Abbreviations

%N	percentage nitrogen by mass
2-NDPA	2-Nitrodiphenylamine
AO	atomic orbital
a.u.	atomic units
B3LYP	Becke, 3-parameter, Lee-Yang-Parr hybrid functional
BCP	bonding critical point
CH_3CH_3	NC repeat unit with two $-OCH_3$ capping groups
CH_3OH	NC repeat unit with $-OCH_3$ capping group on ring 1 and $-OH$ group on ring 2
CCP	cage critical point
CP	critical point
DFT	density functional theory
DSC	differential scanning calorimetry
DOS	degree of substitution
DPA	diphenylamine
ELF	electron localisation function
EM	energetic materials
EN	ethyl nitrate

ESP	electrostatic potential
G09	Gaussian 09 revision D.01
GGA	generalised gradient approximation
GM	genetically modified
GTO	Gaussian type orbitals
GView	Gauss View 5.0.8
HF	Hartree-Fock
HMF	hydroxymethylfurfural
HOMO	highest occupied molecular orbital
IR	infra-red spectroscopy
LDA	local density approximation
LOL	localized orbital locator
MD	molecular dynamics
MEP	minimum energy path
MM	molecular mechanics
MMFF94	Merck molecular force field 94
MO	molecular orbitals
MP2	Møller–Plesset perturbation theory with second order correction
MW	molecular weight
NC	nitrocellulose
NCP	nuclear critical point
NG	nitroglycerine
NMR	nuclear magnetic resonance spectroscopy

OHCH$_3$ NC repeat unit with $-$OH capping group on ring 1 and $-$OCH$_3$ group on ring 2

PCM   polarisable continuum model

PES   potential energy surface

PETN   pentaerythritol tetranitrate

PETRIN   pentaerythritol trinitrate

QM   quantum mechanics

QTAIM   quantum theory of atoms in molecules

RCP   ring critical point

RHF   restricted HF

ROHF   restricted-open HF

UHF   unrestricted HF

SB59   1,4-bis(ethylamino)-9,10-anthraquinone dye

SCF   self-consistent field

SEM   scanning electron microscopy

SMD   solvation model based on density

S$_N$2   bi-molecular nucleophilic substitution reaction

STO   Slater type orbitals

TG   thermogravitmetric analysis

TS   transition state

UFF   universal force field

UV   ultraviolet

UVvis   ultraviolet–visible spectroscopy

ωB97X-D ωB97X-D long-range corrected hybrid functional

ZPE   zero-point energy

Chapter 1

Theory and Implementation

1.1 Electronic structure methods

Electronic structure methods apply the principles of quantum mechanics to the evaluation of electron position and movement, thereby allowing chemists to derive the properties and interactions of molecules. Despite the long history of research and use of nitrocellulose (NC) in industry, experimental analysis has failed to distinguish the fine mechanistic details of its decomposition. This is partly owed to the variation arising from biodiverse NC source materials, combined with the complexity due to the interplay of many different and simultaneous degradation interactions. Electronic structure methods provide a means to untangle the individual facets of decomposition.

At the most fundamental level, the wave function (Ψ) holds the description of a quantum system. In a non-relativistic system, the probability of a particle possessing a given momentum, or residing in a particular location, is given by the probability density. This can be obtained by multiplication of Ψ with its complex conjugate, $|\Psi^2|$. Integration of $|\Psi^2|$ over a region of space returns the probability that a system will be found within, called the Born interpretation. Values of Ψ are chosen to be othonormal; integrating $|\Psi^2|$ over all space gives the probability of 1:

$$\langle \Psi_i | \Psi_j \rangle = \delta_{ij} \tag{1.1}$$

where all states are represented by i and j, and:

$$\delta_{ij} = 0 \text{ for } i \neq j$$

$$\delta_{ij} = 1 \text{ for } i = j \text{ the integral is one.}$$

Operators acting on Ψ yield the observable properties of the system. The operator returning the energy of the system is called the the Hamiltonian operator (**H**). Erwin Schrödinger

proposed his equation in 1926, describing a quantum system using its wave function [1]. Schrödinger's time-independent equation is:

$$\mathbf{H}\Psi = E\Psi \qquad (1.2)$$

and the energy of the system is given by the expectation value of the Hamiltonian operator:

$$E = \langle \Psi | \mathbf{H} | \Psi \rangle \qquad (1.3)$$

where the Hamiltonian operator $\mathbf{H}$ is an eigenvalue of the wave function Ψ, and E is a scalar denoting the energy of the system. A given system may have many acceptable values for Ψ, each with an associated value for E.

