Getting the electrons right for O2-on-metal systems

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2 Theory

In the previous chapter the theoretical framework for molecular modelling in surface science was briefly discussed and somewhat brushed over in light of summarising the scope and main results of this thesis. However, the complete framework of theory required to accurately model chemical reactions, even for "simple" diatomic molecules, is far from trivial and comes with a large set of interwoven complexities. This chapter will discuss the needed theoretical framework more comprehensively such that the methods and new results of Chapters 3-5 may be understood more clearly. Constructing this framework is done in three major sections. Section 2.1 will discuss the starting point for any and all *a priori* chemical models and will discuss the first major approximation needed to reduce complexity and facilitate the splitting of the framework into the next two sections. The first of these two sections (Section 2.2) will discuss the theory needed for describing the electrons in the chemical reaction, and the second (Section 2.3) will consider the procedures for modelling the atoms (nuclei) and how to setup the initial conditions for the motion of diatomic molecules.

2.1 First steps and the Born-Oppenheimer approximation

Let us begin by taking a major step back: we know that chemically relevant matter in the universe will consist of three major building blocks: electrons, protons, and neutrons. Therefore, put simply, chemical interactions, i.e., chemistry, will be due to interactions of these three building blocks. Luckily, for most chemical cases the neutrons and protons are clustered together into the atomic nucleus and we can simplify this to the interactions of the negatively charged electrons with the positively charged atomic nuclei. Nevertheless, this still results in major hurdles we need to overcome. The first problem is that particles with masses as small as electrons, and sometimes light atomic nuclei as well, cannot be described as just point charges or particles, but require a wavefunction description to describe their behaviour accurately. Put differently, we need quantum mechanics to describe them[10]. The wave-like nature of these particles brings with it uncertainties about the locations and states of the

particles[10,64]. Furthermore, any system that contains three or more interacting particles will become very difficult or even impossible to solve exactly because the state of one particle will often depend on the states of all other particles but the states of all the others are dependent on the state of this same one particle, also referred to as the many-body problem[10,112,164].

In this thesis, we will not dwell further on the "why" of quantum mechanics, which, although very interesting, goes far beyond the scope of this thesis. Nevertheless, the rest of this chapter, and arguably this whole thesis, is concerned more with the "how" of quantum mechanics for our specific problems.

To start, the quantum mechanical counter-part to the classical second Newtonian law of motion, i.e., the change of a system with time, for a system of *N* non-relativistic particles with zero spin (more about that in Section 2.2.2) is defined by the time-dependent Schrödinger equation[165]:

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\Psi(\vec{r},\mathrm{t}) = \hat{H}\Psi(\vec{r},\mathrm{t}) \tag{2.1}$$

Here $\hat{H}$ is the (Hermitian) Hamiltonian operator, $\hbar = h/2\pi$, h is Planck's constant, t is time, $\vec{r}$ is the complete spatial (coordinate) vector of all *N* particles, and Ψ is the function describing the complete system in a waveform, hereafter referred to as the wavefunction. The Hamiltonian ($\hat{H}$) operator describes the energy of the system and will take a different form depending on the particles in the system[10,112,118,164,165]. Different observables, like position or momentum, are described by different operators. Furthermore, the wavefunction (Ψ) needs to adhere to a few requirements. First, it needs to be single-valued. Second, it needs to be square-integrable. Third, it and its derivative function need to be continuous everywhere. Furthermore, probabilities of finding the particles in particular regions at a certain time *t* are given by the integral[166]:

$$\int |\Psi(\vec{r},\mathrm{t})|^2 d\vec{r} \tag{2.2}$$

If the region comprises the entire space this integral is equal to 1. Lastly, note that $|\Psi(\vec{r},\mathrm{t})|^2$ in Equation 2.2 describes the probability density of the system.

