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Never trust an experimental result until it has been confirmed by theory.

— Arthur Stanley Eddington

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Theoretical Background

1.1 Computational Chemistry

Computational chemistry is a branch of chemistry where theoretical study of physics and chemistry are implemented in computer programs to simulate and understand chemical reactions that occur both in laboratory settings and in biological systems, using techniques ranging from kinetics and thermodynamics calculations, electronic structure analysis and spectroscopy simulations, amongst many others. Within this field, computer simulations are routinely used to understand and explain chemical reactivity; in some cases, these simulations can predict remarkable and hitherto unperceived chemical phenomena.¹⁻³ Today, computational chemistry has become an indispensable tool in understanding reaction mechanisms in chemical reactions and catalysis.^{4,5} The advent and continued development of computational chemistry has been fuelled by paralleled development in theoretical methods and computational architecture. We should note that computational chemistry is different from theoretical chemistry in that it concerns solving

chemical problems, not directly developing new theoretical techniques. The development of theoretical methods allows new chemical problems to be studied, whereas calculations and insights obtained from computational chemistry can pinpoint the limitations of theory and suggest new areas for further theoretical development.

One of the practical considerations in computational chemistry is that any method employed to study a chemical system is constrained by a compromise between accuracy and cost. In general, the more accurate the methodology, or model chemistry, the more costly it is computationally, although highly parametrised low-cost methods can sometimes obtain this accuracy. A variety of computational methods are available for the study of a range of chemical systems of varying sizes to different degrees of desired accuracy. These methods can be broadly divided into quantum mechanical methods and classical mechanical methods. Quantum mechanical methods aim to understand the electronic structure of a chemical system and include *ab initio* methods based entirely on solving the governing equations in quantum mechanics, without any experimental data input; semi-empirical methods include additional parameters from empirical data for better speed/accuracy in the study of large systems. For even larger systems and where dynamical effects are important, classical mechanical methods based on numerically solving the Newton's equations of motion are employed. Examples of popular quantum mechanical methods include density functional theory (DFT) methods and examples of classical mechanical methods include molecular mechanics (MM) – a form of empirical potential governing the interactions between the atoms of a molecular system – used in molecular dynamics (MD) simulations.

1.2 Quantum Mechanics

As all endeavours in science, quantum mechanics (QM) developed when existing theory could not adequately explain the experimental observations. Classical mechanics provide the physical laws governing the motion and properties of macroscopic systems. However, a series of observations made in the 19th and 20th centuries concerning systems of atomic and subatomic scale could not be reconciled with classical laws. These observations, such as the discovery of cathode rays (Faraday, 1838), the black-body radiation problem (Kirchhoff, 1859) and the photoelectric effect (Hertz, 1887), called for new theoretical framework governing phenomena at the atomic scale. In 1900, in a radical proposal, Max Planck first suggested that the energies emitted by an atomic system come in discrete values, i.e., they are quantised. Then in 1905, in an attempt to explain the photoelectric effect, Einstein proposed, in consistency with Planck, that light is made up of discrete particles, later on termed photons, with quantised energy. As the development of QM progressed, it became clear that not only is light quantised, but also are electrons and atoms. Early contributions from de Broglie, Schrödinger, Heisenberg, Born and others underlie the foundations of theory for modern computational chemistry.

1.2.1 The Schrödinger equation

A chemical system can be described *exactly* by the time-dependent Schrödinger equation (TDSE):

$$\hat{H}\Psi(\mathbf{X}, t) = i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{X}, t) \quad (1.1)$$

where \hat{H} is the Hamiltonian operator, whose measurements yield the total energy of the system; $\Psi(\mathbf{X}, t)$ is the time-dependent wavefunction of the system, whose squared modulus, $|\Psi(\mathbf{X}, t)|^2 = \Psi^*(\mathbf{X}, t)\Psi(\mathbf{X}, t)$, gives the probability density of finding a particle

at position \mathbf{X} (\mathbf{X} is a collection of positions of electrons, at \mathbf{r} , and nuclei, at \mathbf{R}) at time t . For time-independent physical and chemical properties, the solution of the time-independent Schrödinger equation (TISE)

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

is desired.

This is an eigenvalue problem where the eigenfunction is the wavefunction of the system, Ψ , and the eigenvalue is the energy of the system, E . The solution of the TISE cannot be obtained exactly except for the simplest, single-electron systems. For a multi-electronic system with N electrons, at position vectors \mathbf{r}_i 's, and M nuclei, at position vectors \mathbf{R}_A 's, the Hamiltonian of the system, in atomic units, is given by

$$\hat{H} = -\sum_{i=1}^N \frac{1}{2} \nabla_i^2 - \sum_{A=1}^M \frac{1}{2M_A} \nabla_A^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} + \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}} \quad (1.3)$$

where $r_{iA} = |\mathbf{r}_i - \mathbf{R}_A|$ is the distance between i^{th} electron and A^{th} nucleus, $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ is the distance between i^{th} electron and j^{th} electron, $R_{AB} = |\mathbf{R}_A - \mathbf{R}_B|$ is the distance between A^{th} nucleus and B^{th} nucleus; M_A and Z_A are the atomic mass and charge of nucleus A , respectively. The five terms in the total Hamiltonian represent, respectively, the kinetic energy of the electrons, the kinetic energy of the nuclei, the Coulomb attraction between the electrons and nuclei, the electron-electron repulsion and the nucleus-nucleus repulsion. Thus, the total Hamiltonian operator can be written as a sum of the operators for each of these separate contributions, viz.,

$$\hat{H} = \hat{T}_e + \hat{T}_n + \hat{V}_{ne} + \hat{V}_{ee} + \hat{V}_{nn} \quad (1.4)$$

1.2.2 The Born-Oppenheimer approximation

The full Hamiltonian for a molecular system given in Equation (1.3) makes the TISE in Equation (1.2) difficult to be solvable without a number of approximations; the presence of electron-nuclei interactions, \hat{V}_{ne} , makes the Hamiltonian inseparable into electronic and nuclear degrees of freedom. One of the most fundamental approximations employed is the Born-Oppenheimer (BO) approximation.⁶ The validity of this approximation rests on the fact that the mass of a nuclei is much larger than the mass of an electron (1 a.m.u. = 1836 m_e), such that their motions can be separately treated. Within the BO approximation, the nuclei of the system are considered “clamped” in positions; the electrons move in this “clamped-nuclei” framework. By having the nuclei fixed, the nuclear kinetic energy (second term of Equation (1.3)) can be neglected ($\hat{T}_n = 0$); in addition, the nucleus-nucleus repulsion can be considered as a constant at fixed nuclear positions \mathbf{R} ($\hat{V}_{nn} = V_{nn}(\mathbf{R})$). With these simplifications, the Hamiltonian in Equation (1.3) becomes

$$\hat{H} = - \sum_{i=1}^N \frac{1}{2} \nabla_i^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} + V_{nn} \quad (1.5)$$

which is the Hamiltonian describing the motion of N electrons in the field of M fixed nuclear charges. The constant nucleus-nucleus repulsion, V_{nn} , is frequently neglected since it is just a constant within the BO approximation and that adding a constant to a quantum operator just shifts the eigenvalues and does not change the eigenfunctions, i.e., the representation of the system is unaffected. The electronic Hamiltonian is then given by

$$\hat{H}_{el} = - \sum_{i=1}^N \frac{1}{2} \nabla_i^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} \quad (1.6)$$

such that the electronic Schrödinger equation is now

$$\hat{H}_{el} \Psi_{el}(\mathbf{r}, \mathbf{R}) = E_{el}(\mathbf{R}) \Psi_{el}(\mathbf{r}, \mathbf{R}) \quad (1.7)$$

where the electronic wavefunction $\Psi_{el}(\mathbf{r}, \mathbf{R})$ depends on the positions of electrons and the fixed nuclear coordinates. The total energy of the full molecular system, at the fixed nuclear positions, \mathbf{R} , includes the constant nuclear repulsion and is given by

$$E_{tot}(\mathbf{R}) = E_{el}(\mathbf{R}) + V_{nn}(\mathbf{R}) \quad (1.8)$$

By varying the nuclear positions and solving the electronic SE, we are able to arrive at the total energy of the system at different nuclear positions (Equation (1.8)). This total energy, with parametric dependence on the nuclear positions, provides a potential for the nuclear motion. This gives rise to the concept of **potential energy surface** (PES), which is the electronic energy of the system over the nuclear coordinates, $E_{el}(\mathbf{R})$. The nuclear motion can now be solved, with the nuclear Hamiltonian for the motion of nuclei in the field of the electrons given by

$$\hat{H}_{nuc} = - \sum_{A=1}^M \frac{1}{2M_A} \nabla_A^2 + E_{el}(\mathbf{R}) + V_{nn}(\mathbf{R}) = - \sum_{A=1}^M \frac{1}{2M_A} \nabla_A^2 + E_{tot}(\mathbf{R}) \quad (1.9)$$

and with the nuclear SE given by

$$\hat{H}_{nuc} \Psi_{nuc} = E \Psi_{nuc} \quad (1.10)$$

The BO approximated total energy is given by E from Equation (1.10). As a result of this separation, the total molecular wavefunction of the system, Ψ , can be written as a product of the electronic wavefunction and the nuclear wavefunction, as

$$\Psi = \Psi_{el}\Psi_{nuc} \quad (1.11)$$

We focus on solving the electronic TISE given in Equation (1.7).

1.2.3 Quantum mechanical measurements

For any physical observable Q , there is a corresponding Hermitian quantum operator \hat{Q} giving the measurement of the observable. The Hermiticity of the operator ensures that the measured physical observable of a system, represented by the wavefunction Ψ , is real, as is necessary for being physically sound. The mean value of the observable Q in a series of measurements is given by the expectation value of the corresponding operator \hat{Q} , via the formula,

$$Q = \langle \hat{Q} \rangle = \frac{\langle \Psi | \hat{Q} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \quad (1.12)$$

Therefore, if the quantum operator is the total Hamiltonian, then, the total energy of the system is the expectation value of the Hamiltonian, given by

$$E = \langle \hat{H} \rangle = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \quad (1.13)$$

1.2.4 The variational principle

The exact solution of the TISE is possible only for a limited number of systems. In cases where the exact solutions are not available, we can find approximate wavefunctions to the system. In many cases, we are interested in the ground state of a system, represented

by the wavefunction ψ_0 , with ground state energy E_0 . The variational principle asserts that for an arbitrary trial wavefunction $\tilde{\psi}$ satisfying the boundary conditions for a system, the expectation value of its energy \tilde{E} provides an upper bound to the lowest eigenvalue of the Hamiltonian, the true ground state energy E_0 . That is, we have

$$\tilde{E} = \frac{\langle \tilde{\psi} | \hat{H} | \tilde{\psi} \rangle}{\langle \tilde{\psi} | \tilde{\psi} \rangle} \geq E_0 = \frac{\langle \psi_0 | \hat{H} | \psi_0 \rangle}{\langle \psi_0 | \psi_0 \rangle} \quad (1.14)$$

In general, the flexibility of the trial wavefunction can be increased by including in it an adjustable parameter or parameters, so that the energy of the trial wavefunction can be further refined by minimising the trial energy with respect to those parameters. The variational principle (Equation (1.14)) implies that any approximate wavefunction to the true ground state wavefunction will yield an expectation energy that is higher than or equal to the true ground state energy; equality is satisfied when the trial wavefunction is exactly the same as the ground state wavefunction.