The general form of the Hamiltonian is given by:

$$\mathbf{H} = -\sum \frac{\hbar^2}{2m_e}\nabla_i^2 - \sum \frac{\hbar^2}{2m_k}\nabla_k^2 - \sum_i \sum_k \frac{e^2 Z_k}{r_{ik}} + \sum_{i<j} \frac{e^2}{r_{ij}} + \sum_{k<l} \frac{e^2 Z_k Z_l}{r_{kl}} \qquad (1.4)$$

where all electrons are represented by i and j, and all nuclei by k and l [2]. $\hbar$ is the reduced Planck's constant ($\hbar = \frac{h}{2\pi} = 1.055 \times 10^{-34}$), m_e is the mass of an electron, m_k is the mass of the nucleus k, e is the charge of an electron, Z_k is the atomic number of k and r_{ik} is the distance between particles i and k. When using atomic units (a.u.), the value of e, m_e and $\hbar$ are reduced to 1. ∇^2 refers to the Laplacian operator, which describes the divergence of the gradient of a field. In Cartesian space, this is defined as the sum of the second derivatives of the gradient with respect to each of the three dimensions (x,y,z):

$$\nabla_i^2 = \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} \qquad (1.5)$$

The first and second terms of equation (1.4) correspond to the kinetic energy of the electrons and the nuclei, respectively. Electron-nuclear attraction is described by the third term; the fourth term describes inter-electronic repulsion and the final term the inter-nuclear repulsion. The final three potential energy terms are identical to their expression in classical mechanics. The kinetic energy terms can be expressed as the eigenvalue of the kinetic energy operator ($\mathbf{T}$):

$$\mathbf{T} = -\frac{\hbar^2}{2m}\nabla^2 \qquad (1.6)$$

The total, non-relativistic Hamiltonian can therefore be written in terms of the kinetic energy and potential energy operators:

$$\mathbf{H} = \mathbf{T}_e + \mathbf{T}_N + \mathbf{V}_{e-N} + \mathbf{V}_{e-e} + \mathbf{V}_{n-n} \tag{1.7}$$

where the terms are as they were in equation 1.4. $\mathbf{T}_e$ corresponds to the kinetic energy of the electrons, $\mathbf{T}_N$ the kinetic energy of the nuclei, $\mathbf{V}_{e-N}$ the coulombic interaction between electron and nuclei, $\mathbf{V}_{e-e}$ the electron-electron repulsion and $\mathbf{V}_{n-n}$ the nuclear-nuclear interaction.

1.1.1 Born-Oppenheimer approximation

In a real system, the motion of elections and nuclei are coupled. Electron density flows dynamically in response to the change in nuclear position and repulsion from other electrons. The correlated motion of particles is described by the pairwise attractive and repulsive terms of the Schrödinger equation. However, this interdependency makes defining a wave function difficult. Relative to electronic motion, nuclei move far more slowly, owing to their much greater mass (the mass of a proton is around 1836 times larger than that of the electron). Nuclear positions therefore appear essentially stationary when compared to that of the electrons. Exploiting this property, the Born-Oppenheimer approximation fixes the nuclear positions. In this way, the motion of electrons and nuclei can be decoupled, and the electronic properties of the system may be calculated for the given nuclear coordinates. Dependency on the nuclear kinetic energy term ($\mathbf{T}_N$) is removed, as the nuclei are frozen. The nuclear-nuclear repulsive term ($\mathbf{V}_{n-n}$) becomes a constant for the specified geometry. Equation 1.4 is reduced to its electronic components and nuclear constants which in atomic units can be written as:

$$\mathbf{H} = \mathbf{T}_e + \mathbf{V}_{e-N} + \mathbf{V}_{e-e} + \mathbf{V}_{n-n} \tag{1.8}$$

and the electronic terms can be collected into one term, to simplify notation:

$$\mathbf{H} = \mathbf{H}_{el} + \mathbf{V}_{n-n} \tag{1.9}$$

The Schrödinger's equation can now be written in terms of only the electronic coordinates:

$$(\mathbf{H}_{el} + \mathbf{V}_{n-n})\Psi_{el}(\mathbf{q}_i; \mathbf{q}_k) = E_{el}(\mathbf{q}_i; \mathbf{q}_k) \tag{1.10}$$

where the electronic coordinates are given by $\mathbf{q}_i$, the stationary nuclear positions by $\mathbf{q}_k$ and E_{el} is the electronic energy of the system. The values of $\mathbf{q}_i$ are independent variables, whereas the values of $\mathbf{q}_k$ are parameters.

