^\ddagger}{\prod_i q_i} \exp\left(\frac{-\Delta E^\ddagger}{kT}\right) \tag{2.9.1}$$

where $q^\ddagger$ is the (canonical) partition function of the transition state and the q_i are the partition functions for each of the reactants.

To facilitate comparison with experimental data it is useful to re-express rate coefficients in Arrhenius[153] or modified Arrhenius form:

$$k_\infty(T) = A \exp\left(-\frac{E_a}{k_B T}\right) \tag{2.9.2}$$

$$k_\infty(T) = A T^n \exp\left(-\frac{E_a}{k_B T}\right) \tag{2.9.3}$$

where A, E_a and (in the modified Arrhenius fit) n are the fitted parameters. A and E_a are known as the pre-exponential (or simply A) factor and the activation energy respectively.

2.9.2 Variational Transition State Theory (VTST)[154-156]

Many reactions, such as simple bond fissions, do not have a barrier as shown in **Figure 2.9.1**, and thus a transition state cannot be identified by locating a first order saddle point. In such cases a more general definition of the transition state must be used where it is defined as the point corresponding to the maximum value of the free energy along the reaction coordinate; this is equivalent to locating the minimum value of the rate coefficient. This approach is known as variational transition state theory. When the reaction has a barrier, this minimum in the rate coefficient effectively coincides with the top of the barrier. For barrierless reactions, however, calculations of energies and vibrational frequencies need to be performed at several points along the reaction coordinate and rate coefficients calculated at each of these points in order to determine the true (minimum) reaction rate and the associated geometry. This, of course, has a much higher computational cost than for reactions with barriers; in addition, such dissociation reactions often have significant multiconfigurational character so MCSCF or density functional methods must be used.

2.9.3 RRKM Theory[157]

RRKM theory, developed by Rice, Ramsperger, Kassel and Marcus[158-162], is a reliable and widely used formalism for predicting the rates of unimolecular decomposition and recombination reactions. The mechanism for such reactions consists of initial activation of the reactant molecule via collisions with a bath gas, *M*, followed by the actual reaction via a (variational) transition state to form products:

$$A + M \leftrightarrow A^{*} + M \tag{2.9.4}$$

$$A^{*} \xrightarrow{k(E)} A^{\ddagger} \rightarrow P \tag{2.9.5}$$

This collisional activation introduces a pressure dependence to the reaction rate. There are three basic regimes: a high pressure limit where the rate of collisions is sufficiently high that Equation (2.9.5) becomes the rate limiting step and the overall rate coefficient is pressure independent; a low pressure limit where collisions are sufficiently rare that Equation (2.9.4) is the rate limiting step and the rate constant is proportional to the pressure; and a “fall-off” region which connects the two. In order to accurately predict the rate of a unimolecular reaction it is therefore necessary to consider the rates of both processes.

Canonical transition state theory is incapable of correctly describing the low pressure and fall-off regimes and thus RRKM was introduced. The development of RRKM theory rests on two major assumptions: that energy gained by collisional activation is rapidly randomised through all degrees of freedom of the reactant (the so called "ergodicity" assumption); and that all molecules which cross the transition state will go on to form products (the transition state theory assumption as stated earlier). The (microcanonical) RRKM rate coefficient, $k(E)$, is then given by:

$$\begin{aligned} k(E) &= \frac{1}{h}\frac{\int_0^{E-E_0} \rho^{\ddagger}(E_+)\,dE_+}{\rho(E)} \\ &= \frac{1}{h}\frac{W^{\ddagger}(E)}{\rho(E)} \end{aligned} \tag{2.9.6}$$

where h is Planck's constant, E is the energy of the system (with the understanding that most of this will be associated with those modes which have the potential to result in reaction), E_0 is the critical energy, $\rho(E)$ and $\rho^{\ddagger}(E_+)$ are the densities of states of the reactant, A^*, and the transition state, $A^{\ddagger}$, respectively and $W^{\ddagger}(E)$ is the total number of states of the $TS^{\ddagger}$ with energy less than E. It can be shown that, in the limit of high (∞) pressure, averaging $k(E)$ over the Boltzmann distribution yields the canonical transition state formula (Equation (2.9.1)).

In the fall-off and low pressure regions the rate coefficient for the reaction also depends strongly on the rate of collisional energy transfer, $R(E,E')$. This is related to the probability of energy transfer, $P(E,E')$; that is, the probability that a reactant with energy E' will end up with energy E:

$$P(E,E') = \frac{[M]R(E,E')}{\omega(E')} \tag{2.9.7}$$

where $[M]$ is the number concentration of the bath gas and $\omega(E')$ is the total collision frequency.