1.2.5 Linear variation method and the secular equations

Given that we do *not* have the eigenfunctions of the true Hamiltonian, we can write the trial wavefunction $\tilde{\psi}$ as a linear combination of N independent functions $\{\phi_i\}$ (often the atomic orbitals),

$$\tilde{\psi} = \sum_{i=1}^N c_i \phi_i \quad (1.15)$$

so that Equation (1.14) becomes

$$\tilde{E} = \frac{\langle \tilde{\psi} | \hat{H} | \tilde{\psi} \rangle}{\langle \tilde{\psi} | \tilde{\psi} \rangle} = \frac{\sum_i^N \sum_j^N c_i^* c_j \langle \phi_i | \hat{H} | \phi_j \rangle}{\sum_i^N \sum_j^N \langle \phi_i | \phi_j \rangle} = \frac{\sum_{i,j} c_i^* c_j H_{ij}}{\sum_{i,j} c_i^* c_j S_{ij}} \quad (1.16)$$

which can be rearranged to

$$\tilde{E} \sum_{i,j} c_i^* c_j S_{ij} = \sum_{i,j} c_i^* c_j H_{ij} \quad (1.17)$$

To minimise the energy with respect to the coefficients c_i 's, we take the partial derivative of Equation (1.17) with respect to the coefficient c_k and require that

$$\frac{\partial \tilde{E}}{\partial c_k} = 0 \quad (1.18)$$

so that we arrive at

$$\begin{aligned} \frac{\partial \tilde{E}}{\partial c_k} \sum_{i,j} c_i^* c_j S_{ij} + \tilde{E} \sum_{i,j} \left[c_j \frac{\partial c_i^*}{\partial c_k} + c_i^* \frac{\partial c_j}{\partial c_k} \right] S_{ij} &= \sum_{i,j} \left[c_j \frac{\partial c_i^*}{\partial c_k} + c_i^* \frac{\partial c_j}{\partial c_k} \right] H_{ij} \\ \implies \tilde{E} \sum_{i,j} [c_j \delta_{ik} + c_i^* \delta_{jk}] S_{ij} &= \sum_{i,j} [c_j \delta_{ik} + c_i^* \delta_{jk}] H_{ij} \\ \implies \tilde{E} \left[\sum_j c_j S_{kj} + \sum_i c_i^* S_{ik} \right] &= \left[\sum_j c_j H_{kj} + \sum_i c_i^* H_{ik} \right] \quad (1.19) \\ \implies 2\tilde{E} \sum_j c_j S_{kj} &= 2 \sum_j c_j H_{kj} \\ \implies \sum_j (H_{kj} - \tilde{E} S_{kj}) c_j &= 0 \end{aligned}$$

where we have used $S_{ij} = S_{ji}$ and $H_{ij} = H_{ji}$ (due to Hermiticity of the Hamiltonian operator).

Equation (1.19) are the secular equations of the system. In matrix form, this is

$$(\mathbf{H} - E\mathbf{S})\mathbf{c} = \mathbf{0} \quad (1.20)$$

1.2.6 Spin-statistics theorem and Pauli exclusion principle

Due to the indistinguishability of quantum particles, the exchange of labels on any two identical particles should preserve the probability density of the system. This observation is encapsulated by *spin-statistics theorem*, which states that, in exchanging two identical particles (both space and spin coordinates), the total wavefunction is antisymmetric (sign change) for fermions and symmetric (no sign change) for bosons.

Since electrons are fermions, the exchange of two identical electrons requires that the total wavefunction of the system changes sign, viz.,

$$\hat{P}\Psi(\mathbf{r}_1, \mathbf{r}_2) = \Psi(\mathbf{r}_2, \mathbf{r}_1) = -\Psi(\mathbf{r}_1, \mathbf{r}_2), \quad (1.21)$$

where \hat{P} is the exchange/permutation operator. The probability density of the system is preserved since the probability of finding an electron is given by the square modulus of the total wavefunction and is thus not affected by the sign change, that is

$$|\Psi(\mathbf{r}_2, \mathbf{r}_1)|^2 = |-\Psi(\mathbf{r}_1, \mathbf{r}_2)|^2. \quad (1.22)$$

The **Pauli exclusion principle**, which states that no two or more identical fermions can occupy the same quantum state, follows immediately: if we have two fermions in the same state (same spatial and spin coordinates), then, $\mathbf{r}_2 = \mathbf{r}_1 = \mathbf{r}$, Equation (1.21) then becomes $\Psi(\mathbf{r}, \mathbf{r}) = -\Psi(\mathbf{r}, \mathbf{r}) \implies 2\Psi(\mathbf{r}, \mathbf{r}) = 0 \implies \Psi(\mathbf{r}, \mathbf{r}) = 0$, resulting in no such wavefunction.

1.2.7 Spin orbitals, Hartree product and Slater determinants

A spin orbital $\chi(\mathbf{X})$ is a wavefunction for an electron containing a spatial orbital $\psi(\mathbf{r})$, which is a function of the position vector of the electron at \mathbf{r} , multiplied by the spin of the electron σ_{m_s} . The coordinate \mathbf{X} is a collection of individual space coordinates \mathbf{r} and

the associated spin coordinates. Mathematically, $\chi(\mathbf{X}) = \psi(\mathbf{r})\sigma_{m_s}$ where the electron spin takes either spin up (α) or spin down (β). Each spin orbital can accommodate one electron, since, no two electrons can have the same four quantum numbers, as a consequence of Pauli exclusion principle.

For a system with N electrons, we can construct a many-electron wavefunction called the *Hartree product* $\Psi^{\text{HP}}(\mathbf{X})$, which is a product of individual particle wavefunctions, i.e., a product of spin orbitals. Mathematically,

$$\Psi^{\text{HP}}(\mathbf{X}) = \Psi^{\text{HP}}(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = \chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2) \cdots \chi_N(\mathbf{x}_N). \quad (1.23)$$

The Hartree product is a *mean-field* wavefunction where the individual electrons are assumed to be non-interacting; it is an uncorrelated wavefunction. The Hartree product suffers the deficiency that it does not conform to the antisymmetry of the overall wavefunction under the exchange of electron labels, i.e., it violates the Pauli principle.

We can obtain the correct antisymmetric wavefunction of the N -electron system, called a *Slater determinant*, Ψ^{SD} , from the Hartree product, Ψ^{HP} , by applying an antisymmetriser operator, \hat{A} , to it. That is, we have

$$\Psi^{\text{SD}} = \hat{A}\Psi^{\text{HP}} = \hat{A}[\chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2) \cdots \chi_N(\mathbf{x}_N)], \quad (1.24)$$

where the antisymmetriser operator is defined as

$$\hat{A} = \frac{1}{\sqrt{N!}} \sum_u^{N!} \sigma_u \hat{P}_u. \quad (1.25)$$

\hat{P}_u is a permutation operator that permutes the coordinates in the Hartree product; σ_u is the sign of permutation that is even (+1)/odd (-1) if the number of single interchanges is

even/odd. Applying the antisymmetriser on the Hartree product leads us to the Slater determinant, viz.,

$$\Psi^{\text{SD}} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(\mathbf{x}_1) & \chi_2(\mathbf{x}_1) & \cdots & \chi_N(\mathbf{x}_1) \\ \chi_1(\mathbf{x}_2) & \chi_2(\mathbf{x}_2) & \cdots & \chi_N(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(\mathbf{x}_N) & \chi_2(\mathbf{x}_N) & \cdots & \chi_N(\mathbf{x}_N) \end{vmatrix} \quad (1.26)$$

The Slater determinant is correctly antisymmetrised and satisfies the antisymmetry and Pauli exclusion principles since, for example, exchanging the electron labels for any two rows or columns results in sign change, and that having any two electron labels the same results in a vanishing determinant. It can be shown that⁷ for a single Slater determinantal description of an N -electron system, the motion of electrons of parallel spins is correlated (electron exchange) but the motion of electrons of opposite spins is uncorrelated.

1.3 Basis sets

A basis set is a collection of known vectors/functions used to span a vector/Hilbert space. The simplest example of a basis set is the collection of unit vectors, $\{\hat{i}, \hat{j}, \hat{k}\}$, which spans the Euclidean 3D space. In other words, any vector in space can be represented as a linear combination of the unit vectors. Similarly, in quantum chemistry, a basis set is a collection of known functions, usually one-particle functions such as the atomic orbitals (AOs), used to represent the molecular orbitals (MOs) of a system of interest. The MOs can be written as a linear combination of AOs where their coefficients can be variationally determined. In almost all quantum chemical calculations, a finite set of basis functions is used. If the finite basis set is expanded toward completeness of an infinite basis set, then calculations using such an infinite basis set are said to approach the **basis set limit**.

1.3.1 Slater-type orbitals vs Gaussian-type orbitals

There are two types of basis functions in quantum chemistry. The **Slater-type orbitals** (STOs; named after John C. Slater) are similar to the eigenfunctions of the hydrogen atom and have the following functional form,

$$\chi_{\zeta,n,l,m}(r, \theta, \varphi) = NY_{l,m}(\theta, \phi)r^{n-1}e^{-\zeta r} \quad (1.27)$$

where N is a normalisation constant, $Y_{l,m}$ are the spherical harmonics; the radial part is given by r^{n-1} , with ζ the Slater exponent that controls the width of the orbital. Note the exponential dependence on r . Since the STOs have resemblance to the hydrogen atomic orbitals, they are naturally good for molecular orbitals. In addition, they have the correct behaviours at short ($R \rightarrow 0$) and long ($R \rightarrow \infty$) ranges. However, the evaluation of integrals using these STOs are difficult and computationally resource-consuming.