Given the example of a diatomic molecule, a potential energy curve can be obtained by calculating the value of E_{el} at different inter-nuclear distances. A series of these calculations generates a potential energy profile, allowing identification of an equilibrium bond length at the minimum of the curve. Calculation of E_{el} for all possible nuclear coordinates in a system of three or more atoms facilitates the construction of a hypersurface on which the potential energy is defined by the nuclear geometry, called a potential energy surface (PES). Exploration of the PES allows for discovery of global and local minimum energy structures, intermediate products on a reaction coordinate and transition states, through scrutiny of the at a particular set of nuclear coordinates.

Molecular structure theories adopt the Born-Oppenheimer approximation for its effective simplification of the coupled nuclear-electronic motion problem, in addition to its accuracy; this assumption works well for ground state molecules and only introduces very small errors. The model breaks down in the situation where there are multiple PES close in energy to one another, or even intersecting. In these cases the coupled equations must be considered. However for the work within this study, the Born-Oppenheimer approximation is successfully applied for all calculations involving electronic structure determination.

1.1.2   Slater determinants

In a system of multiple electrons, each electron is indistinguishable. If the positions of two electrons are swapped, the distribution of electron density in the system remains the same. The Pauli exclusion principle states that no two identical fermions, such as electrons, may simultaneously occupy the same quantum state within the same system. When considering an atom with two or more electrons, this means that none may have the same set of quantum numbers. As a result, for two equivalent electrons, the wave function of the system is antisymmetric with respect to the exchange of their coordinates:

$$\Psi(1,2..i,...j..N) = -\Psi(1,2..i,...j..N) \tag{1.11}$$

This requirement is fulfilled by expressing the wave function as a Slater determinant, which changes sign with permutation of the coordinates of two electrons. In the case of a

multi-electronic system, the generalised Slater determinant for N total electrons is as follows:

$$\psi_{SD} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(1) & \chi_2(1) & \cdots & \chi_N(1) \\ \chi_1(2) & \chi_2(2) & \cdots & \chi_N(2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(N) & \chi_2(N) & \cdots & \chi_N(N) \end{vmatrix} \qquad (1.12)$$

where χ_N represents single electron wave functions, or spin-orbitals [3]. In the context of a molecule, the single electron wave functions are molecular orbitals. Rows are labelled by the coordinates of each electron: (1), (2) $\cdots$ (N), whereas each column uses a different orbital function: χ_1, $\chi_2 \cdots$, χ_N. If the labels of (1) and (2) are exchanged, the rows of the determinant are exchanged; a general property of determinants is that the interchange of two rows leads to a change of sign. The expanded form of the determinant (ψ_{SD}) will have the opposite sign when a pair of electronic coordinates are switched, by switching rows within the determinant, thereby fulfilling the antisymmetry requirement. In the dis-allowed case of two equivalent electrons occupying the same spin-orbital, two columns would be identical [4]. The evaluation of the determinant would then be zero, indicating that the probability of two electrons with identical spin occupying the same orbital was zero.

1.1.3 Variational principle

In order to obtain the ground state energy of a system, the wave function giving the lowest energy must be found. This corresponds to the electronic configuration with lowest value of E_{el}. Difficulty then arises, as ground state energy cannot be computed exactly. The variational theorem states that the calculated energy of any guess wave function can only be greater than or equal to the real ground-state energy (E_0) of the system. This provides a criterion for selection of the best guess wave function, as the energy is always bounded from below, where:

$$E = \langle \Psi | \mathbf{H} | \Psi \rangle \geq E_0 \qquad (1.13)$$

for a normalised wave function. Thus, when choosing between different trial wave functions, the solution with the lowest energy is the one closest to the exact value.

1.1.4 Hartree-Fock self-consistent field method

In practice, equation 1.10 can only be solved *exactly* in very few circumstances; no exact solutions can be found for problems involving three or more interacting particles, such as

in the case of a helium atom possessing two electrons and one proton. For systems of complexity greater than one electron, further approximations must be made.