The first moment of $R(E,E')$ with respect to energy is the mean energy transferred per collision, $\langle \Delta E \rangle$, while the second moment is the mean-square energy transferred per collision, $\langle \Delta E^2 \rangle$; the moments are formally defined by:

$$\langle \Delta E^n \rangle = \int_o^\infty (E-E')^n P(E,E') dE \tag{2.9.8}$$

It has been found that the pressure dependence of the overall rate constant is fairly insensitive to the functional form of $R(E,E')$, instead depending largely on the moments alone. This means that it is usually sufficient to use the simple exponential-down and Gaussian forms for $R(E,E')$:

$$R(E,E') = \frac{1}{n(E')} \exp\left[-\frac{E'-E}{\alpha}\right] \tag{2.9.9}$$

and

$$R(E,E') = \frac{1}{n(E')} \exp\left[-\left(\frac{E'-E}{\alpha}\right)^2\right] \tag{2.9.10}$$

respectively, where $n(E')$ is a normalisation factor to ensure the correct overall collision frequency and α is a constant chosen to yield reasonable values for the moments, that is, the values obtained from accurate trajectory calculations of collisional energy transfer.

The overall thermal unimolecular rate constant, k_{uni}, can finally be obtained by solving the master equation

$$-k_{uni}g(E)=[M]\int_0^\infty\left[R(E,E')g(E')-R(E',E)g(E)\right]dE'-k(E)g(E) \qquad (2.9.11)$$

where $g(E)$ is the population of reactant molecules with energy *E*. In practice, k_{uni} for a given temperature and pressure is usually calculated at a range of energies and averaged. Recombination reaction rates can also be obtained by RRKM using the rate of the reverse (unimolecular decomposition) reaction and the principle of microscopic reversibility.

2.10 Population Analysis

Quantum chemical calculations, as described in **Sections 2.2** and **2.3**, yield total molecular wavefunctions and/or total molecular probability densities. From a chemical point of view, however, it is often useful to describe a molecule in terms of electrons associated with individual nuclei and with covalent bonds. A range of schemes have been proposed for extracting such localised information (atomic and bond populations) from the delocalised one-particle density function; of these, the most commonly used is the simple Mulliken method.[163] Assumptions and definitions vary widely amongst the various population analysis models, thus different methods are often found to give significantly different results. One of the more respected methods, however, is the Roby-Davidson population analysis[164-166], which has been used in this thesis.

The Roby-Davidson procedure involves partitioning the electron density of a molecule, *ABC*…, into populations (numbers of electrons) which can be associated with each atom, with pairs of atoms, with triples of atoms, and so on. This is achieved by applying appropriate projection operators to the total density as obtained from quantum chemical calculations. These projection operators, $\hat{P}_A$, $\hat{P}_B$, $\hat{P}_C$, …, $\hat{P}_{AB}$, $\hat{P}_{AC}$, $\hat{P}_{BC}$, …, $\hat{P}_{ABC}$, … are constructed from the atomic orbitals of the molecule so as to span the space of individual atoms, *A*, *B*, *C*, …, pairs of atoms, *AB*, *AC*, *BC*, …, triples of atoms, *ABC*, … etc. Thus

$$\hat{P}_A = \sum_{\mu,\nu \in A} \left|\varphi_\mu\right\rangle \left(S^{-1}\right)_{\mu\nu} \left\langle\varphi_\nu\right| \tag{2.10.1}$$

$$\hat{P}_B = \sum_{\mu,\nu \in B} \left|\varphi_\mu\right\rangle \left(S^{-1}\right)_{\mu\nu} \left\langle\varphi_\nu\right| \tag{2.10.2}$$

$$\hat{P}_{AB} = \sum_{\mu,\nu \in A,B} \left|\varphi_\mu\right\rangle \left(S^{-1}\right)_{\mu\nu} \left\langle\varphi_\nu\right| \tag{2.10.3}$$

etc.

where μ and ν run over the (non-orthogonal) spin orbitals of the relevant atoms and $\left(S^{-1}\right)_{\mu\nu}$ is an element of the inverse of the overlap matrix, $\boldsymbol{S}$.

As $\hat{P}_A$ is constructed from the spin orbitals of atom *A*, it can act on the total (one-electron) density, ***D***, to project out the density associated with atom *A*; likewise for $\hat{P}_B$, while $\hat{P}_{AB}$, being built from the spin orbitals of both atoms *A* and *B*, projects out the density associated with the pair of atoms. The occupation numbers, n_A, n_B, n_{AB}, etc. (that is, the number of electrons associated with each atom, pair of atoms, etc.) are therefore given by

$$\begin{aligned} n_A &= \mathrm{Tr}\left(\boldsymbol{DP}_A\right) \\ &= \sum_{\lambda,\sigma} \sum_{\mu,\nu \in A} D_{\lambda\sigma} S_{\sigma\mu} \left(S^{-1}\right)_{\mu\nu} S_{\nu\lambda} \end{aligned} \tag{2.10.4}$$

$$n_B = \mathrm{Tr}\left(\boldsymbol{DP}_B\right) \tag{2.10.5}$$

$$n_{AB} = \mathrm{Tr}\left(\boldsymbol{DP}_{AB}\right) \tag{2.10.6}$$

etc.