An alternative and much more popular type of basis set employed in quantum chemistry is the **Gaussian-type orbitals** (GTOs; first proposed by Francis Boys). The functional forms of the GTOs are given below,

$$\begin{aligned} \chi_{\alpha,l_x,l_y,l_z}(x, y, z) &= Nx^{l_x}y^{l_y}z^{l_z}e^{-\alpha r^2} \quad (\text{Cartesian}) \\ \chi_{\alpha,n,l,m}(r, \theta, \phi) &= NY_{l,m}(\theta, \phi)r^{n-1}e^{-\alpha r^2} \quad (\text{Spherical}) \end{aligned} \quad (1.28)$$

where α is the Gaussian orbital exponent that controls the width of the GTOs (the larger the value of α , the more contracted the GTO is) and l_x , l_y and l_z are non-negative integers. The sum of these numbers, $l = l_x + l_y + l_z$, is analogous to the angular momentum quantum number and gives an indication of the type of functions as s -type ($l = 0$), p -type ($l = 1$), d -type ($l = 2$) etc. The GTOs have the advantage that they are simpler to handle than STOs computationally since the calculation of multi-centre electron repulsion integrals

are easier using GTOs due to the Gaussian product theorem (the product of two Gaussians at different centres is another Gaussian at a new centre). The GTOs, however, have incorrect behaviours both at short ($R \rightarrow 0$; no nuclear cusp) and long ($R \rightarrow \infty$; too fast decay) ranges. To overcome these shortcomings, a number of GTOs (primitives) are commonly taken as a linear combination to create *contracted* Gaussian functions (CGFs) to resemble the STOs as much as possible:

$$\chi^{\text{CGF}} = \sum_i a_i \chi_i^{\text{GTO}} \quad (1.29)$$

The CGFs are variationally optimised with respect to the Hartree-Fock (HF) energy of free atoms to produce an optimal set of contraction coefficients and Gaussian exponents of the primitives, which are then fixed. The optimised CGFs are then used to construct Gaussian-type basis sets.

1.3.2 Single- ζ , multiple- ζ and split-valence basis sets

A minimal basis set, or **single- ζ** basis set, is one where a single basis function is used for each orbital in a Hartree-Fock (*vide infra*) calculation on the free atom. The most common example of minimal basis set is STO- n G, first proposed by John Pople, where n Gaussian primitives are used to approximate a single STO. For example, an STO-3G basis function is a linear combination of 3 primitive Gaussian functions with the coefficients determined via a least square fit to the single STO. Using this basis set, a carbon atom, for example, will have only one STO-3G orbital for each of 1s, 2s and three 2p orbitals. This minimal basis set is generally considered to be insufficient for accurate representation of orbitals in quantum chemistry.

To increase the accuracy of orbital descriptions by the basis sets, two or more functions can be used to describe each type of orbital, giving rise to **double- ζ (DZ)**, **triple- ζ (TZ)**, and **quadruple- ζ (QZ)** basis sets. For example, a carbon atom with DZ basis set will have two functions for each of 1s, 2s and three 2p orbitals (1s, 1s', 2s, 2s' and two sets of p-functions 2p and 2p').

In chemical bonding, the core orbitals are only weakly affected whereas the valence orbitals can change substantially. The majority of chemistry is governed by the movement of valence electrons. It is therefore more computationally efficient to implement basis set that allows for a greater flexibility in the valence orbitals rather than the core orbitals. The **split-valence (SV)** basis set introduced by Pople aims to achieve this balance of flexibility and cost. In a SV basis set, single- ζ basis functions are used for core orbitals and double- and higher- ζ basis functions for valence orbitals. These SV basis sets are represented as n - ij G or n - ijk G where n is the number of Gaussian primitives used for the core shells; the numbers i , j , k are the numbers of Gaussian primitives used for contractions in the *first*, *second* and *third* STO of the valence shells, respectively. The ij notation is used for basis set of valence double- ζ (VDZ) quality (two functions for the valence orbitals) while the ijk notation is used for basis set of valence triple- ζ (VTZ) quality (three functions for the valence orbitals). For example, the split-valence triple- ζ basis set 6-311G uses 6 Gaussian functions to describe the core orbital, and respectively 3, 1, 1 Gaussian function(s) for the first, second, third STO of the valence orbital.

1.3.3 Polarisation functions

The GTOs in the previous subsections are optimised by minimising the HF energy of the atoms. This gives the basis functions that have the same angular momentum l as those in atoms. However, during bonding in the formation of molecules, these atomic orbitals are

distorted. Under these situations, the s-orbital acquires p-character while the p-orbital acquires d-character and so on. These changes are not satisfactorily represented by the Gaussian AOs. To account for these orbital distortions upon molecular bonding, functions of higher angular momentum are usually added. These additional functions are called *polarisation functions* and when added to the basis set, is denoted by the letter “P”. Thus, DZP means double- ζ basis set with polarisation functions added. In the Pople-type basis sets, the polarisation functions are denoted by the parenthesis behind the basis set names, for example, in 6-31G(d,p) basis set, the notation “(d,p)” denotes that a set of d-orbital functions are added to the heavy atoms and that a set of p-orbital functions are added to the H atoms.

The addition of polarisation functions removes the spherical symmetry of the AOs so that the basis set can give a better description of bonding environment. Polarisation functions introduce an additional node. For example, when polarisation is added to 1s AO of a hydrogen atom, a p-function is added; similarly, when polarisation is added to valence p-orbitals, d-type functions are added to the basis set. For heavy atoms, higher angular momentum polarisation functions (d, f, ...) may be important. In all calculations where electron correlation is important, it is necessary to include polarisation functions.

1.3.4 Diffuse functions

For anionic systems or systems in excited states, the electrons are usually loosely bound. This necessitates an accurate description of the wavefunction towards the tail region. *Diffuse functions*, having very small exponents and decaying more slowly with distance from the nucleus, are included to provide improved description of the tail region. These Gaussian functions are usually of s- and p-type functions and their inclusion allow better description of anions, weak bonds (e.g. hydrogen bonds) and calculation of properties

such as dipole moments and polarizabilities etc. The addition of diffuse functions to a Pople-type basis set is indicated by “+” in $n-ij+G$ or $n-ij++G$ where a single “+” indicates that one diffuse s-type and p-type Gaussian functions are added on heavy atoms and a double “++” indicates that on top of the functions added on heavy atoms in “+” basis set, an additional diffuse s-type Gaussian function is added on hydrogen atoms.

1.3.5 Correlation-consistent (cc) basis sets

Correlation-consistent (cc) basis sets are widely used basis sets developed by Dunning and co-workers⁸⁻¹⁶ for wavefunction-based calculations. They are primarily designed for correlated calculations and are optimised using correlated (CISD) wavefunctions. They are designed to converge systematically to the complete basis set (CBS) limit. These basis sets are denoted cc-pVXZ ($X = D, T, Q, 5, 6, 7\dots$) which means correlation-consistent, polarised valence, X-zeta basis. Additional set of tight functions with large exponents can be added to recover core-core and core-valence electron correlation, producing the cc-pCVXZ basis sets (where C stands for core). A prefix “aug” can be added to show that a set of diffuse functions has been included for every angular momentum present in the basis set, therefore, aug-cc-pVDZ for C atom for example, has diffuse s, p, d functions added.

1.3.6 Karlsruhe basis sets

The basis sets discussed previously are rather expensive computationally (non-linear dependence) and suffer from basis set incompleteness if a finite basis set is used. The Karlsruhe basis sets provide an attractive alternative as they are property-optimised balanced basis sets of quality for all elements up to radon ($Z = 86$). These basis sets show similar convergence for SV, DZ, TZ and QZ quality and are more computationally economical.¹⁷

Def2-basis sets are examples of segmented contracted basis sets.^{18,19} These are designed for all the elements H-Rn for varying flexibility and accuracy. The basis sets are named def2-SV(P) to def2-QZVPP. They were tested for a set of *ca.* 300 molecules representing nearly all elements in nearly all common oxidation states and are designed to give similar errors for all the elements across the periodic table for a given basis set type. It is recommended that¹⁸ for DFT calculations, one uses def2-SV(P) basis sets to obtain qualitative results and def2-TZVP basis sets to obtain results close to DFT basis set limit. For similar accuracies in HF and MP2 and other post-HF calculations, larger polarisation sets are required and that def2-SVP and def2-TZVPP bases are recommended, for the above purposes respectively. For first-order property calculations, such as bond energies, using DFT, def2-TZVPP bases are recommended to approach the DFT basis set limit.¹⁸

1.3.7 Effective core potentials

For systems involving heavier elements such as those from the third period and beyond of the periodic table, there is a large number of core electrons for these elements. To reach a proper description of the valence electrons, a large number of basis functions are first required to describe the core electrons, which are relatively less important in chemical reactions. The situation is complicated by the increasing importance of relativistic effects for heavy elements. To overcome these problems, effective core potentials (ECP), also called pseudopotentials, are introduced to represent the chemically inert core electrons and capture the dominant effects of relativity. This has the advantage that the size of the basis set needed for the molecular description can be significantly reduced. The ECPs from Hay and Wadt, also called Los Alamos National Laboratory (LANL) ECPs^{20,21} (non-relativistic for the first-row transition metals), is an example of popular ECPs in modern use.

1.3.8 Basis set superposition error

Calculations of a molecular system using a finite (especially small) basis set are prone to *basis set superposition error* (BSSE).^{22,23} The interaction energy between two monomers A and B is given by the energy difference between the complex AB and the sum of the individual energy of A and B. As the two monomers A and B approach each other in the complex formation, the complex AB can be artificially stabilised as monomer A utilises the basis functions from monomer B and vice versa. Each monomer is able to access the basis functions on the other monomer at short, but not long, intermolecular distance. This differential treatment of monomers at varying intermolecular distances is the source of BSSE. In the event that BSSE can be eliminated by treating the monomers with same number of basis functions at different intermolecular distances, the system can still be subject to basis set incompleteness errors (BSIEs) due to the finite size of the basis set used.

The Boys and Bernardi counterpoise correction (CP) is commonly used to remove BSSE.²⁴ Briefly, the BSSE is calculated by additional calculations using the dimer basis for all species and subtracting the energy difference between the monomer in dimer basis and the monomer in monomer basis.