The Hartree-Fock (HF) approximation was the first practically applicable method for calculation of the ground-state energy of atoms with fixed nuclear positions. The self-consistent field (SCF) method was proposed by Hartree in 1928 [5, 6]. *N* electrons are treated as individual particles occupying single-electron spin orbitals and move independently of the dynamics of any other fermions in the system. The effective interaction of one electron with all other fermions is averaged and applied as a static external field, in the form of a spherical potential around the electron (called the mean-field approximation). In this way, the *N*-body problem is reduced to a 1-body problem. The approximation neglects exchange in the electron-electron interaction; the calculated Hartree wavefunction alone does not include any contribution from electron correlation, and incorrectly implies that the electrons are distinguishable. Fock developed this idea by introducing Slater determinant wave functions [7]. The effects of exchange on the coulombic repulsion were incorporated, achieved by taking the trial wave function as a single Slater determinant.

For an electron in orbital χ_i in the field of nuclei *M* and other electrons χ_j, the Hamiltonian operator is comprised of three terms, corresponding to the three contributions to the energy. The core Hamiltonian operator, $\mathbf{H}^{core}$ comprises of the kinetic energy of each electron, and the electron-nuclear interaction:

$$\mathbf{H}^{core}(1) = -\frac{1}{2}\nabla_1^2 - \sum_{A=1}^{M} \frac{Z_A}{r_{1A}} \tag{1.14}$$

where Z_A is the nuclear charge and r_{1A} is the separation of electron (1) with nucleus A. In a mono-electronic system, this would be the only operator present.

The coulomb operator, $\mathbf{J}_j$ corresponds to the averaged interaction potential between each pair of electrons in the same orbital, and with other electrons in other orbitals χ_j:

$$\mathbf{J}_j(1) = \int d\tau_2 \chi_j(2) \frac{1}{r_{12}} \chi_j(2) \tag{1.15}$$

where $d\tau_i$ indicates the integration is over the spatial and spin coordinates of electron *i*, and r_{12} is the distance between the two electrons.

The exchange operator $\mathbf{K}_j$, is only non-zero for electrons with the same spin, arising

due to the antisymmetry of the wavefunction:

$$\mathbf{K}_j(1)\chi_i(1) = \left[\int d\tau_2 \chi_j(2)\frac{1}{r_{12}}\chi_j(2)\right]\chi_j(1) \tag{1.16}$$

defined in terms of its effect when acting on χ_i. The Hamiltonian operator written in terms of its core, coulomb and exchange contributions is as follows:

$$\left[\mathbf{H}^{core}(1) + \sum_{j=1}^{N}\{\mathbf{J}_j(1) - \mathbf{K}_j(1)\}\right]\chi_i(1) = \sum_{j=1}^{N}\varepsilon_{ij}\chi_j(1) \tag{1.17}$$

and can be simplified to:

$$\mathbf{F}_i\chi_i = \sum_j \varepsilon_{ij}\chi_j \tag{1.18}$$

where $\mathbf{F}_i$ is the Fock operator, and ε_{ij} is the energy of orbital χ_j. The operator is a one electron Hamiltonian for an electron in a multi-electron system. For "closed shell" problems where there are no unpaired electrons, the operator has the form:

$$\mathbf{F}_i(1) = \mathbf{H}^{core}(1) + \sum_{j=1}^{N/2}\{2\mathbf{J}_j(1) - \mathbf{K}_j(1)\} \tag{1.19}$$
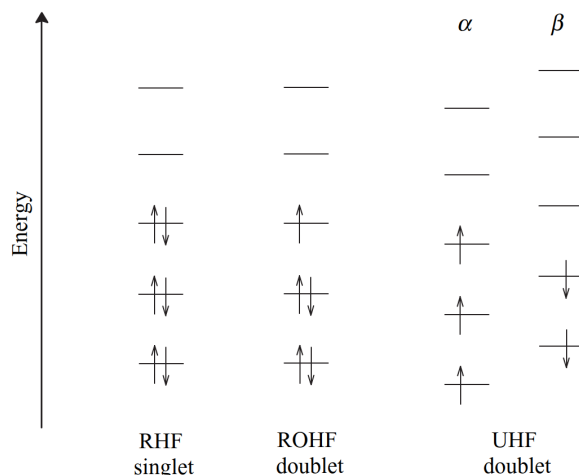
$\mathbf{H}^{core}$ consisting of the kinetic energy terms can be solved exactly, the electron-electron repulsion $\mathbf{J}_j$ must apply the mean-field approximation but the exchange component $\mathbf{K}_j$ is solved iteratively. Starting with an initial guess wave functions for the occupied for the occupied orbitals χ_i, solution of the one-electron HF eigenvalue equations generates a new set of orbitals. Applying the variational principle, the spin orbitals are varied to minimise the energy. This process propagates using the newly generated orbitals for the next optimisation, until the difference between the final solution and its previous iteration falls within an acceptable threshold and is "self-consistent".