Once the occupation numbers are known, the degree of electron sharing between pairs or multiplets of atoms can also be quantified by defining shared electron numbers, σ_{AB}, σ_{AC}, σ_{BC}, σ_{ABC}, etc. as

$$\sigma_{AB} = n_A + n_B - n_{AB} \tag{2.10.7}$$

$$\sigma_{ABC} = n_A + n_B + n_C - n_{AB} - n_{AC} - n_{BC} + n_{ABC} \tag{2.10.8}$$

The degree of electron sharing between two atoms can be considered as a measure of the covalent bonding between them. While single and double covalent bonds have been found to have shared electron numbers of approximately 1 and 2 respectively, it is important to calibrate the shared electron numbers for any *A*-*B* bond before using them to investigate and interpret the bonding in new molecules. For example, the S-O bond in SO only has a population of 1.47 even though it is formally a double bond.

The partial charge on each atom, q_A, q_B, etc. is the difference between its nuclear charge and the electron density associated with that atom; the latter is found by equally partitioning any shared electron density.

$$q_A = n_A - \frac{1}{2}\sum_{B(\neq A)} \sigma_{AB} - \frac{1}{3}\sum_{C(\neq B(\neq A))} \sigma_{ABC} \cdots \tag{2.10.9}$$

One of the most important issues affecting the reliability of the Roby-Davidson population analysis is the choice of the spin orbital basis used in the construction of the projection operators. Ahlrichs and coworkers[166,167] have proposed the use of a minimal set of modified atomic orbitals (MAO's), $\boldsymbol{\varphi}$, consisting of individual atom centred minimal basis sets, $\boldsymbol{\varphi}^A$, $\boldsymbol{\varphi}^B$, etc. These MAO's are constructed by firstly partitioning the molecular density matrix, $\boldsymbol{D}$, (expressed in terms of the original atomic orbitals, $\boldsymbol{\chi}$) into diagonal blocks associated with each atom, $\boldsymbol{D}_A$, $\boldsymbol{D}_B$, etc.:

$$\boldsymbol{D} = \begin{array}{c} \\ A \\ B \\ C \\ \vdots \end{array} \left(\begin{array}{c|c|c|c} \overset{A}{\chi_1\ \chi_2\ \chi_3 \ldots} & B & C & \ldots \\ \begin{matrix}\chi_1\\ \chi_2\\ \chi_3\\ \vdots\end{matrix}\ \ \boldsymbol{D}_A & & & \\ \hline & \boldsymbol{D}_B & & \\ \hline & & \boldsymbol{D}_C & \\ \hline & & & \end{array} \right) \tag{2.10.10}$$

Each block is then diagonalised in order to give the MAO's, $\boldsymbol{\varphi}$, for the associated atom; for example,

$$\begin{aligned} \boldsymbol{U}^{A+}\boldsymbol{D}^{A}\boldsymbol{U}^{A} &= \boldsymbol{U}^{A+}\boldsymbol{S}^{A}\boldsymbol{U}^{A}\boldsymbol{d}^{A} \\ &= \boldsymbol{d}^{A} \end{aligned} \tag{2.10.11}$$

and hence

$$\boldsymbol{\varphi}^{A} = \boldsymbol{\chi}^{A}\boldsymbol{U}^{A} \tag{2.10.12}$$

Only a minimal number of these MAO's on each atom are used to construct the projection operators; that is, only the MAO's with the highest occupation numbers (eigenvalues) are included. This means that the set of projection operators may not, in fact, fully span the space of the molecule and some fraction of the total charge is left unassigned. This unassigned charge, ε, is defined as:

$$\varepsilon = n - Tr\left(\boldsymbol{DP}\right) \tag{2.10.13}$$

where n is the total number of electrons in the system and $\boldsymbol{P}$ is the total projection operator for all atoms in the molecule:

$$\boldsymbol{P} = \boldsymbol{P}_{A} + \boldsymbol{P}_{B} + \boldsymbol{P}_{C} + \ldots \tag{2.10.14}$$

In practice ε is usually very small (less than 0.05) and can be safely neglected. A large unassigned charge (0.2 or larger) is, however, believed to be indicative of hypervalency in the molecule.[168] The concept of the unshared population, u_A, associated with an atom has been introduced in an effort to quantify this hypervalency:

$$u_{A} = n - \mathrm{Tr}\left(\boldsymbol{DP}_{AB'C'\ldots}\right) \tag{2.10.15}$$

where $\boldsymbol{P}_{AB'C'\ldots}$ is a projection operator defined in terms of the minimal MAO basis for atom A but the non-minimal (full) MAO sets for all other atoms.

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