1.3.9 Basis sets used in this thesis

We used GTOs throughout this thesis. For systems where small organic molecules are involved (Chapters 2 and 3), we used a small Pople-type basis set for geometry optimisation. For example, in Chapter 2, we study the radical cationic system involving small organic molecules, we used a small basis set 6-31G(d) for geometry optimisation. For Chapter 3, in the study of hydroxyphosphine bifunctional catalyst, where hydrogen bonding and proton movements are potentially important, we used 6-31+G(d,p) basis set

for geometry optimisation. Here we added in diffuse functions for a better description of hydrogen bonding and additional polarisation functions for the hydrogen atom for better bonding description of the formation and breaking of O–H and N–H bonds.

For the study of transition metal (TM) catalysed reactions (Chapters 4 to 7), the initial geometry optimisations were all performed with a small basis set of def2-SVP quality. The Karlsruhe basis set was chosen as it provides a balanced description of all elements, up to Rn, on the periodic table. The Pople basis sets were not used as these do not provide descriptions of elements beyond Kr (such as Pd, and Ir that we use in our catalytic system). For a finer geometry optimisation, we used a mixture of bases for the description of these organometallic systems. Typically, a larger basis set, such as def2-TZVPPD used for the TMs in this thesis, is needed to provide a sufficient description of the d-orbitals.¹⁸ The diffused functions (indicated by the letter “D” in the basis name) are also included to better describe the second (e.g. Pd) and third row (e.g. Ir) TM p- and d-orbitals.¹⁸

For single-point (SP) calculations, we generally use a large basis set from the Karlsruhe basis set family, such as def2-QZVPP, which provides a good description for all elements and yields a good accuracy.

1.4 The Hartree-Fock or Self-Consistent Field Method

The Hartree-Fock (HF) method is central to quantum chemistry. HF commonly serves as a starting point for more sophisticated methods such as those accounting for the effects of electron correlation. The underlying idea of HF is that a single Slater determinantal wavefunction can be used to approximate a multi-electronic system where electron-electron interactions are treated in an average way.

1.4.1 Hartree-Fock equations

For an N -electron system, we can use a single Slater determinant of the form in Equation (1.26) to approximate the ground state wavefunction. We aim to minimise the electronic energy to find the best spin orbitals using the variational method. That is, we want to minimise

$$E_0 = \frac{\langle \Psi_{\text{HF}} | \hat{H} | \Psi_{\text{HF}} \rangle}{\langle \Psi_{\text{HF}} | \Psi_{\text{HF}} \rangle} = \langle \Psi_{\text{HF}} | \hat{H} | \Psi_{\text{HF}} \rangle \text{ if } \Psi_{\text{HF}} \text{ is normalised} \quad (1.30)$$

by systematically varying the spin orbitals $\{\chi_i\}$, subject to the constraint that these spin orbitals remain orthonormal, $\langle \chi_i | \chi_j \rangle = \delta_{ij}$. Doing this formally leads to a set of one-electron Fock equations

$$\hat{f}_i \chi_i = \varepsilon_i \chi_i \quad (1.31)$$

where the Fock operator \hat{f}_i gives the effective *one-particle* Hamiltonian:

$$\hat{f}_i = \hat{h}_i + \hat{V}_i^{\text{HF}} = -\frac{1}{2} \nabla_i^2 - \sum_{A=1}^M \frac{Z_A}{r_{iA}} + \sum_j \left(\hat{J}_j(1) - \hat{K}_j(1) \right) \quad (1.32)$$

The Fock operator is a sum of the core Hamiltonian operator \hat{h}_i ,

$$\hat{h}_i = -\frac{1}{2} \nabla_i^2 - \sum_{A=1}^M \frac{Z_A}{r_{iA}}, \quad (1.33)$$

and the effective *one-electron* HF potential operator, \hat{V}_i^{HF} ,

$$\hat{V}_i^{\text{HF}} = \sum_j \left(\hat{J}_j(1) - \hat{K}_j(1) \right) \quad (1.34)$$

where \hat{J}_i and \hat{K}_i are the Coulomb and exchange operators, respectively, defined as

$$\begin{aligned}
\hat{J}_j(1) |\chi_i(1)\rangle &= \left\langle \chi_j(2) \left| \frac{1}{r_{12}} \right| \chi_j(2) \right\rangle |\chi_i(1)\rangle \\
\hat{K}_j(1) |\chi_i(1)\rangle &= \left\langle \chi_j(2) \left| \frac{1}{r_{12}} \right| \chi_i(2) \right\rangle |\chi_j(1)\rangle
\end{aligned}
\tag{1.35}$$

The *Coulomb operator* \hat{J}_i accounts for the Coulombic repulsion between electrons and is local in nature in the sense that it gives the averaged potential due to other electrons at a point in space and does not depend on other points in space. The *exchange operator* \hat{K}_i is, on the other hand, non-local since there does not exist a simple potential that uniquely define the exchange at a local point in space. The exchange energy accounts for the effects of electron exchange interactions due to the indistinguishability of identical particles and results from the antisymmetry of the Slater determinantal wavefunction.

The HF equations are a set of non-linear coupled differential equations in that the Fock operator \hat{f}_i for one electron depends on the spin orbitals of all other electrons and that each spin orbitals χ_i is obtained as a solution of the Fock equation. As a result, an iterative approach is needed to solve the HF equations. This is done by first proposing a set of guess orbitals, from which the average HF potential operator \hat{V}_i^{HF} is constructed. The Fock equations (Equation (1.31)) can then be solved to obtain a new set of orbitals. This procedure is iterated until the difference between the new orbitals and the input orbitals falls below a predefined threshold value. As a result, this method is known as the **self-consistent field** (SCF) method.

1.4.2 Restricted close-shell, restricted open-shell and unrestricted HF

The presence of electron spins gives rise to different energy expressions for the HF procedures. In a restricted close-shell HF (**RHF**), the electron spins are all paired up in orbitals. It can be shown the energy expression for the RHF single Slater determinantal wavefunction is given by

$$E^{RHF} = 2 \sum_i^n h_{ii} + \sum_{ij}^n [2(ii|jj) - (ij|ij)] \quad (1.36)$$

where the spin of the system has been taken into account and factored out so that only spatial orbitals $\{\psi_i\}$ are used. In the expression,

$$h_{ii} = \langle \psi_i | \hat{h} | \psi_i \rangle \quad (1.37)$$

is the matrix element of the core Hamiltonian, Equation (1.33), representing the electronic energy of an electron in spatial orbital i in the combined electrostatic potential averaged over *all other* electrons;

$$(ii|jj) = \left\langle \psi_i(i)\psi_j(j) \left| \frac{1}{r_{ij}} \right| \psi_i(i)\psi_j(j) \right\rangle \quad (1.38)$$

is the Coulomb energy between electrons i and j (labels in parenthesis) in orbitals i and j (labels in subscripts of the wavefunctions); and that

$$(ij|ij) = \left\langle \psi_i(i)\psi_j(j) \left| \frac{1}{r_{ij}} \right| \psi_i(j)\psi_j(i) \right\rangle \quad (1.39)$$

is the exchange energy. Note that the direct Coulomb energy results from pairwise interactions between *all* electrons whereas the exchange energy results from the pairwise interactions between electrons of *parallel* spins only.

For openshell systems, two approaches are generally adopted. Using unrestricted HF (**UHF**), the lowest energy for the single Slater determinantal wavefunction is given by

$$E^{\text{UHF}} = \sum_i^{\alpha+\beta} h_{ii} + \frac{1}{2} \sum_{ij}^{\alpha+\beta} (ii|jj) - \frac{1}{2} \sum_{ij}^{\alpha} (ij|ij) - \frac{1}{2} \sum_{ij}^{\beta} (ij|ij) \quad (1.40)$$

where the α and β orbitals have different spatial parts. The Slater determinant is an eigenfunction of \hat{S}_z but not an eigenfunction of \hat{S}^2 . Spin contamination, the artificial mixing of electronic states of different spins, can lead to inaccurate energies. Techniques exist, however, to eliminate spin contamination.²⁵⁻²⁷ UHF is commonly used to study openshell systems due to its simplicity, computational efficiency and ease for post-Hartree Fock method implementation.

Another method for dealing with openshell system is restricted open-shell HF (**ROHF**). In this method, electrons are first paired up in doubly occupied spatial orbitals, leaving unpaired electrons in singly occupied orbitals. The energy expression for ROHF is given by

$$\begin{aligned}
 E = & \sum_i 2h_{ii} + \sum_{ij} [2(ii|jj) - (ij|ij)] \\
 & + \sum_m h_{mm} + \frac{1}{2} \sum_{mn} [(mm|nn) - (mn|mn)] \\
 & + \sum_{im} [2(mm|ii) - (im|im)]
 \end{aligned} \tag{1.41}$$

where $i, j \dots$ denote doubly occupied orbitals and $m, n \dots$ denote singly occupied α orbitals; the last term gives the mixing between doubly and singly occupied orbitals since they are chemically distinct. The ROHF picture is chemically accurate in that the wavefunction is an eigenfunction of the total spin operator \hat{S}^2 . In other words, the ROHF wavefunction does not suffer from spin contamination. However, this method is much less frequently used than the UHF method in modern quantum chemistry due to its higher difficulty in implementation and higher computational cost. The ROHF method lacks a unique effective Fock operator,²⁸ such that the resulting orbitals and orbital energies are

different depending on the choice of Fock operators, making the physical interpretation somewhat difficult.

1.4.3 Roothaan-Hall equations

The direct solution of the Fock equations (Equation (1.31)) is non-trivial. In 1951-52, Roothaan²⁹ and Hall³⁰ independently proposed a method of converting the set of integro-differential equations into a set of algebraic equations by introducing basis functions (section 1.3). Taking electron spin out of consideration by adopting the appropriate HF method, we consider only the spatial orbitals. A set of K known basis functions or AOs $\{\phi_\mu(\mathbf{r})\}$ is commonly employed, so that each MO ψ_i can be expressed as a linear combination of these AOs, viz.,

$$\psi_i = \sum_{\mu=1}^K c_{\mu i} \phi_\mu(\mathbf{r}) \quad (1.42)$$

Substituting the above expression into the Fock equations $\hat{f}_i \chi_i = \varepsilon_i \chi_i$, we have

$$\hat{f}_i \sum_{\mu=1}^K c_{\mu i} \phi_\mu(\mathbf{r}) = \varepsilon_i \sum_{\mu=1}^K c_{\mu i} \phi_\mu(\mathbf{r}) \quad (1.43)$$

which is equivalent to the following matrix equation for the expansion coefficients:

$$\mathbf{FC} = \mathbf{SC}\boldsymbol{\varepsilon} \quad (1.44)$$

These are the Roothaan-Hall equations. \mathbf{F} is the Fock matrix with the matrix element $F_{\mu\nu} = \langle \phi_\mu | \hat{f} | \phi_\nu \rangle$; \mathbf{S} is the overlap matrix with the $S_{\mu\nu} = \langle \phi_\mu | \phi_\nu \rangle$ giving the overlap between the basis functions; \mathbf{C} is the coefficient matrix containing the expansion coefficients $c_{\mu i}$; $\boldsymbol{\varepsilon}$ is a diagonal matrix of orbital energies. All these matrices are $K \times K$ in

dimension. The integro-differential HF equations, using the Roothaan-Hall formalism, is thus converted to standard algebraic matrix equations.

