

Abbreviations

ψ	wavefunction
%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
CH₃CH₃	NC repeat unit with two –OCH ₃ capping groups
CH₃OH	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
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 theory
HOMO	highest occupied molecular orbital
IR	infra-red spectroscopy
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
OHCH₃	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
SEM	scanning electron microscopy
S_N2	bi-molecular nucleophilic substitution reaction
TG	thermogravimetric analysis
TS	transition state
UFF	universal force field
UV	ultraviolet
UVvis	ultraviolet–visible spectroscopy
ωB97X-D	ω B97X-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 place, 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 orthonormal; integrating $|\Psi^2|$ over all space gives the probability of 1:

$$\langle \Psi_i | \Psi_j \rangle = \delta_{ij} \quad (1.1)$$

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

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

$$\delta_{ij} = 1 \text{ for } i = j$$

Operators acting on Ψ yield the observable properties of the system. The operator returning the energy of the system is called the Hamiltonian operator (\mathbf{H}). Erwin Schrödinger first proposed his equation for the description of the wavefunction of a quantum system in 1926 [1]. The time-independent equation is:

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

where the Hamiltonian operator \mathbf{H} is an eigenvalue of the wavefunction Ψ , and E is a scalar denoting the energy of the system. The general form of the Hamiltonian is given by:

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

where all electrons are represented by i and j , and all nuclei by k and l . \hbar is the reduced Planck's constant ($\hbar = \frac{h}{2\pi}$), 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_{xy} is the distance between particles x and y . When using atomic units (a.u.), the electronic mass, charge and reduced Planck's constant are reduced to a value of 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 second derivative of the gradient in the three dimensions:

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

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, followed by the interelectronic and internuclear repulsive terms. The three latter potential energy terms are described just as in classical mechanics. The kinetic energy terms are expressed as the eigenvalue of the kinetic energy operator (\mathbf{T}):

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

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

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

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 electrons. The correlated motion of particles is described by the pairwise attractive and repulsive terms of the Schrödinger's equation. However, this interdependency results in a wavefuction that is difficult to define. Relative to electronic motion, nuclei move far more slowly, owing to

their mass. The difference is such, that the nuclear positions appear essentially stationary compared to 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. 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. The equation is reduced to its electronic components and nuclear constants which in atomic units can be written as:

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

The Schrödinger's equation only dependent on the electronic coordinates is as follows:

$$(\mathbf{H}_{el} + \mathbf{V}_{NN})\Psi_{el}(\mathbf{q}_i; \mathbf{q}_k) = E_{el}(\mathbf{q}_i; \mathbf{q}_k) \quad (1.8)$$

where \mathbf{H}_{el} is the pure electronic Hamiltonian, that is, only including the electronic kinetic energy, electron-nuclear attractive term, and electron-electron repulsion term from the total Hamiltonian given in 1.3. \mathbf{V}_{NN} is the nuclear-nuclear repulsion, constant for the fixed positions. The electronic coordinates are given by \mathbf{q}_i , and the nuclear positions, \mathbf{q}_k . E_{el} is the electronic energy of the system, which is now only dependent on the electronic coordinates.

1.1.2 Variational principle

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 of the system. This provides a criterion for selection of the best guess wavefunction.

1.1.3 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, or “closed shell”, this treatment is sufficient. For radicals and other species with unpaired electron spin such as transition metal complexes, 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). This is singly occupied. An alternative model is Unrestricted, 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 where the bond has not completely broken.

1.1.4 Density functional theory

Solutions to the Schrödinger's equation using reference Density functional theory derives from the Thomas-Fermi-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:

$$E = E^T + E^V + E^J + E^{XC}$$

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:

$$E^{XC}(\rho) = E^X(\rho) + E^C(\rho) \quad (1.9)$$

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:

$$E_{B3LYP^{XC}} = E_{LDA}^X + c_0(E_{HF^X} - E_{LDA^X}) + c_X \Delta E_{B88^X} + E_{VWN3^C} + c_C(E_{LYP^C} - E_{VWN3^C}) \quad (1.10)$$

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.

1.1.5 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 Analysis

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

The topology analysis technique proposed by Bader was firstly used for analyzing electron density in "atoms in molecules" (AIM) theory, which is also known as "the quantum theory of atoms in molecules" (QTAIM), this technique has also been extended to other real space functions, e.g. the first topology analysis research of ELF for small molecules is given by Silvi and Savin. In topology analysis language, the points at where gradient norm of function value is zero (except at infinity) are called as critical points (CPs), CPs can be classified into four types according to how many eigenvalues of Hessian matrix of real space function are negative.

(3,-3): All three eigenvalues of Hessian matrix of function are negative, namely the local maximum. For electron density analysis and for heavy atoms, the position of (3,-3) are nearly identical to nuclear positions, hence (3,-3) is also called nuclear critical point (NCP). Generally the number of (3,-3) is equal to the number of atoms, only in rarely cases the former can be more than (e.g. Li₂) or less than (e.g. KrH⁺) the latter.

(3,-1): Two eigenvalues of Hessian matrix of function are negative, namely the second-order saddle point. For electron density analysis, (3,-1) generally appears between attractive atom pairs and hence commonly called as bond critical point (BCP). The value of real space functions at BCP have great significance. The sign of at BCP is closely related to bonding strength and bonding type respectively in analogous bonding type. 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	2 nd order saddle point	Bonding site
Ring (RCP)	(3,+1)	1 eigenvalue of Hessian matrix is -ve	1 st 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)

$$n(3, -3) - n(3, -1) + n(3, +1) - n(3, +3) = 1 \quad (1.11)$$

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.

1.2.2 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 [2].

Frequency calculations

1.2.3 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.

1.2.4 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 degrada-

tion 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.

Bibliography

- [1] E. Schrödinger. An Undulatory Theory of the Mechanics of Atoms and Molecules. *Physical Review*, 28(6):1049–1070, dec 1926.
- [2] 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.