In chemistry, we are mostly interested in the energy of the system. The *N* particle Hamiltonian operator for energy can be split into two major components, the kinetic energy operator ($\hat{T}$) and the potential energy operator ($\hat{V}$), such that:

$$\hat{\mathrm{H}} = \hat{T} + \hat{V} \tag{2.3}$$

If there is no external force or torque on the system, e.g., no electric or magnetic field is applied, then the potential energy can be described by the Coulomb interaction between all the particles in the system. Then, the Hamiltonian for the energy of a chemical system with *N* particles is described by

$$\hat{\mathrm{H}} = \underbrace{-\sum_{i=1}^{N} \frac{\hbar^2}{2m_i} \nabla_i^2}_{\hat{T}} + \underbrace{\frac{1}{2} \sum_{i=1}^{N} \sum_{i \neq j}^{N} \frac{1}{4\pi\varepsilon_0} \frac{q_i q_j}{|\vec{r}_i - \vec{r}_j|}}_{\hat{V}} \tag{2.4}$$

Here m_i is the mass of particular particle *i*, ∇_i^2 is the Laplacian operator for particle *i* (when using Cartesian spatial coordinates: the sum of the three unmixed second-order partial derivatives to the Cartesian coordinates), ε_0 is the electric constant or vacuum permittivity, q_i the charge of particle *i*, and $\vec{r}_i$ is the three-dimensional Cartesian position vector of particle *i*.

It follows from Equation 2.4 that the Hamiltonian in the Schrödinger equation is not explicitly dependent on time (t), and thus, if the wavefunction $\Psi(\vec{r}, \mathrm{t})$ is a non-degenerate eigenfunction of this Hamiltonian (Eq. 2.4) we can make the "product ansatz", i.e., the wavefunction can be taken as a product of two independent parts:

$$\Psi(\vec{r}, \mathrm{t}) = \Psi(t)\Psi(\vec{r}) \tag{2.5}$$

The time dependency of Equation 2.5 can then be described by

$$\Psi(t) = Ce^{\pm iEt} \tag{2.6}$$

Equation 2.6 shows us that the time dependence of the energy of a system is given by a phase-factor in the complex plane This phase-factor can be divided out to arrive at the time-independent Schrödinger equation, or commonly just referred to as the Schrödinger equation:

$$\hat{H}\Psi(\vec{r}) = E\Psi(\vec{r}) \tag{2.7}$$

More generally, the expectation value for the total energy ($\langle E \rangle$) of a system that is described by the wavefunction $\Psi(\vec{r})$ is described analogous to Eq. 2.2 by

$$\langle E \rangle = \int \Psi^*(\vec{r}) \hat{H} \Psi(\vec{r}) d\vec{r} \tag{2.8}$$

Furthermore, Equation 2.8 is often written as

$$\langle E \rangle = \langle \Psi | \hat{H} | \Psi \rangle \tag{2.9}$$

using the Bra-Ket or Dirac notation, which is a shorter method of writing the integral[167], and will henceforth also be used.

We can break down the Hamiltonian even further. That is, we know that the only relevant interactions in chemical systems are those of the *N* number of electrons and *M* number of atomic nuclei, thus, we can split the Hamiltonian into the relevant parts such that:

$$\begin{aligned} \hat{\mathrm{H}} = &-\sum_{i=1}^{N} \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_{I=1}^{M} \frac{\hbar^2}{2M_I} \nabla_I^2 \\ &- \sum_{i=1}^{N} \sum_{I=1}^{M} \frac{Z_I q_e^2}{4\pi\varepsilon_0 |\vec{r}_i - \vec{R}_I|} + \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{q_e^2}{4\pi\varepsilon_0 |\vec{r}_i - \vec{r}_j|} \\ &+ \sum_{I=1}^{M} \sum_{J>I}^{M} \frac{Z_I Z_J q_e^2}{4\pi\varepsilon_0 |\vec{R}_I - \vec{R}_J|} \end{aligned} \tag{2.10}$$

Although it may look like we only made Equation 2.4 longer, Equation 2.10 has a few benefits. First, the mass (m_e) and charge (q_e) of electrons are well-defined constants, such that we only need the mass (M_I) and the number of protons (Z_I) of the nuclei in the system to proceed. Moreover, note that we limit the number of calculations by avoiding double-counting the pair interactions (in Equation 2.4 this is compensated by the 1/2). Lastly, the operator is now clearly split into five different "types" of energy. Namely, the kinetic energies of the electrons and the nuclei, the attractive force between the negatively charged electrons and positively charged nuclei, the repulsion between the nuclei, and the repulsion between electrons. The use of atomic units will make it possible to simplify Equation 2.10 further. In this unit system, all the natural constants in the Hamiltonian are taken equal to 1, reducing the writing of constants that would otherwise be required[168].