If the set of basis functions used is complete, then the expansion Equation (1.42) would be exact, and we would be able to obtain the lowest possible variational energy, the **HF limit**, within the single Slater determinantal approximation. In practice, however, limited by computational resources, a *finite* set of K basis functions is used. For a system of N electrons, using a set of K basis functions gives a total of $2K$ spin orbitals, consisting of N occupied spin orbitals and $2K - N$ unoccupied, or virtual, orbitals. The single Slater determinantal wavefunction formed from the occupied spin orbitals is then the best approximation to the ground state of the system.

1.4.4 Electron correlation

Because the HF potential uses central field approximation, electron-electron interactions are not directly taken into account and are only treated in an averaged manner. As a result, there is a finite probability that, within the HF approximation, two electrons will occupy the same space, which is unphysical. The deficiency of HF theory is that the motion of an electron can be affected by the motion of other electrons and this *electron correlation* is not captured by HF theory. The correlation energy E_{corr} is defined as

$$E_{\text{corr}} = E_{\text{exact}} - E_{\text{HF}} \quad (1.45)$$

This correlation due to electron-electron interactions is sometimes called *dynamical* electron correlation as it results from the motion of these electrons. As the HF is single Slater determinantal, it also fails to account for *non-dynamical* correlation, arising from different determinants contributing similar weights to a system due to their near or exact degeneracy in frontier orbitals.

E_{corr} is always negative as the HF limit, E_{HF} , is an upper bound to the true ground state energy, as dictated by the variational principle. Although this correlation energy is normally only 1% of the total energy, its exclusion can lead to major errors in chemistry. This is particularly true for cases such as transition metal systems, where the neglect of electron correlation can result in huge errors. Therefore, methods accounting for electron correlation are required for high accuracy quantum chemistry.

1.5 Post-Hartree-Fock Methods

To account for electron correlation, it is essential to go beyond Hartree-Fock. Broadly speaking, two classes of methods can be distinguished – the variational and perturbative. Variational methods, such as configuration interaction (CI), uses a linear combination of discrete solution sets whereas perturbative methods, such as many-body perturbation theory (MBPT), separate the problem into an exactly solvable part and a difficult part with no general analytic solution as a small perturbation to that solvable part.

1.5.1 Configuration interaction

The configuration interaction (CI) wavefunction is constructed from a linear combination of Slater determinants called the *configuration state functions*, that is

$$\Psi_{\text{CI}} = \sum_i c_i |\Psi_i\rangle = c_0 \Psi_{\text{HF}} + \sum_S c_S \Psi_S + \sum_D c_D \Psi_D + \sum_T c_T \Psi_T + \sum_Q c_Q \Psi_Q + \dots \quad (1.46)$$

where the Slater determinants are obtained by promoting electrons from the occupied orbitals to the virtual orbitals in the reference HF Slater determinant. The number of electrons promoted determines the nature of these configuration state functions: promotion of one electron generates the singly excited state functions Ψ_S , and two

electrons, doubly excited state functions Ψ_D , etc. The CI coefficients are obtained by variationally minimising the electronic energy for the ground state:

$$E_{\text{CI}} = \min_{\Psi_{\text{CI}}} \frac{\langle \Psi_{\text{CI}} | \hat{H} | \Psi_{\text{CI}} \rangle}{\langle \Psi_{\text{CI}} | \Psi_{\text{CI}} \rangle} \quad (1.47)$$

For a given basis set, a full CI (FCI) wavefunction can be constructed by considering all the configurations that can be generated from the reference Slater determinant and including them in the calculation. A full CI calculation is highly computationally expensive due to its poor scaling with the number of electrons and basis functions, it is thus only achievable for very small systems. For most cases, it is necessary to truncate the CI expansion, Equation (1.46), so that only a subset of the determinants is included. In general, since lower-order excitations are more important than higher-order ones, *hierarchical truncation* is used. As an illustration, the CI singles-and-doubles (CISD) wavefunction recovers $\sim 94.5\%$ of the correlation energy while CISDT with triples recovers $\sim 95.9\%$. This goes up to 99.9% at CISDTQ with quadruple excitations.

The method above of using a single HF Slater determinant as a reference state function is called *single-reference* CI. In systems where a single determinant is insufficient to represent the ground state due to (near-)degeneracy (source of non-dynamical electron correlation), a *multi-reference* CI (MRCI) wavefunction is necessary. A reference space consisting of more than one dominant determinant is constructed, from which excitation determinants are generated from each of the reference determinants.

1.5.2 Many-body perturbation theory

Another systematic approach to recover the electron correlation energy is the many-body perturbation theory (MBPT). This perturbative method treats electron correlation as a

small perturbation to the ground state wavefunction; this method is not variational but size-consistent. The simplest example is the Møller-Plesset (MP) theory³¹ – an example of Rayleigh Schrödinger perturbation theory – denoted by MP n where n is the order at which the perturbation is truncated. The starting point for the MP theory are the eigensolutions of the Fock equations, $\hat{f}_i \chi_i = \varepsilon_i \chi_i$. Using MBPT, we wish to solve the eigenvalue problem for electronic state n :

$$\hat{H} |\Psi_n\rangle = (\hat{H}_0 + \hat{V}) |\Psi_n\rangle = E_n |\Psi_n\rangle \quad (1.48)$$

Expanding the wavefunction and energy as power series, we have

$$\begin{aligned} (\hat{H}^{(0)} + \lambda \hat{V}) \left(\sum_{i=0} \lambda^i \Psi_n^{(i)} \right) &= \left(\sum_{i=0} \lambda^i E_n^{(i)} \right) \left(\sum_{i=0} \lambda^i \Psi_n^{(i)} \right) \iff \\ (\hat{H}_0 + \lambda \hat{V}) \left| \Psi_n^{(0)} + \lambda \Psi_n^{(1)} + \dots \right\rangle &= (E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots) \left| \Psi_n^{(0)} + \lambda \Psi_n^{(1)} + \dots \right\rangle \end{aligned} \quad (1.49)$$

We choose the reference Hamiltonian to be the sum of the Fock operators,

$$\hat{H}_0 = \sum_i^N \hat{f}_i, \quad (1.50)$$

such that the perturbation is defined as

$$\hat{V} = \hat{H} - \hat{H}_0 = \hat{H} - \sum_i^N \hat{f}_i. \quad (1.51)$$

The zeroth order reference determinant is the HF Slater determinant $\Psi^{(0)} = \Psi_{\text{HF}}$.

Equating the different power terms in λ in the series expansion of Equation (1.49), we find that the first-order change in the n^{th} state wavefunction is given by

$$|\Psi_n^{(1)}\rangle = \sum_{m \neq n} \frac{\langle \Psi_m^{(0)} | V | \Psi_n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}} |\Psi_m^{(0)}\rangle \quad (1.52)$$

and has contributions from each of the eigenstates with $m \neq n$. The second order (MP2) perturbation energy is given by

$$E_n^{(2)} = \sum_{m \neq n} \frac{|\langle \Psi_m^{(0)} | V | \Psi_n^{(0)} \rangle|^2}{E_n^{(0)} - E_m^{(0)}} \quad (1.53)$$

which is proportional to the square of the matrix element of the perturbation that mixes the eigenstates m and n (the numerator), and inversely proportional to the energy difference between eigenstates m and n , showing that the contribution to the perturbation energy is the largest if the other eigenstates are close in energy to the state of interest.

Although higher order energy corrections can be calculated (MP3, MP4...), they are rarely used since the MP theory is non-variational and frequently the inclusion of higher orders, at additional computational cost, does not improve the calculated results.

1.5.3 Coupled-cluster theory

The coupled-cluster (CC) theory, originally proposed for problems in physics, is one of the most accurate methods that treat electron correlation for practical *ab initio* quantum chemistry. It has wide-ranging applications in the study of molecular structures and properties, excited states and spectroscopy. The basic equations for CC theory have a rather simple appearance. Instead of using a linear expansion of wavefunctions as in CI, CC uses an exponential ansatz for the wavefunction, viz.,

$$|\Psi\rangle = e^{\hat{T}} |\Phi_0\rangle = \left(1 + \hat{T} + \frac{1}{2}\hat{T}^2 + \frac{1}{3!}\hat{T}^3 + \dots \right) |\Phi_0\rangle \quad (1.54)$$

where $|\Phi_0\rangle$ is the reference wavefunction, which is typically a Hartree-Fock determinant, but can also be other wavefunction arising from, for example, CI. The cluster operator \hat{T} can be written as a sum of operators that, for an N -electron system, generate single (\hat{T}_1), double (\hat{T}_2) and triple (\hat{T}_3), ..., up to N -tuple excitations (\hat{T}_N),

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \dots + \hat{T}_N \quad (1.55)$$

in the reference wavefunction. The CC energy, which is not variational, is given by

$$E = \langle \Phi_0 | e^{-\hat{T}} H e^{\hat{T}} | \Phi_0 \rangle = \langle \Phi_0 | \bar{H} | \Phi_0 \rangle \quad (1.56)$$

where $\bar{H} = e^{-\hat{T}} H e^{\hat{T}}$ is the similarity-transformed (rotated) Hamiltonian of the system. The CC energy is a function of unknown amplitudes which can be obtained by solving the amplitude equation

$$\langle \Phi_{ij\dots}^{ab\dots} | \bar{H} | \Phi_0 \rangle = 0 \quad (1.57)$$

The cluster operator is usually truncated to give different models. One of the most popular ones is the coupled cluster singles-and-doubles (**CCSD**)³² where the cluster operator is taken as $\hat{T} = \hat{T}_1 + \hat{T}_2$. This CCSD method has the same number of parameters as CISD but has better approximations as it also accounts for higher order terms using the products of lower order terms – for example, substituting $\hat{T} = \hat{T}_1 + \hat{T}_2$ in the exponential wavefunction ansatz Equation (1.54) gives \hat{T}_2^2 and \hat{T}_2^3 terms (and others), which approximately accounts for quadruple and sextuple (and other) excitations, respectively. For coupled cluster singles-doubles-and-triples (CCSDT), we take $\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3$.