1.1.5 Open shell systems

The forced pairing of electrons of opposing spin into a shared orbital is referred to as the *restricted* scheme (figure 1.1). For closed shell systems, this treatment is appropriate. For species with unpaired electron spin such as in transition metal complexes or radicals, an alternative model allowing singly occupied orbitals must be adopted.

The *restricted-open* scheme maintains electron pairing within orbitals except in the case of the highest occupied molecular orbital (HOMO), which is singly occupied. An al-

ternative model is the *unrestricted* scheme, where all electrons are unpaired and reside in their own orbitals. A caveat of the unrestricted model is its susceptibility to spin contamination, which has consequences at large bond separations.

Figure 1.1: The electron ordering schemes corresponding to the restricted Hartree-Fock (HF), restricted-open HF (ROHF) and unrestricted HF (UHF) methods of calculation for closed and open shell systems [8].

1.1.6 Electron correlation

The energy difference between the real energy and the result obtained from HF is called the correlation energy, $E_{corr.}$.

$$E_{corr.} = E_{exact} - E_{HF} \tag{1.20}$$

The $E_{corr.}$ term can be divided into two components. The static correlation component arises as a system cannot be fully described by a single set of molecular orbitals (MO)s, and the dynamic correlation contribution derives from the neglect of instantaneous electron repulsion interactions. The latter includes the description of instantaneous dipolar interactions, leading to Van der Waals forces, which are lost when the electron repulsion terms are averaged. Post-HF methods such as perturbation theory and coupled-cluster techniques aim to account for the difference by inclusion of the contribution from correlation as an additive term, or *via* multi-electron wave functions. However, these methods become prohibitively expensive with increasing numbers of electrons, such that the system size is limited to small molecules for calculations of high accuracy. The high computational demand associated with handling a many-electron wave function is circumvented in density functional theory (DFT), by expression of the total energy in terms of electron density.

1.2 Density functional theory

There are two approaches for solving the Schrödinger equation for a polyatomic system with many electrons. *Ab initio* methods generate solutions from "first principles", without information gained from experimental results. By contrast, *semi-empirical* methods deal with parameters fitted to experimental quantities, such as enthalpies of formation or dipole moments. DFT derives from the Thomas-Femi-Dirac model, whereby electron correlation is modelled via functionals of the electron density, $\rho(r)$. Electron density has reduced dimensionality when compared with the wave function, and can be obtained both *via* theoretical methods as well as experimentally, such as through x-ray diffraction. Currently, it forms the most widely used approach for quantum mechanics (QM) problems. When compared to HF and post-HF methods, DFT provides increased computational efficiency. Modern hybrid functionals are able to produce results on the order of MP2 accuracy, utilising only the resource of a HF calculation. The NC monomers, dimer and trimer models examined in this study consist of between 30 - 75 atoms; DFT provided the best pay-off between accuracy and efficiency for application on a system of this size.

1.2.1 Hohenberg-Kohn formalism

Modern DFT is based on two fundamental theorems proposed by Hohenberg and Kohn in 1964 [**?**]. The first theorem states that for the ground state of system, there exists a unique energy and non-degenerate electron density. The density can therefore be used to determine the Hamiltonian of a system, thereby also describing its ground state energy $E[\rho(r)]$, wave function and other properties of the system. The energy is a functional of the density:

$$E[\rho(r)] = \int \rho(r)V(r)\,d(r) + F[\rho(r)] \qquad (1.21)$$

where $V(r)$ is the external potential, with the first term of the equation arising from the interaction of electrons with $V(r)$ (usually a coulombic attraction between electrons and nuclei). $F[\rho(r)]$ is a universal functional of the density, representing the total kinetic energy and electron-electron repulsion. It is not possible to explicitly express $F[\rho(r)]$ in terms of $\rho(r)$, so its exact form is not known.

