Abbreviations

%N   percentage nitrogen by mass

2-NDPA   2-Nitrodiphenylamine

a.u.   atomic units

B3LYP   Becke, 3-parameter, Lee-Yang-Parr hybrid functional

BCP   bonding critical point

CH$_3$CH$_3$ NC repeat unit with two $-$OCH$_3$ capping groups

CH$_3$OH   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

GM   genetically modified

GView   Gauss View 5.0.8

HF   Hartree-Fock

HMF   hydroxymethylfurfural

HOMO   highest occupied molecular orbital

IR   infra-red spectroscopy

LOL   localized orbital locator

MD   molecular dynamics

MEP   minimum energy path

MM   molecular mechanics

MMFF94   Merck molecular force field 94

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

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

SCF   self-consistent field

SEM   scanning electron microscopy

S_N2   bi-molecular nucleophilic substitution reaction

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. At the most fundamental level, the wavefunction (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. 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 wavefunction [1]. Schrödinger's time independent equation is:

$$\mathbf{H}\Psi = E\Psi \tag{1.2}$$

where the Hamiltonian operator **H** is an eigenvalue of the wavefunction 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

$$\mathbf{H} = -\sum \frac{\hbar^2}{2m_e}\nabla_i^2 - \sum \frac{\hbar^2}{2m_k}\nabla_k^2 - \sum_i \sum_k \frac{e^2 Z_k}{r_{ik}} + \sum_{i<j} \frac{e^2}{r_{ij}} + \sum_{k<l} \frac{e^2 Z_k Z_l}{r_{kl}} \qquad (1.3)$$

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):

$$\nabla_i^2 = \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} \qquad (1.4)$$

The first and second terms of equation (1.3) 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 ($\mathbf{T}$):

$$\mathbf{T} = -\frac{\hbar^2}{2m}\nabla^2 \qquad (1.5)$$

The Hamiltonian can therefore be written in terms of the kinetic energy and potential energy operators:

$$\mathbf{H} = \mathbf{T}_e + \mathbf{T}_N + \mathbf{V}_{e-N} + \mathbf{V}_{e-e} + \mathbf{V}_{NN} \qquad (1.6)$$

where the terms are as they were in equation 1.3.

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 elec-

trons. The correlated motion of particles is described by the pairwise attractive and repulsive terms of the Schrödinger equation. However, this interdependency makes defining a wavefunction 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 ($\mathbf{T}_N$) of the Hamiltonian is removed, as the nuclei are frozen. The nuclear-nuclear repulsive term ($\mathbf{V}_{NN}$) becomes a constant for the specified geometry. Equation 1.3 is reduced to its electronic components and nuclear constants which in atomic units can be written as:

$$\mathbf{H} = -\frac{1}{2}\sum \nabla_i^2 - \sum_i \sum_k \frac{Z_k}{r_{ik}} + \sum_{i<j} \frac{1}{r_{ij}} + \mathbf{V}_{NN} \tag{1.7}$$

The electronic terms can be factorised into one term, to simplify notation:

$$\mathbf{H} = \mathbf{H}_{el} + \mathbf{V}_{NN} \tag{1.8}$$

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

$$(\mathbf{H}_{el} + \mathbf{V}_{NN})\Psi_{el}(\mathbf{q}_i;\mathbf{q}_k) = E_{el}(\mathbf{q}_i;\mathbf{q}_k) \tag{1.9}$$

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} for a particular inter-nuclear separation, increasing the separation distance and again calculating the energy. A series of these calculations along different fixed nuclear separations 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 allows the construction of the potential energy surface (PES) , a hypersurface on which nuclear motion occurs, with the potential energy defined by the nuclear

geometry.

Molecular structure theories adopt the Born-Oppenheimer approximation for its effective simplification of the coupled nuclear-electronic motion problem, in addition to its relative accuracy; this assumption works well for ground state molecules and only introduces very small errors. This model breaks down in the situation where there are multiple PES, similar 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 electronic structure calculations.

1.1.2 Variational principle

In order to determine the ground state energy of a system, the wavefunction giving the lowest energy must be found. Within the Born-Oppenheimer approximation, this corresponds to the electronic configuration with smallest value of E_{el}. The variational theorem states that the calculated energy of any guess wavefunction 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 wavefunction, as the energy is always bound from below:

$$E_{el} = \frac{\langle \Psi | \mathbf{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \leq E_0 \qquad (1.10)$$

1.1.3 Slater determinants

Equation 1.9 can be solved exactly in only a 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.

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 an identical set of quantum numbers. As a result, for two indistinguishable electrons, the wavefunction of the system is antisymmetric with respect to the exchange of their coordinates.

$$\Psi(1, 2..i, ...j..N) = -\Psi(1, 2..i, ...j..N) \qquad (1.11)$$

This requirement is fulfilled by expressing the wavefunction 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:

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

where χ_n represents single electron wavefunctions, or spin-orbitals [3]. In the context of a molecule, the single electron wavefunctions are molecular orbitals.

Rows are labelled by the coordinates of each electron: $\mathbf{x}_1, \mathbf{x}_2 \cdots \mathbf{x}_N$, whereas each column uses a different orbital function: $\chi_1, \chi_2 \cdots, \chi_N$. If the labels of $\mathbf{x}_1$ and $\mathbf{x}_2$ 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 when a pair of electronic coordinates are switched, by switching rows within the determinant, thereby fulfilling the antisymmetry requirement. In the disallowed case of two 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 to be zero.