As CCSDT is rather expensive, a popular method for improving upon CCSD calculations is the **CCSD(T)** method,³³ which consists of full CCSD treatment with an estimate of the connected triples contribution by a non-iterative calculation of MBPT. This is frequently considered the “gold standard” in quantum chemistry.

1.6 Density Functional Theory

The *ab initio* wavefunction-based methods discussed earlier are rather expensive and are practical only for systems with a small number of atoms. Density functional theory (DFT) aims to provide an alternative framework within which the electronic structure problem is tackled. The central idea behind DFT is that it is not necessary to solve the Schrödinger equation for the wavefunction of the system (a $4N$ -variable quantity – $3N$ spatial and N spin coordinates – for an N -electron system) to compute the ground state energy, but rather it is sufficient to express the energy (and other properties) as a functional of the electron density, which is a 3-dimensional quantity.

1.6.1 Hohenberg-Kohn theorems

The foundations of modern DFT are grounded in two theorems developed by Hohenberg and Kohn (HK) in 1964.³⁴ The first theorem (HK1) states that the ground state electron density uniquely determines the external potential, thus the total energy, of a system. This means that the total energy is a unique functional of the ground state electron density. We know that the Hamiltonian of a system depends on the nuclear positions $\{R_A\}$ and atomic numbers $\{Z_A\}$ of the atoms and the total number of electrons, N (Equation (1.3)). It is quite easy to see that knowing the ground state electron density immediately gives us these *three* quantities since, 1) the integral of the density over all space gives the number of electrons N , viz.,

$$\int \rho(\mathbf{r}) d\tau = N; \quad (1.58)$$

2) the electron density maxima give the positions of the nuclei $\{R_A\}$; and 3) for any nucleus A at density maximum, the atomic number Z_A is given by

$$\left. \frac{\partial \bar{\rho}(r)}{\partial r} \right|_{r=0} = -2Z_A \rho(0) \quad (1.59)$$

where r is the radial distance from nucleus A , $\bar{\rho}(r)$ is the spherically averaged density. In words, this means that the radial derivative of the spherically averaged electron density, at the nuclear position, gives twice the density at the nucleus, $\rho(0)$, multiplied by the negative of the atomic number. At this stage, we see that given a known electron density, one can form the Hamiltonian for the system, solve the Schrödinger equation and thus determine the wavefunctions and energies of the system:

$$\rho(\mathbf{r}) \Rightarrow \{N, Z_A, R_A\} \Rightarrow \hat{H} \Rightarrow \Psi_0 \Rightarrow E_0 \text{ (and all other properties)} \quad (1.60)$$

The second theorem (HK2) guarantees that the ground state energy can be variationally found, provided that we can find an *exact* energy functional of the electron density $E[\rho]$; it states that any trial density satisfying the boundary conditions delivers an energy that is an upper bound to the true ground state energy and that the energy is exactly the same as the true ground state energy only if the trial density is exactly the true density, that is,

$$E_0 = E_0[\rho_0] \leq E[\tilde{\rho}] \quad (1.61)$$

These theorems prove the existence of the functional for finding the energies but they do not prescribe how one can find the functional!

1.6.2 The energy functional

The electronic Hamiltonian Equation (1.6) contains three terms: the kinetic energy of the electrons, the electron-electron interactions and electron-nucleus interactions and can be written as

$$\hat{H} = \hat{T} + \hat{V}_{ee} + \hat{V}_{Ne} \quad (1.62)$$

and that the energy functional is given by

$$E[\rho] = T[\rho] + V_{ee}[\rho] + V_{Ne}[\rho] = F[\rho] + \int \rho(\mathbf{r})v(\mathbf{r})d\mathbf{r} \quad (1.63)$$

where

$$v(\mathbf{r}) = - \sum_{A=1}^M \frac{Z_A}{r_A} \quad (1.64)$$

is the external potential that depends on the system. This term can be trivially evaluated once the system is specified, that is, once the potential $v(\mathbf{r})$ is known;

$$F[\rho] = T[\rho] + V_{ee}[\rho] = T[\rho] + (J[\rho] + E_{nc}[\rho]) \quad (1.65)$$

is the internal energy functional or the Hohenberg-Kohn functional that is *independent* of the external potential $v(\mathbf{r})$ and is thus universal for all systems (depends only on the total density). The electron-electron interaction energy functional $V_{ee}[\rho]$ can be further separated into the functional due to classical Coulomb interaction, $J[\rho]$, and *non-classical* contributions, $E_{nc}[\rho]$. If this functional $F[\rho]$ were known, we would have solved the SE for *all* systems. However, the explicit form of this functional is unknown and this is a major challenge for DFT development.

1.6.3 The Kohn-Sham approach

The quest for the universal functional $F[\rho]$ is not directly in sight. The method of Kohn and Sham³⁵ gives us one way to proceed with practical DFT. The essential idea behind the KS approach is the introduction of a fictitious system of non-interacting particles that generate the same density as the true system of interacting particles. In doing so, a special type of one-particle orbitals $\{\phi_i\}$ is reintroduced. The internal energy functional $F[\rho]$ can then be written as

$$F[\rho] = T[\rho] + J[\rho] + E_{nc}[\rho] = T_s[\rho] + J[\rho] + E_{xc}[\rho] \quad (1.66)$$

where the exchange-correlation functional $E_{xc}[\rho]$, given by

$$E_{xc}[\rho] = (T[\rho] - T_s[\rho]) + (V_{ee}[\rho] - J[\rho]), \quad (1.67)$$

is a collection of all portions of the total energy that are not exactly known.

In this approach, the bulk of the kinetic energy of the true system can be recovered using the kinetic energy of the fictitious non-interacting systems, $T_s[\rho]$, given by

$$T_s[\rho] = -\frac{1}{2} \sum_i^N \langle \phi_i | \nabla^2 | \phi_i \rangle \quad (1.68)$$

The electron density of the system is also exactly known in term of these orbitals,

$$\rho(\mathbf{r}) = \sum_i^N f_i |\phi_i|^2 \quad (1.69)$$

where f_i is the occupation number of i^{th} orbital.

To find the set of orbitals $\{\phi_i\}$ that minimises the energy functional, we apply the variational principle and take the functional derivative of the energy functional to arrive at the Kohn-Sham equations:

$$\left(-\frac{1}{2}\nabla^2 + v(\mathbf{r}) + v_J(\mathbf{r}) + v_{xc}(\mathbf{r})\right) \phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r}) \quad (1.70)$$

The external potential due to the electron-nucleus interactions is given by $v(\mathbf{r})$ in Equation (1.64); the Coulomb potential $v_J(\mathbf{r})$ is given by

$$v_J(\mathbf{r}) = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \quad (1.71)$$

and the exchange-correlation potential $v_{xc}(\mathbf{r})$ is given by the functional derivative of the exchange-correlation functional E_{xc} , viz.,

$$v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}}{\delta \rho(\mathbf{r})} \quad (1.72)$$

The KS equations (1.70) is a set of coupled *one-particle* Schrödinger equations that can only be solved self-consistently, as the sum of the potential terms depends on the density, and thus the orbitals, of the system that we are trying to solve for.

1.6.4 Hartree-Fock vs DFT

The HF method is a single Slater-determinantal approximation to the true ground state wavefunction and that the HF equations are obtained by optimising the MOs of the trial wavefunction to get the best energy. DFT is formally exact. The KS formalism is one approach to DFT that tries to optimise the particle density that maps a non-interacting system to a physical, interacting system to get the best energy. Thus, to get a property from wavefunction-based methods, one needs to know the correct quantum operator

corresponding to that property, but to get the property from DFT, one only needs to know how that property depends on the density of the system.

The KS orbitals are introduced to reproduce the particle density of the true interacting systems and have no strict physical meanings, except for the HOMO, whose energy gives the negative of the ionisation energy.³⁶⁻³⁹ In practice, however, these KS orbitals have similar shapes to the HF orbitals, allowing for qualitative analysis.

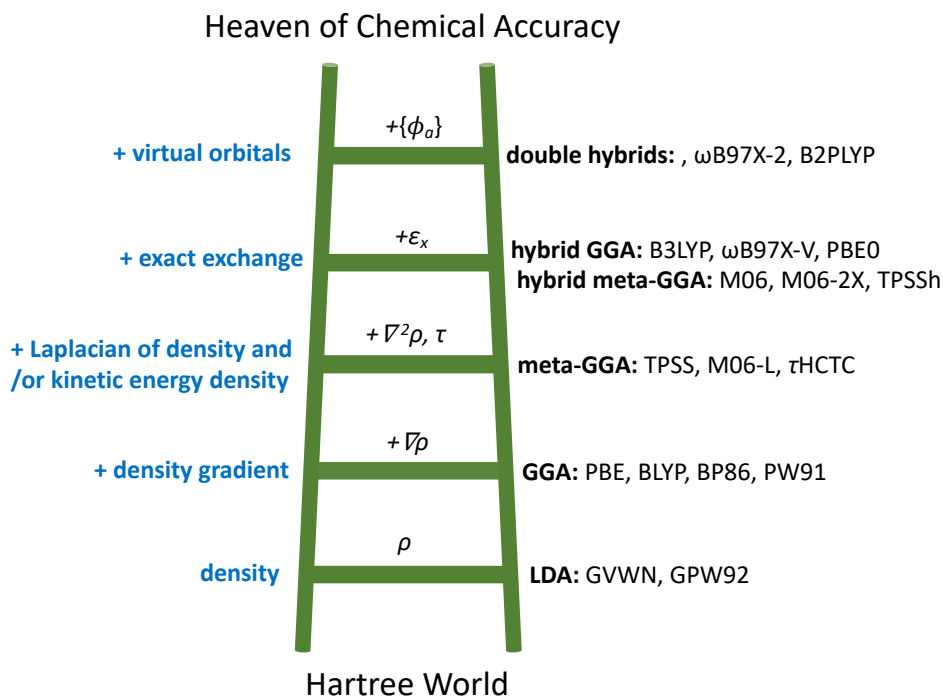
1.6.5 The exchange-correlation energy

The exchange-correlation energy is commonly separated into the exchange energy and the correlation energy. The exchange energy results from Pauli Exclusion principle and arises due to the antisymmetry requirement of the total electronic wavefunction of the system. It describes the non-classical effect (interactions not due to the electronic charges but electronic spins) that electrons of parallel spins avoid each other in space. This energy gives the lowering of total energy due to the presence of this “exchange hole”.