Equations 2.7 and 2.10 show us "what" we have to solve to fully describe the energy of a chemical system but it does not show us "how". For instance, in the Hamiltonian, the Coulomb potential operator is a function of all the distances between the particles and in quantum mechanics (when solving for the energy of the system) the particle locations cannot be exactly defined because of their

delocalised wave-like nature[10,112,118,164]. Additionally, finding a suitable (eigen-) wavefunction to properly describe a chemical system is not trivial. Lastly, there is also still the many-body problem that will need to be addressed as well. However, setting up Equation 2.10 like this will allow us to make the first important fundamental approximation to start working on the "how" of quantum mechanics in chemical systems. This is the Born-Oppenheimer approximation (BOA)[117].

The BOA means that we decouple the motion of the electrons from the motion of the nuclei, which is often allowed because the nuclei have a mass of at least three orders of magnitude higher than the electrons. The handwaving argument is that the electrons can "instantly" move and adjust to any motion of the nuclei. For a complete and detailed derivation of the BOA, the reader is referred to Refs. [117,119]. However, for this thesis, it is convenient to note that the BOA results in splitting the quantum mechanical problem into two, such that we have to first solve the electronic problem:

$$\hat{H}_{Elec}\Psi\left(\vec{r}_{Elec};\ \vec{R}_{nuc}\right) = E_{Elec}\left(\vec{R}_{nuc}\right)\Psi\left(\vec{r}_{Elec};\ \vec{R}_{nuc}\right) \quad (2.11),$$

where the electronic energy (E_{Elec}) is still dependent on the parametric position of the nuclei ($\vec{R}_{nuc}$) as the electronic Hamiltonian is now (using atomic units)

$$\hat{H}_{Elec} = -\sum_{i=1}^{N}\frac{1}{2}\nabla_i^2 - \sum_{i=1}^{N}\sum_{I=1}^{M}\frac{Z_I}{\left|\vec{r}_i - \vec{R}_I\right|} + \sum_{i=1}^{N}\sum_{j>i}^{N}\frac{1}{\left|\vec{r}_i - \vec{r}_j\right|} \quad (2.12).$$

$E_{Elec}\left(\vec{R}_{nuc}\right)$ has a set of solutions which represent the different electronic states. Often, and especially in this thesis, we are only interested in the ground-state solution, i.e., the lowest energy solution. Then, by applying the BOA and thus completely neglecting the, often small, coupling between the motion of electrons and nuclei[112] we can, for every value of $\vec{R}_{nuc}$, i.e., for every possible geometry of the nuclei, compute the potential energy for the nuclei with:

$$\begin{aligned}\hat{V}_{Pot}\left(\vec{R}_{nuc}\right) &= E_{Elec}\left(\vec{R}_{nuc}\right) + E_{repulsion}\left(\vec{R}_{nuc}\right) \\ &= E_{Elec}\left(\vec{R}_{nuc}\right) + \sum_{I=1}^{M}\sum_{J>I}^{M}\frac{Z_I Z_J}{\left|\vec{R}_I - \vec{R}_J\right|}\end{aligned} \quad (2.13),$$

such that we can now solve the Schrödinger equation for the nuclei separately using our resulting potential energy surface (PES) for the movement of the nuclei such that:

$$\left[\hat{T}_{Nuc} + \hat{V}_{Pot}(\vec{R}_{nuc})\right] \Phi(\vec{R}_{nuc}) = E_{Total}\, \Phi(\vec{R}_{nuc}) \qquad (2.14).$$

Note, that the use of a PES is also possible without necessarily applying the BOA, however, in this work, the BOA is the foundation of all PESs used in Chapters 3,4 and 5.

In the end, the consequence of the BOA is that we are now able to separately solve two "easier" problems instead of one more complicated one. That is, for every "snapshot" of the positions of the nuclei we need to find the energy of the resulting electronic structure. The electronic structure energy gives us the potential energy of the nuclei such that we can calculate either the total energy of the chemical system or we can use the potential energy to calculate where and how the nuclei are going to move in time. Even more powerful is that, at least for this thesis, the atomic nuclei are all considered "heavy". Therefore, we even resort to treating the motion of the nuclei with classical mechanics[112] (see Section 2.3). Thus, we only need to proceed with using quantum mechanics to build the PES for the nuclei, i.e., for a good approximation of the systems described in this thesis quantum mechanics is only required to solve the electronic structure of the system. There are known scenarios where the BOA cannot be applied, i.e., where the coupling between the motion of nuclei and electrons cannot be neglected[59–61,169–171]. These scenarios will be discussed in later chapters when needed.

