

# Abbreviations

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

<b>ESP</b>	electrostatic potential
<b>G09</b>	Gaussian 09 revision D.01
<b>GM</b>	genetically modified
<b>GTO</b>	Gaussian type orbitals
<b>GView</b>	Gauss View 5.0.8
<b>HF</b>	Hartree Fock
<b>HMF</b>	hydroxymethylfurfural
<b>HOMO</b>	highest occupied molecular orbital
<b>IR</b>	infra-red spectroscopy
<b>LOL</b>	localized orbital locator
<b>MD</b>	molecular dynamics
<b>MEP</b>	minimum energy path
<b>MM</b>	molecular mechanics
<b>MMFF94</b>	Merck molecular force field 94
<b>MO</b>	molecular orbital
<b>MP2</b>	Møller–Plesset perturbation theory with second order correction
<b>MW</b>	molecular weight
<b>NC</b>	nitrocellulose
<b>NCP</b>	nuclear critical point
<b>NG</b>	nitroglycerine
<b>NMR</b>	nuclear magnetic resonance spectroscopy
<b>OHCH<sub>3</sub></b>	NC repeat unit with –OH capping group on ring 1 and –OCH <sub>3</sub> group on ring 2

<b>PCM</b>	polarisable continuum model
<b>PES</b>	potential energy surface
<b>PETN</b>	pentaerythritol tetranitrate
<b>PETRIN</b>	pentaerythritol trinitrate
<b>QM</b>	quantum mechanics
<b>QTAIM</b>	quantum theory of atoms in molecules
<b>RCP</b>	ring critical point
<b>SB59</b>	1,4-bis(ethylamino)-9,10-anthraquinone dye
<b>SCF</b>	self-consistent field
<b>SEM</b>	scanning electron microscopy
<b>SMD</b>	solvation model based on density
<b>S<sub>N</sub>2</b>	bi-molecular nucleophilic substitution reaction
<b>STO</b>	Slater type orbitals
<b>TG</b>	thermogravimetric analysis
<b>TS</b>	transition state
<b>UFF</b>	universal force field
<b>UV</b>	ultraviolet
<b>UVvis</b>	ultraviolet–visible spectroscopy
<b><math>\omega</math>B97X-D</b>	$\omega$ B97X-D long-range corrected hybrid functional
<b>ZPE</b>	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 NC decomposition, in part owing to the variation arising from NC source material, but also 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 ( $\Psi$ ) 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  $\Psi$  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  $\Psi$  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:

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

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

Operators acting on  $\Psi$  yield the observable properties of the system. The operator returning the energy of the system is called the Hamiltonian operator ( $\mathbf{H}$ ). Erwin Schrödinger

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

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

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

The general form of the Hamiltonian is given by

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

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.  $\nabla^2$  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):

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

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; 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 ( $\mathbf{T}$ ):

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

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

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

where the terms are as they were in equation 1.3.

### 1.1.1 Born-Oppenheimer approximation

In a real system, the motion of electrons 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 ( $\mathbf{V}_{NN}$ ) 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:

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

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

$$\mathbf{H} = \mathbf{H}_{el} + \mathbf{V}_{NN} \quad (1.8)$$

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

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

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  $E_{el}$  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

Equation 1.9 can be solved *exactly* in only 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.

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:

$$\Psi(1, 2..i, \dots j..N) = -\Psi(1, 2..i, \dots j..N) \quad (1.10)$$

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 fol-

lows:

$$\psi_{SD} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(1) & \chi_2(1) & \cdots & \chi_N(1) \\ \chi_1(2) & \chi_2(2) & \cdots & \chi_N(2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(N) & \chi_2(N) & \cdots & \chi_N(N) \end{vmatrix} \quad (1.11)$$

where  $\chi_n$  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:  $\chi_1, \chi_2 \cdots, \chi_N$ . 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 ( $\psi_{SD}$ ) 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:

$$E_0 \leq \langle \Psi | \mathbf{H} | \Psi \rangle \quad (1.12)$$

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

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 [?, ?].  $N$  electrons are treated as

individual particles occupying single-electron spin orbitals and moving 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 further by introducing Slater determinantal wave functions [?]. The effects of exchange on the Coulomb repulsion were incorporated, achieved by taking the trial wave function as a single Slater determinant.