The correlation energy is what remains of the true total energy after taking away the kinetic and exchange energies. Unlike the exchange energy, correlation energy is more pronounced for electrons with anti-parallel spins, as these have higher likelihood of occupying the same region in space. This energy lowering can be understood as the effect arising from quantum fluctuations of electrons of anti-parallel spins as they coordinate their movements to minimise their Coulomb energy. The energy difference between the true kinetic energy and the non-interacting kinetic energy is also a major contribution to the exchange energy in KS-DFT.

1.6.6 Density functional approximations

The exchange-correlation functional can be approximated to varying degrees of accuracy, generally at increasing computational cost. These density functional approximations (DFAs) can be described as rungs of the Jacob's ladder (Scheme 1.1).



Scheme 1.1. Jacob's ladder of Density Functional Approximations (DFAs).

The crudest form of approximations is the local density approximation (**LDA**) which assumes that the electron density is the same at every position in space (the uniform electron gas (UEG)). The exchange energy (of the UEG) can be obtained exactly and is given by

$$E_x^{\text{LDA}}[\rho] = C \int \rho^{4/3}(\mathbf{r}) d\mathbf{r} \quad (1.73)$$

The correlation energy from the LDA is generally obtained by fitting to the results of accurate numerical quantum Monte Carlo simulations of the UEG (e.g. the correlation

functional $E_c^{\text{VWN}}[\rho]$ due to Vosko, Wilk and Nusair⁴⁰). LDA functionals are widely used in the study of solid-state systems but are considered inadequate for the study of molecular systems.

To account for the rapidly varying electron densities in molecules, generalised gradient approximation (**GGA**) functionals are developed. These functionals take into account the gradients of the density (thus “semi-local”) and have the general form of

$$E_{xc}^{\text{GGA}}[\rho] = \int \rho(\mathbf{r}) \varepsilon_{xc}(\rho(\mathbf{r}), |\nabla \rho(\mathbf{r})|) d\mathbf{r} \quad (1.74)$$

Most GGA functionals are constructed as correction terms that are added to the LDA functionals. These GGA functionals reproduce the LDA functionals in the limit of zero density gradient. GGAs can give better results than LDAs in predicting geometries and ground state energies of molecules and solids and in the description of covalent bonds and systems with weak bonding. However, they are not necessarily accurate due to, for example in B88 exchange functional, incorrect asymptotic behaviour.

In **meta-GGA** functionals, the Laplacian/second derivative of the density $\nabla^2 \rho(\mathbf{r})$ is included to improve accuracy. Additionally, the kinetic energy density τ is also included as it is numerically more stable and helps to reduce self-interaction error (SIE; *vide infra*) present in DFAs. Examples of meta-GGAs include TPSS⁴¹ functional. These functionals have been shown in various cases to perform better than LDAs and GGAs in the study of molecular properties,^{42–45} although hybrid GGAs (*vide infra*) can perform better than pure meta-GGAs for many applications.

Since LDA and GGA functionals overbind, whereas HF underbinds, another strategy is to mix in a portion of exact HF exchange to form the so-called **hybrid GGA** functionals.

When the same amount of HF is added for all molecular ranges, these are called *global* hybrid functionals. The most popular one is B3LYP.^{40,46-48} This functional has 3 parameters (fitted to empirical data) that control the amount of HF exchange added. The exchange-correlation has the general form

$$E_{xc} = E_{xc}^{LDA} + a_1 (E_x^{HF} - E_x^{LDA}) + a_2 \Delta E_x^{GGA} + a_3 \Delta E_c^{GGA}. \quad (1.75)$$

These hybrid functionals have been shown to be further improvements for molecular and solid-state properties over LDAs and GGAs.^{44,45,49-51}

Range-separated functionals are a subclass of hybrid functionals. In these functionals, the inter-electron interaction is divided into a short-range (SR) and a long-range (LR) part:

$$\frac{1}{r_{12}} = \frac{1 - [\alpha + \beta (1 - \omega_{RSF}(\gamma, r_{12}))]}{r_{12}} + \frac{\alpha + \beta (1 - \omega_{RSF}(\gamma, r_{12}))}{r_{12}} \quad (1.76)$$

where the first term is the SR part described by exchange from (semi-)local functionals such as PBE and the second term is the LR part described by exchange from HF; α and β are the mixing parameters and ω is the range parameter that depend on the functional.

The general form of the exchange-correlation is given by

$$E_{XC} = aE_X^{SR-DFT} + bE_X^{LR-HF} + c\Delta E_C^{DFT} \quad (1.77)$$

Range-separated functionals include CAM-B3LYP and ω B97X-D and are popular for the study of excited states and other time-dependent phenomena.

In the next rung of the Jacob’s ladder is the **double hybrid GGAs** which include the exchange energy from MP2 to improve the dispersion and exact exchange. Virtual orbitals are used. The exchange-correlation has the form

$$E_{XC} = aE_X^{DFT} + (1 - a)E_X^{HF} + c\Delta E_C^{DFT} + (1 - c)\Delta E_C^{PT}. \quad (1.78)$$

This class of functionals include B2PLYP and ω B97X-2. These functionals have much higher formal computational scaling than HF.

1.6.7 Dispersion

The failure to capture London dispersion interaction is a major inadequacy in accurately accounting for thermochemistry, kinetics and non-covalent interactions.^{52–54} Most DFT functionals cannot reproduce the long-range London dispersion of the form $-C_6/R^6$, but instead fall off exponentially. Empirical dispersion correction of the form

$$E_{\text{disp}} = - \sum_{j>i} f_{\text{damp}}(R_{ij}) \frac{C_{6ij}}{R_{ij}^6} \quad (1.79)$$

which is in fact Grimme’s D2 dispersion correction⁵⁵ used in functionals such as ω B97X-D⁵⁶, has been widely added to DFT functionals to improve calculations, especially in the study of systems with weak bonding. The interatomic coefficients C_{6ij} are obtained by fitting to accurate data and the damping function f_{damp} is required to ensure R^{-6} convergence at small internuclear separation. More recent developments in the dispersion correction include the so-called Grimme’s D3 dispersion correction,⁵⁷ where in addition to the (unscaled) C_6 terms, additional C_8 terms are included.

1.6.8 Self-interaction error

The self-interaction is a spurious interaction arising from the approximate nature of DFAs.⁵⁸ In HF theory, the exchange energy is computed exactly, the correlation energy is absent and the self-interaction is exactly cancelled out. The Coulomb interaction results from the interaction of two different electrons and this is accurately captured by wavefunction theory. In KS-DFT, the energy is a functional of single-particle electron density; the two-electron Coulomb interaction cannot be distinguished from the self-interaction. The Coulomb energy in DFT results from the interactions of each electron with the entire electron density, including its own density, thus giving rise to SIEs. SIEs have been shown to cause inaccuracy in the study of numerous phenomena including orbital localisation,^{58–61} ionisation,^{62–65} charge transfer^{66–68} and photoemission^{36,69–71} processes. In DFT development, one generally includes the self-interaction and then tries to remove it from the Coulomb energy in the exchange-correlation functional.⁵⁸

1.6.9 Density functionals used in this thesis

M06-2X.⁷² M06-2X is a global hybrid meta-GGA exchange-correlation functional. It is a functional parametrised for non-metals only and has twice the amount of nonlocal exchange (2X) as compared to similar functional M06 (*vide infra*) which is parametrised for transition metal and non-metals. The parametrisation of M06-2X uses 314 data points, out of a total of 496 data points from bond lengths, vibrational frequencies, vibrational zero-point energies (ZPEs) and so on. This functional is recommended for applications involving main-group thermochemistry, kinetics and non-covalent interactions (NCIs).

This is the DFT functional we used for the study of radical cationic system in Chapter 2 of this thesis. M06-2X includes 54% of exact Hartree-Fock exchange (HFX), which was shown to be in the optimal range of 50%-60% HFX in successful spin density localisation

of a single hole in a cluster of 64 water molecules.⁷³ It has been shown to perform very well for describing neutral and anionic model system having dispersion and hydrogen-bonding interactions^{74,75} and for ionisation energies and aqueous redox potentials of organic molecules.⁷⁶ (see subsection 2.3.1 for a detailed discussion on the choice of DFT functional).

ω B97X-D.⁵⁶ ω B97X-D is a range-separated hybrid functional where the inter-electronic interactions are separated to short-range and long-range interactions controlled by a separation parameter ω . This functional, with the inclusion of Grimme's D2 dispersion correction, captures weak NCIs, such as the attractive London dispersion component of van der Waals interactions, which can influence the structures and energetics.⁵⁴ We applied this functional to study the phosphorus-containing system in Chapter 3, as this functional has been successfully employed in the study of similar phosphorus-containing catalytic reaction mechanisms.⁷⁷

MN15.⁷⁸ MN15 is a recently developed global hybrid meta-NGA (non-separable gradient approximation; so called since the approximations to the exchange and the correlation of the energy functional are not separated) functional from Truhlar and co-workers. According to the developers of this functional, it has greater accuracy than any previously available ones for a broad range of applications. This functional uses a wide range of physical and chemical properties, including energies, thermochemistry, reaction barrier heights, NCIs, excited state energies, and molecular structures, for parametrisation. It has overall the best performance for both single-reference and multi-reference chemical systems amongst 83 functionals tested. This is the functional we used for the study of TM catalysis in this thesis. MN15 was used as it performs better than many others in predicting TM dimer bond lengths and bond energies (TMBE33 dataset⁷⁹⁻⁸³) and barrier

heights (TMBH21 dataset⁸⁴⁻⁸⁶) for reactions involving TMs.^{78,87,88} Its accuracy for barrier heights are comparable to the popular M06 functional⁷² employed for the study of TM catalysis.⁸⁹⁻⁹⁶ MN15 also performs the best for TM coordination database (WCCR10⁹⁷). In a recent study of tri-copper complex catalysed methane-to-methanol conversion,⁹⁸ MN15 came out the best amongst 31 functionals tested, including TPSS, M06, B2PLYP, ω B97X and ω B97X-D3. It has been employed in a number of theoretical study of TM catalysis⁹⁸⁻¹⁰³ and spectroscopy¹⁰⁴, giving good quantitative experimental agreements. The combination of MN15 with ECP basis sets has been shown to perform well for bond lengths and dissociation energies for bimetallic diatomic molecules.¹⁰⁵

1.7 Solvation Models

Two classes of solvation can be distinguished: the explicit solvation model includes the individual solvent molecules and considers their molecular detail together with the solute molecules; the implicit solvation model treats the solvent as a continuous medium within which the solute molecules are dissolved. Due to the large number of solvent molecules in a chemical reaction, in quantum chemical calculations, implicit solvation is almost always the choice of solvation model used.