The second theorem states that the ground state energy can be obtained *via* minimisation of $E[\rho(r)]$. Since equation 1.21 gives the exact energy of the original Hamiltonian, by applying the variational principle, the lowest possible value of $E[\rho(r)]$ gives the real solu-

tion for the ground state energy, and therefore $\rho(r)$. It is not possible to verify that the found $\rho(r)$ giving the lowest value of $E[\rho(r)]$ corresponds to a wave function obeying the Pauli exclusion principle requirement for antisymmetry. This problem and the unknown identity of $F[\rho(r)]$ were addressed by the Kohn-Sham equations.

1.2.2   Kohn-Sham DFT

The Kohn-Sham scheme establishes a system with N non-interacting electrons, in a similar manner to HF [?]. The wave function is described by a single Slater determinant of one-electron orbitals, and the electron density is set to be identical to that of the exact ground state wave function. Using this approximation, the energy of the system can again be divided up into its component contributions:

$$E[\rho] = E_{KE}[\rho(r)] + E_H[\rho(r)] + E_V[\rho(r)] + E_{XC}[\rho(r)] \tag{1.22}$$

where E_{KE} is the kinetic energy of the non-interacting electrons, E_H the Hartree electrostatic energy corresponding to the electron-electron repulsion between electrons, E_V the interaction between the electrons and the external potential due to the nuclei, and E_{XC} the exchange-correlation energy, encapsulating non-classical exchange and correlation contributions not accounted for by the other terms. Referring back to the Born interpretation (equation 1.1), the density can be obtained from the sum of the square moduli of the wave function:

$$\rho(r) = \sum_{i=1}^{N} |\psi_i(r)|^2 = |\Psi|^2 \tag{1.23}$$

Aside from the kinetic energy term in equation 1.22, the remaining terms can be summarised into an effective potential v_{eff}:

$$v_{eff} = v_H(r) + v_V(r) + v_{XC}(r) \tag{1.24}$$

where $v_H(r)$ is the electron repulsion potential and $v_V(r)$ the electron-ion potential. The exchange-correlation potential $v_{XC}(r)$ is the functional derivative of E_{XC}. If E_{XC} is known then $v_{XC}(r)$ can be computed from the following equation:

$$v_{XC}(r) = \frac{\delta E_{XC}}{\delta \rho} \tag{1.25}$$

The kinetic energy term in equation 1.22 can be expressed in terms of the one-electron

wave function:

$$E_{KE}[\rho(r)] = -\frac{1}{2}\nabla^2 \sum_{i=1}^{N} \langle \psi_i | \nabla^2 | \psi_i \rangle \tag{1.26}$$

Combining equations 1.24 and 1.26, a new Hamiltonian can be written, only considering the non-interacting system:

$$\mathbf{H} = -\frac{\nabla^2}{2} + v_{eff} \tag{1.27}$$

Using the Kohn-Sham formulation of the Schrödinger equation, the one-electron orbitals $\psi_i(r)$ have the form:

$$\left(-\frac{\nabla^2}{2} + v_{eff}(r) \right) \psi_i(r) = \varepsilon_i \psi_i(r) \tag{1.28}$$

where $v_{eff}(r)$ is the effective potential, $\psi_i(r)$ the Kohn-Sham orbitals and ε_i the Kohn-Sham orbital energies.

The Kohn-Sham equations are solved self-consistently. Evaluation of equation 1.22 gives the total electronic energy. A guess density is supplied for the evaluation of equation 1.28, to generate a set of orbitals. This in turn informs the next iteration with an improved density value, until convergence is reached.

1.2.2.1 Exchange-correlation functionals

In practice, the exact solution for E_{XC} in equation 1.24 is not known, so an approximation is used. The simplest method is the local density approximation (LDA), based upon a uniform electron gas. ε_{XC} is calculated per electron as function of the density, and integration over all space gives the E_{XC} for the whole system:

$$E_{XC}^{LDA}[\rho(r)] = \int \rho(r)\varepsilon_{XC}[\rho(r)] \, dr \tag{1.29}$$

This method has demonstrated good results for structural properties such as bond lengths and lattice constants, often improving on HF results. The model falls down when considering systems with many molecules, overestimating binding energies and atomisation energies, and performing worse than HF for open shell atoms.