1.1.4 Hartree Fock self-consistent field method

As the The self-consistent field (SCF) method was developed by Hartree and Fock in XX to iteratively determine a set of molecular orbitals that minimised the energy of the wavefunction

Hartree approximation neglects electron-electron interaction, describing the energy of electrons as individual particles without the effect of the surrounding fermions.

Fock and Slater improved upon this by introducing electron exchange. This assumption places a static spherical potential around the electron, derived from the average effect of the nucleus and other electrons in the system.

The Hartree-Fock (HF) method starts

$$E = \frac{\int \psi^*(\mathbf{x}) H \psi(\mathbf{x}) d\mathbf{x}}{\int \psi^*(\mathbf{x}) \psi(\mathbf{x}) d\mathbf{x}} \tag{1.13}$$

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. For systems without unpaired electrons, called "closed shell", 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 alternative 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.

1.1.6 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", where calculations are performed By contrast, semi-epirical methods deal with parameters fitted to experimental quantities, such as enthalpies of formation or dipole moments. Density functional theory derives from the Thomas-Femi-Dirac model, whereby the electron correlation is modelled via functionals of the electron density.The total energy is defined by functionals split into the following terms:

$$E = E^T + E^V + E^J + E^X C$$

Where E^T is the kinetic energy term, arising from electron motion; E^V is the potential energy term arising from nuclear-electron attraction and nuclear-nuclear repulsion; E^J is the columbic repulsion term arising from electron-electron repulsion and E^{XC} is the exchange correlation term containing the remainder of the electron-electron interactions. The first three terms are purely classical, and correspond to the classical energy of the charge distribution (ρ). The exchange term is non-classical encompasses the exchange energy due to the antisymmetry of the wavefunction, and dynamic correlation of electron motion. It can be further divided into the exchange and correlation components:

$$E^{XC}(\rho) = E^X(\rho) + E^C(\rho) \tag{1.14}$$

LDA, GGA etc and development of functionals. The different treatment of exchange.

In the context of this report, the Becke, 3-parameter, Lee-Yang-Parr hybrid functional (B3LYP) functional will be used where the exchange is described as follows:

$$E_{B3LYP^{xc}} = E_{LDA^x} + c_0(E_{HF^x} - E_{LDA^x}) + c_X \Delta E_{B88^x} + E_{VWN3^c} + c_C(E_{LYP^c} - E_{VWN3^c})$$

$$(1.15)$$

Where $c_0 = 0.2$, $c_X = 0.72$ and $c_C = 0.81$. The coefficient c_0 allows mixing of E_{HF^x} (Hartree Fock) and E_{LDA^x} (Local Density Approximation). E_{VWN3^c} (VWN3 local correlation) is mixed with E_{LYP^c} (Lee, Yang, Parr correlation function) via c_C. E_{B88^x} is Becke's gradient-corrected exchange functional.

1.1.7 Basis sets

A basis set is the collection of mathematical basis functions used in linear combination to construct the molecular orbitals.

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.

1.2 Implementation & Analysis

1.2.1 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) method42. 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 [5].

1.2.2 Intrinsic Reaction Coordinate

IRC calculations begin at the saddle point and descend the PES in both the forwards and backwards direction of the reaction co-ordinate dictated by the normal mode of the imaginary frequency. In a similar manner to a geometry scan, geometry optimisations are performed at each step point. Its purpose is to connect the two minima leading to the found transition state, thereby confirming whether the found transition state corresponds to your reactants and products of interest. IRC calculations are called via the IRC keyword, with specifications of whether the forward or backward reaction is to be scanned, step size and maximum number of steps allowed.

1.2.3 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.

1.2.4 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 [6]. 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. [7] 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).

The positions of CPs are searched by Newton method, one need to assign an initial

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

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)

$$n(3,-3)\!-\!n(3,-1)+n(3,+1)\!-\!n(3,+3) = 1 \qquad (1.16)$$

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.

Bibliography

[1] E. Schrödinger. An Undulatory Theory of the Mechanics of Atoms and Molecules. *Physical Review*, 28(6):1049–1070, dec 1926.

[2] Christopher J Cramer. *Essentials of Computational Chemistry Theories and Models*, volume 42. 2004.

[3] J. C. Slater. The theory of complex spectra. *Physical Review*, 34(10):1293–1322, 1929.

[4] Clifford E. Dykstra. *Introduction to quantum chemistry*. Prentice Hall, 1994.

[5] Qian Yao, Xiao Mei Cao, Wen Gang Zong, Xiao Hui Sun, Ze Rong Li, and Xiang Yuan Li. Potential Energy Surface for Large Barrierless Reaction Systems: Application to the Kinetic Calculations of the Dissociation of Alkanes and the Reverse Recombination Reactions. *Journal of Physical Chemistry A*, 122(21):4869–4881, may 2018.

[6] Richard F. W. Bader. A quantum theory of molecular structure and its applications. *Chemical Reviews*, 91(5):893–928, jul 1991.

[7] Chérif F. Matta and Russell J. Boyd. *The Quantum Theory of Atoms in Molecules: From Solid State to DNA and Drug Design*. 2007.