In the implicit model, the free energy of solvation is given by

$$\Delta G_{\text{solv}} = \Delta G_{\text{cav}} + \Delta G_{\text{disp}} + \Delta G_{\text{elec}} (+\Delta G_{\text{hb}}) \quad (1.80)$$

where ΔG_{cav} is the free energy required to create the solute cavity; ΔG_{disp} is the van der Waals interaction between the solute and solvent; ΔG_{elec} is the electrostatic component due to the charge redistribution and reorientation induced by the polarisation between solute and solvent; ΔG_{hb} accounts for hydrogen bonding interactions. The

implicit solvation models can differ in the descriptions of the cavity and the dielectric media and the cavity calculation methods.

Two major classes of implicit models can be distinguished: the conductor-like screening models and the continuum models. In the conductor-like screening models, the solvent is treated as a conductor of infinite permittivity.¹⁰⁶ Examples of this class include COSMO¹⁰⁷ and COSMO-RS^{108,109}. In COSMO, the cavity is based on the solvent accessible surface and the electrostatic interactions are treated approximately. This model can be a good approximation for very polar solvents. In COSMO-RS, the “conductor-like screening model for real solvents”, the COSMO results are additionally augmented with statistical thermodynamic treatment of the screening charge density on the surface of the solute.

In the continuum models, a parametrised dielectric medium is used to surround the solute cavity and represent the solvent polarisation caused by the solute.¹⁰⁶ Due to the mutual polarisation between solute molecules and the solvent medium, the screening of the solute’s electrostatic field by the continuum is calculated iteratively. Examples of such models include polarizable continuum models (PCMs) such as IEF-PCM¹¹⁰⁻¹¹² and C-PCM^{107,113,114} and the SMx^{115,116} and SMD¹¹⁷ models. In PCMs, the cavity is formed from the overlapping van der Waals spheres and the electrostatic interactions between the solute and the polarisation of solvent is obtained by solving the Poisson equation.

1.7.1 Solvation model used in this thesis

For this thesis, we have generally used the SMD model, from Truhlar and co-workers, to account for implicit solvation effect of the reaction solvents. This model is parametrised using a training set of 2821 solvation data including 2346 solvation free energies for 318

neutral solutes in 91 solvents and 143 transfer free energies for 93 neutral solutes between water and 15 organic solvents. The elements present in the solutes are H, C, N, O, F, Si, P, S, Cl, and Br. The SMD model employs a single set of optimised parameters (intrinsic atomic Coulomb radii and atomic surface tension coefficients). This model was found to be the most accurate in computational redox potential studies¹¹⁸ and was thus used in Chapter 2. For other systems, this solvation model is favoured, especially when used in combination with DFT functionals from the Truhlar group (e.g., M06-2X and MN15), since the parametrisation of the SMD parameters are optimised using the functionals (M05-2X) from the same research group.¹¹⁷

1.8 Chemical Reactivity and Selectivity

1.8.1 Transition state theory

In chemical systems, the interesting transitions from the reactants to the products occur in a very small timescale. These transitions through the transition states (TSs), which are first-order saddle points on the PES, are rare events. We want to study the rates of reaction using results from, for example, conventional DFT calculations. Transition state theory (TST), also known as activated complex theory (ACT), is a method for calculating the thermal rates of change in such chemical reactions.^{119–121} This theory assumes that there is a quasi-equilibrium between the reactant molecule and the activated complex at the transition state in that the redistribution of internal vibrational energies of the reacting solute and solvent species is much faster than the timescale for bond breaking/formation. As a result, kinetic theory using Maxwell-Boltzmann statistics can be applied at the activated complex to study the rates of the conversion of the activated complex to the products, without re-crossing. TST further assumes that the PES is adiabatic, that is Born-Oppenheimer separation of the electronic and nuclear motions applies. Within this

framework, the macroscopic rate constant for the formation of the product is given by the Eyring equation:

$$k = \frac{k_{\text{B}}T}{h} e^{-\Delta G^{\ddagger}/RT} \quad (1.81)$$

where ΔG^{\ddagger} is the activation free energy for the formation of the activated complex.

It is helpful to mention **Hammond's postulate** which states that the TS of a reaction resembles either one of the reactants or the products that is closer to it in energy. Thus, in an exergonic reaction, the TS is closer to the reactants in energy and thus resembles the reactants in structure, as usually the case in early-TS formation. Conversely, in an endergonic reaction, the TS is closer to the products in energy, and resembles the products, as in late-TS formation.

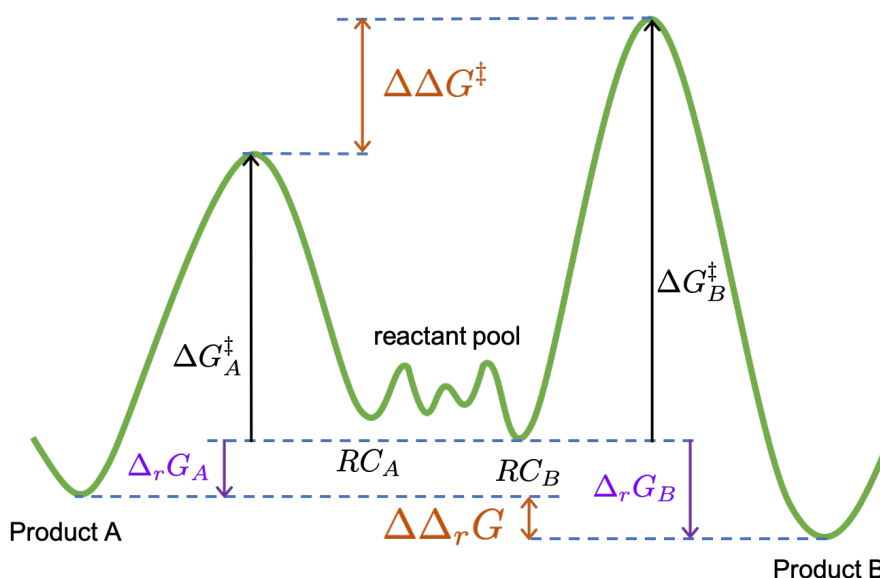
It is necessary to bear in mind that despite the successes of simple TST to account for the rates and selectivities of many thermal reactions, TST is only valid under the assumptions outlined before, and recently there have been studies showing examples where TST is insufficient to describe the chemical reactions due to the breakdown of the underlying assumptions.^{122,123}

1.8.2 Kinetic vs thermodynamic control of reactions

In a chemical reaction where two products are possible from the same reactants, different sets of products can be formed under different reaction conditions, as first observed in the formation of both *endo*- and *exo*-diastereoisomers in the Diels-Alder reaction between 6,6-pentamethylenefulvene and maleic anhydride, first described by Woodward and Baer in 1944.¹²⁴ The exact outcomes for such reactions are determined by a balance between kinetic and thermodynamic influences.

A possible simplified PES for such a reaction is shown in Scheme 1.2. Under kinetic control, typically at low temperature, the reaction proceeds irreversibly such that the ratio between the two products, A and B, is solely determined by the difference in the activation barriers, $\Delta\Delta G^\ddagger$, for the rate-determining steps and is quantitatively given, using simple TST, as the ratio of the relative rates of formation, viz.,

$$\frac{[A]}{[B]} = \frac{k_1}{k_2} = \frac{(k_B T/h)e^{-\Delta G_A^\ddagger/RT}}{(k_B T/h)e^{-\Delta G_B^\ddagger/RT}} = e^{-(\Delta G_A^\ddagger - \Delta G_B^\ddagger)/RT} = e^{-\Delta\Delta G^\ddagger/RT} \quad (1.82)$$



Scheme 1.2. Schematic potential free energy surface.

We here assume that the **Curtin-Hammett principle** applies: the reaction complexes in the reactant pool equilibrate amongst themselves very rapidly, at rates that are much faster than product formation, such that the lowest energy reaction complex (RC) is taken as the reference energy zero. In this framework, the activation barrier for the formation of product A is given by ΔG_A^\ddagger , taken from the lowest energy RC (RC_B here) to the activated complex, in accordance with the energetic span model.¹²⁵

Under thermodynamic control, typically at high reaction temperature and prolonged reaction time, the reaction becomes reversible and is under thermodynamic control. That is, both activation barriers for the product formations become thermally accessible, so that the product ratio is dictated by the difference in their thermodynamic stabilities, measured by their difference in the Gibbs energies of reaction, $\Delta\Delta_rG$, and is given quantitatively by

$$\frac{[A]}{[B]} = K_{\text{eq}} = \frac{e^{-\Delta_rG_A/RT}}{e^{-\Delta_rG_B/RT}} = e^{-(\Delta G_A - \Delta G_B)/RT} = e^{-\Delta\Delta_rG/RT} \quad (1.83)$$

1.8.3 Conformational sampling and Boltzmann weighting

In many cases, different conformations of the TSs exist that lead to the same product at the given reaction temperature. In those cases, the ratio of product selectivity is dictated by all the thermally accessible TSs for the competing product formations. All the rate-limiting TS conformers are then used for Boltzmann weighting to give the selectivity ratio. Standard procedures for Boltzmann weighting can be found in, for example, Equation (2) of reference¹²⁶ and the SI of reference¹²⁷. Specifically, the selectivity between two products A and B is calculated via

$$\frac{[A]}{[B]} = \frac{\sum_{i \in \text{all confs}, A}^{N_A} e^{-\Delta\Delta G_{0i,A}^\ddagger/RT}}{\sum_{j \in \text{all confs}, B}^{N_B} e^{-\Delta\Delta G_{0j,B}^\ddagger/RT}} \quad (1.84)$$

where $\Delta\Delta G_{0i,X}^\ddagger = \Delta G_{i,X}^\ddagger - \Delta G_0^\ddagger$ is the energy difference between the i^{th} conformer of product X ($X = A, B$) and the lowest energy conformer of all products, state 0, having the lowest activation barrier of ΔG_0^\ddagger .

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