To account for inhomogenous electron density present in real systems, the local gradient of the density $\nabla\rho$ is taken into account at each coordinate, on top of the existing dependency on the density ρ. This gradient corrected approach is called the generalised

gradient approximation (GGA):

$$E_{XC}^{GGA}[\rho(r)] = \int \rho(r)\nabla\rho(r)\,dr \qquad (1.30)$$

The results obtained using GGA greatly improve upon the LDA, such as in the calculation of bond dissociation energies. The GGA is split into its exchange and correlation contributions, which can be solved individually:

$$E_{XC}^{GGA} = E_X^{GGA} + E_C^{GGA} \qquad (1.31)$$

The function of $\nabla\rho(r)$ is not uniquely defined; further developments saw the proposal of numerous gradient correction schemes, often fitting to experimental parameters. Functionals well established in literature, include:

- B88: is the exchange functional developed by Becke, and contains a parameter β that was fitted to give the best agreement with the HF energies of the noble gases [?].

- LYP: is the most widely used GGA correlation functional, developed by Lee, Yang and Parr, with empirical fitting to the helium atom. Combination with the B88 exchange functional gives the BLYP method [?].

- PBE: is the functional developed by Perdew, Burke and Ernzerhof derived purely from *ab initio* calculations [?]. The PBE family of functionals have parameterisations optimised for different materials and interfaces, such as solids and surfaces [?, ?, ?].

1.2.3   Hybrid functionals

1.2.4   Basis set approximation

A basis set is the collection of mathematical basis functions, used in linear combination, to construct the MO. An individual MO can be defined as:

$$\psi_i = \sum_{\mu=1}^{K} c_{\mu i}\chi_\mu \qquad (1.32)$$

where $c_{\mu i}$ is the molecular orbital expansion coefficient and χ_μ corresponds to the one-electron occupied orbitals, often atomic orbitals, also called *basis functions*. K is the total number of basis functions, which are all chosen to be normalised. The convention is that Roman subscripts are used for molecular orbital functions, but Greek used on the basis

functions. The smallest possible basis set is a single basis per occupied orbital on each atom in a molecular system, termed the "minimal basis". The HF limit is when the addition of further bases does not lower the energy of the system any further.

Slater type orbitals (STO) with exponential dependence $Ae^{-\alpha r}$, were the first choice for atomic functions; α controls how quickly the function decays (radial extent), with higher values for higher effective nuclear charge. They are extremely similar in their mathematical expression to the real atomic orbital, however, are difficult to implement in molecular orbital calculations. Gaussian type orbitals (GTO) of dependence $Ae^{-\alpha r^2}$, offered a more practically viable approximation.

Split valence basis sets describe the core electrons with fewer basis functions than the interacting valence electrons, as they are not as significant in bonding or intermolecular interactions. In this study, the widely used Pople basis sets will be applied.

Basis set superposition error (BSSE) is a false lowering of the energy that can occur when two species in a system approach one another to form a complex. Particle A borrows the extra basis functions belonging to particle B and an artificial stabilisation is observed. The error arises from the inconsistency in treatment between the individual particles at long separations and the complex at short distances. The effect is particularly pronounced for smaller basis sets.

1.3 Implementation & Analysis

1.3.1 Transition state searches

Transition state searches are called through the Opt=TS, QST or QST3 keywords. The Opt=TS method in Gaussian 09 revision D.01 (G09) attempts to optimise the given "guess" geometry to a transition state. The guess structure can be obtained from a geometry scan, manually constructed or generated using the QST2 function. In many cases, a TS alone will not be able to isolate the suitable transition state and is usually used in conjunction the QST2 or QST3 methods, and combined with other techniques such as frequency calculations. The QST2 option is able to generate a transition state geometry using the Synchronous Transit Quasi-Newton (STQN) method. Here the transition geometry is midway between a given reactant and product. The corresponding atoms labels must match in both the starting and end products. QST3 performs similarly, but also considers a guess transition state. It is widely acknowledged that transition state searching is challenging; in addition to the techniques above, the task requires perhaps a certain measure of chemical intuition. "Scan"

means that the reaction coordinates are changed gradually and "relaxed" means that the reaction coordinates are fixed, while other coordinates that are orthogonal to the reaction coordinates are relaxed during the energy minimisation [9].