2.2 The electronic structure

The electronic state has been separated from the rest of the system, specifically the motion of the nuclei, by applying the BOA and this has simplified our problem to a certain degree. Yet, the major challenges of "how" still remain, however, for the this section these challenges are limited to those of the electrons in the system. This section will discuss the basics of how electronic structure calculations can be done. It will first show that there is a strategy we can employ to find the best possible approximation for the electronic wavefunction (Section 2.2.1). Then, we will briefly discuss the basics of Hartree-Fock wavefunction-based solutions to the electronic structure(2.2.2), and the method employed to solve the resulting eigenvalue equations to come to a converged electronic energy (2.2.3). After this, we will pivot to Density

Functional Theory (DFT) (2.2.4 and 2.2.5) as an alternative approach to solving the electronic Schrödinger equation. Thereafter, the discussion will move to the DFT implementation that is best for periodic systems (2.2.6).

2.2.1 The variational theorem

The exact wavefunctions for systems with at least two atoms and more than one electron, which interact, are not known, so the only path to solving the electronic structure problem is by trying a so-called "trial wavefunction", or $\widetilde{\Psi}(\vec{r})$. Fortunately, we can use the Hermitian nature of the Hamiltonian operator to come up with a strategy for finding the best possible trial wavefunction. By selecting a trial wavefunction that maintains the required boundary conditions of the system and adheres to the wavefunction demands of Section 2.1, we can prove that the expectation value of the energy for that trial wavefunction must always be larger than or equivalent to the true ground state energy of the system, i.e.,

$$\left\langle E(\widetilde{\Psi}(\vec{r}))\right\rangle \geq E_0(\Psi(\vec{r})) \qquad (2.15).$$

Equation 2.15 is easily proven by expressing the trial wavefunction as a linear combination, i.e., as a superposition, of all possible eigenfunctions of the electronic Hamiltonian and calculating the resulting expectation value using Equation 2.8.

In the end, the result of Equation 2.15 means that we can now formulate a strategy for optimising our wavefunctions. That is, the lower the expectation value of the energy of the system, the better the trial wavefunction is as an approximation of the true wavefunction of that system (as long as the boundary conditions remain satisfied). Thus, for any trial wavefunction that fulfils the normalisation constraint and that is dependent on a defined set of parameters we can optimise that trial wavefunction by minimising the expectation value of the energy as a function of those trial wavefunction parameters. This procedure is referred to as the variational method and Eq. 2.15 as the variational theorem[10,112,118,164].

2.2.2 Building a wavefunction

Randomly trying trial wavefunctions and minimising their energy expectation value may still not be an optimal approach to finding a good trial wavefunction. It may, however, be a good idea to use solutions for more easily solvable systems as a basis for our trial wavefunction. It so happens that the Hamiltonian is fully separatable and the Schrödinger equation is exactly solvable in the context of a one-electron system that also adheres to the BOA, like an H atom, He^+ ion, etc.[10]. The resulting one-electron wavefunctions, or orbitals, could then serve as a basis for the much harder multi-electron system. This means that for a system of *N* electrons and *M* nuclei, it may be possible to start constructing a trial wavefunction by starting with a system of *N* non-interacting electrons such that the electrons in the wavefunction can be separated by the product ansatz, similar to Equation 2.5, i.e., we would describe the wavefunction of the system with

$$\Psi_{HP}(\vec{r};\vec{R}) = \prod_{i=1}^{N} \psi_i(\vec{r}_i;\vec{R}) \tag{2.16}$$

Equation 2.16 is also referred to as the Hartree product (HP) wavefunction[10,112,118,164,168] . The benefit of the product ansatz of the HP is that we could then express the Hamiltonian as a sum of *N* one-electron Hamiltonians, i.e.,

$$\hat{H} = \sum_{i=1}^{N} \hat{h}_i \tag{2.17}$$

Here each one-electron Hamiltonian $\hat{h}_i$ would then satisfy the *N* one-electron Schrödinger equations

$$\hat{h}_i \psi_i(\vec{r}_i;\vec{R}) = \varepsilon_i \psi_i(\vec{r}_i;\vec{R}) \tag{2.18}$$