For an electron in orbital  $\chi_i$  in the field of nuclei  $M$  and other electrons  $\chi_j$ , 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:

$$\mathbf{H}^{core}(1) = -\frac{1}{2}\nabla_1^2 - \sum_{A=1}^M \frac{Z_A}{r_{1A}} \quad (1.13)$$

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  $\chi_j$ :

$$\mathbf{J}_j(1) = \int d\tau_2 \chi_j(2) \frac{1}{r_{12}} \chi_j(2) \quad (1.14)$$

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:

$$\mathbf{K}_j(1)\chi_i(1) = \left[ \int d\tau_2 \chi_j(2) \frac{1}{r_{12}} \chi_j(2) \right] \chi_j(1) \quad (1.15)$$

defined in terms of its effect when acting on  $\chi_i$ . The Hamiltonian operator written in terms

of its core, coulomb and exchange contributions:

$$\left[ \mathbf{H}^{core}(1) + \sum_{j=1}^N \{ \mathbf{J}_j(1) - \mathbf{K}_j(1) \} \right] \chi_i(1) = \sum_{j=1}^N \varepsilon_{ij} \chi_j(1) \quad (1.16)$$

can be simplified to:

$$\mathbf{F}_i \chi_i = \sum_j \varepsilon_{ij} \chi_j \quad (1.17)$$

where  $\mathbf{F}_i$  is the Fock operator, and  $\varepsilon_{ij}$  is the energy of orbital  $\chi_j$ . 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:

$$\mathbf{F}_i(1) = \mathbf{H}^{core}(1) + \sum_{j=1}^{N/2} \{ 2\mathbf{J}_j(1) - \mathbf{K}_j(1) \} \quad (1.18)$$

Rearranging to the standard eigenvalue form:

$$\mathbf{F}_i \chi_i = \varepsilon_i \chi_i \quad (1.19)$$

$\mathbf{H}^{core}$  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 solutions for the occupied orbitals  $\chi_i$ , 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, thus, 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. 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 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”, 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. 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 ( $\rho$ ). The exchange term is non-classical encompasses the exchange energy due to the antisymmetry of the wave function, and dynamic correlation of electron motion. It can be further divided into the exchange and correlation components:

$$E^{XC}(\rho) = E^X(\rho) + E^C(\rho) \quad (1.20)$$

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:

$$E_{B3LYP^X} = E_{LDA^X} + c_0(E_{HF^X} - E_{LDA^X}) + c_X \Delta E_{B88^X} + E_{VWN3^C} + c_C(E_{LYP^C} - E_{VWN3^C}) \quad (1.21)$$

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 set approximation

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

$$\psi_i = \sum_{v=1}^N c_{vi} \chi_v \quad (1.22)$$

where  $c_{vi}$  is the molecular orbital expansion coefficient and  $\chi_v$  corresponds to the one-electron occupied orbitals, often atomic orbitals, also called *basis functions*. N 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 do not further lower the energy of the system.

Slater type orbitals (STO) of the form  $Ae^{-\alpha r}$  were the first choice for atomic functions;  $\alpha$  controls how quickly the function decays (radial extent), with higher values for higher effective nuclear charge,  $r$ . However, they are mathematically difficult to implement in molecular orbital calculations. Gaussian type orbitals (GTO) of the form  $Ae^{-\alpha r^2}$  offered a more 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.

## 1.2 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) method<sup>42</sup>. 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 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.

### 1.2.3 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 [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<sub>2</sub> or a lower number for KrH<sup>+</sup>.

(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 P<sub>4</sub> 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 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

**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 <sup>nd</sup> order saddle point	Bonding site
Ring (RCP)	(3,+1)	1 eigenvalue of Hessian matrix is -ve	1 <sup>st</sup> 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

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

$$n(3, -3) - n(3, -1) + n(3, +1) - n(3, +3) = 1 \quad (1.23)$$

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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