1.3.2 PES Scans

Relaxed potential energy surface (PES) scans, or geometry scans are used to probe the local energy landscape corresponding to specific change in geometry. During the course of a scan, a selected bond length, angle or dihedral is adjusted in incremental steps, as specified by the given scan parameters. At each step, the adjusted parameter is frozen and a geometry optimisation is performed, allowing the rest of the system to relax around the modified bond. Each scan yields a PES of the explored pathway, presented in a reaction co-ordinate diagram. An energy maximum followed by a trough indicates a transition state and intermediate reaction product, respectively. The structural co-ordinates at the points of interest are extracted and used for subsequent frequency calculations, transition state searches and validated using intrinsic reaction co-ordinate methods. To explore the predicted degradation mechanisms, the scanning parameter was assigned to the bond undergoing the most significant transformation during a particular step of the mechanism. In the case that more than one significant bond was altered, multiple scans with different bond specifications were compared. Geometry scans were performed on the optimised reactant geometry using the Opt=ModRedundant keyword.

A rigid scan consists of a single point energy calculation of the structure at each of step the scan. A relaxed scans calls for a geometry optimisation at each of these points. Two-dimensional scans may be used to probe simultaneous processes in the system. These are specified in G09 by selecting two internal coordinates to be scanned, and stating the number of steps.

1.3.3 Topology analysis using quantum theory of atoms in molecules (QTAIM)

Topology analysis is a method of obtaining useful properties from the 3D representation of ...Bader proposed a technique to analyse the electron density in the QTAIM [10]. The points in the topological landscape at which the gradient norm is zero, excluding points at infinity, signify a stationary point. These are deemed Critical Points (CP). In the context of electron density, these point can be classified into four types:

nuclear critical point (NCP): All three eigenvalues of Hessian matrix of the function

are negative, also known as the local maximum. As the position of (3,-3) are generally located at nuclear positions, these are referred to as Nuclear Critical Points (NCP). The number of NCP is usually equal to the number of atoms, though there are exceptions, such as a greater number of NCP for Li_2 or a lower number for KrH^+.

(3,-1): Two eigenvalues of Hessian matrix of function are negative, or a second-order saddle point. (3,-1) usually appears between attractive atom pairs and so are referred to as a Bonding Critical Points (BCP). As the electron density af bonding critical point (BCP) is closely related to bonding strength and bonding type respectively in analogous bonding type. [11] The potential energy density at BCP has been shown to be highly correlated with hydrogen bond energies; local information entropy at BCP is a good indicator of aromaticity.

(3,+1): Only one eigenvalue of Hessian matrix of function is negative, namely first-order saddle point (like transition state in potential energy surface). For electron density analysis, (3,+1) generally appears in the center of ring system and displays steric effect, hence (3,+1) is often named as ring critical point (RCP).

(3,+3): None of eigenvalues of Hessian matrix of function are negative, namely the local minimum. For electron density analysis, (3,+3) generally appears in the center of cage system (e.g. pyramid P4 molecule), hence is often referred to as cage critical point (CCP).

Table 1.1: Features of different types of critical point from QTAIM topological analysis.

Critical Point	Label	Derivation	Attribute	Representation
Nuclear (NCP)	(3,-3)	3 eigenvalues of Hessian matrix are -ve	Local maximum	Atomic nuclei
Bonding (BCP)	(3,-1)	2 eigenvalues of Hessian matrix are -ve	2nd order saddle point	Bonding site
Ring (RCP)	(3,+1)	1 eigenvalue of Hessian matrix is -ve	1st order saddle point	Steric point or centre of ring system
Cage (CCP)	(3,+3)	No negative eigenvalue of Hessian matrix	Local minimum	Centre of cage system

The positions of CPs are searched by Newton method, one need to assign an initial guess point, then the Newton iteration always converge to the CP that is closest to the guess point. By assigning different guesses and doing iteration for each of them, all CPs could be found. Once searches of CPs are finished, one should use Poincaré-Hopf relationship to

verify if all CPs may have been found, the relationship states that (for isolated system)

$$n(3,-3) - n(3,-1) + n(3,+1) - n(3,+3) = 1 \tag{1.33}$$

The maximal gradient path linking BCP and associated two local maxima of density is termed as "bond path", which reveals atomic interaction path for all kinds of bonding. The collection of bond paths is known as molecular graph, which provides an unambiguous definition of molecular structure. Bond path can be straight line or curve, obviously for the latter case the length of bond path is longer than the sum of the distances between BCP and associated two (3,-3) CPs.

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