Then, using the HP for the wavefunction, it follows that the Schrödinger equation for the complete electronic system would be expressed as

$$\hat{H}\Psi_{HP}(\vec{r};\vec{R}) = \sum_{i=1}^{N} \varepsilon_i \, \Psi_{HP}(\vec{r};\vec{R}) \tag{2.19}$$

In a real system of *N* electrons there will be a repulsive force between all the electrons, i.e., the *N* number of electrons do interact with each other. However, to maintain the ease of solving *N* one-electron systems this repulsive force can be approximated as the electronic repulsion force on any one electron *i*, as a

mean field force created by all other *N-1* electrons. This mean-field approximation will then result in the following expression for the one-electron Hamiltonians:

$$\hat{h}_i = -\frac{1}{2}\nabla_i^2 - \sum_{I=1}^{M}\frac{Z_I}{\left|\vec{r}_i - \vec{R}_I\right|} + \sum_{j\neq i}^{N}\int \frac{\left|\psi_j(\vec{r}_j;\vec{R})\right|^2}{\left|\vec{r}_i - \vec{r}_j\right|} d\vec{r}_j \qquad (2.20).$$

It can be shown that the HP of Equation 2.16 will still be an eigenfunction of the one-electron Hamiltonian of Equation 2.20. Still, the mean-field force is dependent on the one-electron wavefunctions of all other electrons in the system but each of those one-electron wavefunctions will have to be optimised, using variational calculus, with their "own" one-electron Hamiltonian which will, in turn, be dependent on the wavefunctions of all other electrons. It is here that the infamous many-body problem clearly shows up. Luckily, Hartree[168] came up with an iterative solution strategy to this problem that we will discuss more in Section 2.2.3, making the mean-field approximation a useful approach to deal with and 'solve' electron interactions.

Note that in Equation 2.20 we need to loop over all other electrons to compute the mean-field repulsion force but this does mean we are systematically double counting our electron-electron interaction thus, to compute the total energy of a HP(-like) solution to a many-electron system we would need to apply a Coulombic interaction correction:

$$E^{HP} = \sum_{i=1}^{N}\varepsilon_i - \frac{1}{2}\sum_{i=1}^{N}\sum_{j\neq i}^{N}\int\int \frac{\left|\psi_i(\vec{r}_i;\vec{R})\right|^2\left|\psi_j(\vec{r}_j;\vec{R})\right|^2}{\left|\vec{r}_i - \vec{r}_j\right|} d\vec{r}_j\, d\vec{r}_j \qquad (2.21).$$

At this point, we need to address a larger elephant in the room. The Hartree product is still not a great approximation for electrons as it ignores a few key features of the electron[10]. The first key feature is the Pauli exclusion principle[172] which states that no two electrons can have the same set of quantum numbers. This feature can be addressed by adding the electronic spin-function into the wavefunction. Electron spin it not only added to address the Pauli exclusion principle and the spin of an electron is also observed, but for more details on the "what, why, and how" of electron spin the reader is referred to Refs. [10,112,164]. For this thesis, it is important to note that a spin coordinate S_i needs to be added to

the wavefunction such that an *N* electron (HP-like) wavefunction would take the form:

$$\Psi^{HP-like}(\vec{r}, \vec{S}; \vec{R}) = \prod_{i=1}^{N} \psi_i(\vec{r}_i; \vec{R})\sigma(S_i) \quad (2.22).$$

Here $\sigma(S_i)$ is an eigenfunction of the $\hat{S}_z$ spin operator with only two eigenvalues, i.e., *±ħ/2* (or *±1/2* in atomic units), and its two orthonormal eigenfunctions are often denoted as *α* and *β*.

However, Equation 2.22 is still not a good approximated wavefunction as we also need to account for two other important physical features of electrons. Namely, electrons are non-distinguishable, i.e., we cannot tell one apart from the other, and most importantly, we need to adhere to the fact that electrons are fermions. Crucially, this means that the total wavefunction needs to be anti-symmetric, i.e., if we were to exchange two electrons in our wavefunction then the wavefunction would need to change sign. These demands may seem a little arbitrary when we describe them here so briefly, and the "why" thereof is a very interesting piece of physics but entirely out of scope for this work, so here it is convenient to take these features as given assertions and proceed. For further clarification, the reader is encouraged to read to Refs. [10,173].

To satisfy all three assertions, discussed above, the *N*-electron wavefunction needs to take the form of a Slater determinant (SD)[118,174] instead of an HP wavefunction or the spin-modified HP wavefunction of Equation 2.22. An N-electron SD takes the following form:

$$\Psi_{SD}(\vec{r}, \vec{S}; \vec{R}) \quad (2.23),$$
$$= \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(\vec{r}_1, S_1; \vec{R}) & \chi_2(\vec{r}_1, S_1; \vec{R}) & \cdots & \chi_N(\vec{r}_1, S_1; \vec{R}) \\ \chi_1(\vec{r}_2, S_2; \vec{R}) & \chi_2(\vec{r}_2, S_2; \vec{R}) & \cdots & \chi_N(\vec{r}_2, S_2; \vec{R}) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(\vec{r}_N, S_N; \vec{R}) & \chi_2(\vec{r}_N, S_N; \vec{R}) & \dots & \chi_N(\vec{r}_N, S_N; \vec{R}) \end{vmatrix}$$

in which, analogously to Equation 2.22, each spin-orbital is defined by

$$\chi_i(\vec{r}_i, S_i; \vec{R}) = \varphi_i(\vec{r}_i; \vec{R})\sigma(S_i) \quad (2.24).$$

In the Slater determinant every electron *i* can be contained in each occupied spin-orbital (*χ*), as we cannot distinguish between electrons. Moreover, the SD

enforces that the exchange of two electrons (*i* and *j*) results in a sign change of the SD-wavefunction.

Fulfilling the three assertions means that the wavefunction has gotten more complicated and that the Coulombic electron interaction in the Hamiltonian requires a compensation component for the possible exchange of electrons, i.e., we need to subtract the exchange energy from the Coulomb potential in the Hamiltonian. The proof for this can be found in Refs. [112,118]. In the end, this means that the *N*-electron, *M*-nuclei (BOA, one-electron) Fock operator, as it is called, will (in atomic units) take a slightly different form to accommodate for this exchange compensation. This form is

$$\hat{f}_i^{HF} = -\frac{1}{2}\nabla_i^2 - \sum_I^M \frac{Z_I}{\left|\vec{r}_i - \vec{R}_I\right|} + \underbrace{\sum_{j\neq i}^{N} \int \frac{\left|\chi_j(\vec{r}_j, S_j; \vec{R})\right|^2}{\left|\vec{r}_i - \vec{r}_j\right|} d\vec{r}_j}_{\hat{J}(\vec{r}_i, S_i; \vec{R})} - \underbrace{\sum_{j\neq i}^{N} \chi_j(\vec{r}_i, S_i; \vec{R}) \int \frac{\chi_j(\vec{r}_j, S_j; \vec{R})\chi_i(\vec{r}_j, S_j; \vec{R})}{\left|\vec{r}_i - \vec{r}_j\right|} d\vec{r}_j}_{\hat{K}(\vec{r}_i, S_i; \vec{R})} \tag{2.25}$$

Here $\hat{J}(\vec{r}_i, S_i; \vec{R})$ is the Coulomb operator and $\hat{K}(\vec{r}_i, S_i; \vec{R})$ is the exchange operator. The Fock operator has the Slater determinant as eigenfunction and the resulting eigenvalues of this operator are the orbital energies of the system where the set of *N* eigenfunction problems that come from this are called the Hartree-Fock (HF) equations. Similar to the Hartree operator we employ a mean-field theory to describe the electronic interactions with each other. Lastly, the total energy of the chemical system is now given by

$$\begin{aligned} &\mathrm{E}_{pot}^{HF}(\vec{r}, \vec{S}; \vec{R}) \\ &= \sum_{i=1}^{N} \left\langle \chi_i(\vec{r}_i, S_i; \vec{R}) \middle| -\frac{1}{2}\nabla_i^2 - \textstyle\sum_I^M \frac{Z_I}{\left|\vec{r}_i - \vec{R}_I\right|} \middle| \chi_i(\vec{r}_i, S_i; \vec{R}) \right\rangle \\ &+ \sum_{i=1}^{N} \sum_{j=1}^{N/2} \left(2\langle \chi_i(\vec{r}_i, S_i; \vec{R}) | \hat{J}(\vec{r}_i, S_i; \vec{R}) | \chi_j(\vec{r}_j, S_j; \vec{R}) \rangle \right. \\ &\left. - \langle \chi_i(\vec{r}_i, S_i; \vec{R}) | \hat{K}(\vec{r}_i, S_i; \vec{R}) | \chi_j(\vec{r}_j, S_j; \vec{R}) \rangle \right) + E_{repulsion}(\vec{R}) \end{aligned} \tag{2.26}$$

We can parametrize the spin-orbitals in the SD-wavefunction (Equation 2.24) and then optimise them using the variational theorem (Section 2.2.1). The parametrisation can be done in many different ways but often the orbital wavefunctions in a molecular system are set up as a linear combination of all contributing atom-centred wavefunctions (or atomic orbitals (AO)).

$$\chi_i(\vec{r}_i, S_i; \vec{R}) = \sum_k^K c_{k,i}\phi_k(\vec{r}_i, S_i; \vec{R}) \quad (2.27).$$

The atom-centred wavefunctions (ϕ_k), are themselves normally constructed via another linear combination of basis functions that represent the shapes of the atom-centred wavefunctions (or AOs). These basis functions come in collections that are called basis sets, and these sets can be based on so-called Gaussian-type orbitals[112,175], Slater-type orbitals[112,176], Numerical orbitals[112,164,177], or in principle any other type that will fulfil the required constraints. The choice of basis set will influence the results of the electronic structure calculations, where the general trend is that a larger, more complex, and more complete basis set will improve the results, but increase the demands of the electronic structure calculation. In the following chapters, a very different type of basis sets are used. These types are constructed with an entirely different philosophy and method in mind and these will be discussed in more detail in Sections 2.2.4, 2.2.5, and 2.2.6.

2.2.3 Solving the electronic structure

At this point, we have a description of the multi-electron wavefunction and a strategy to optimise that wavefunction via the variational method. Still, we need to find a way to solve the “chicken-egg problem”, or many-body problem, that arose from applying the mean-field theory in the one-electron operator, the Fock operator, and the HF equations.

To start, an initial guess of the wavefunction can be made for any initial configuration or geometry of the system, i.e., nuclei positions. This guessed wavefunction is used to construct the mean-field theory (Hartree-Fock or any other) many-body operator. This initial operator, with the initial guess of the wavefunction, is used to optimise the wavefunction it works on, i.e., the wavefunction is minimised with respect to the total energy via the variational

theorem. Then, the optimised wavefunction of this new iteration is used to construct a new mean-field operator, which in turn is used to re-optimise the wavefunction for the next iteration. Then the resulting energy of the new wavefunction is tested against the energy of the previous iteration. If these energies are the same (within a certain threshold) then the calculation is considered converged and is stopped. Otherwise, the procedure is repeated, i.e. the new wavefunction will make a new operator, will make a new wavefunction, and is tested against the previous energy again. The process is continued until the energy is self-consistent, i.e., the value essentially does not change anymore between iterations. This is why this method is referred to as the self-consistent-field (SCF) method. A simplified flowchart of a SCF procedure is shown in **Figure 2.1**.

The procedure as described above, and shown in **Figure 2.1**, is in reality somewhat more complicated and especially optimising the parameters in the wavefunction is far from trivial. For a more complete understanding, the reader is encouraged to read Refs. [112,118]. However, for our purposes, we now have a complete picture of how to "solve" the electronic structure for multi-electron atoms and molecules. A good example of this method in practice for the "simple" H_2 molecule was published already in 1971 by Dewar *et al.* [120].

Lastly, we must note that the HF method does not yield the exact electronic energy of a molecular system. We have thus far neglected the tendency of electrons to correlate, that is, the movement of electrons is also influenced by the presence and movement of other electrons individually and not by their average overall momentum[112]. This, in turn, influences the total energy of the system. This is why correlation energy is usually defined as the residual energy difference between the converged Hartree-Fock energy and the exact energy of the system. The correlation energy can be included via methods like full configuration interaction[112,120], but these are computationally very demanding and out-of-scope for this work. Moreover, in Sections 2.2.4. and 2.2.5. a different method of including some correlation effects within a different electronic structure method is discussed.

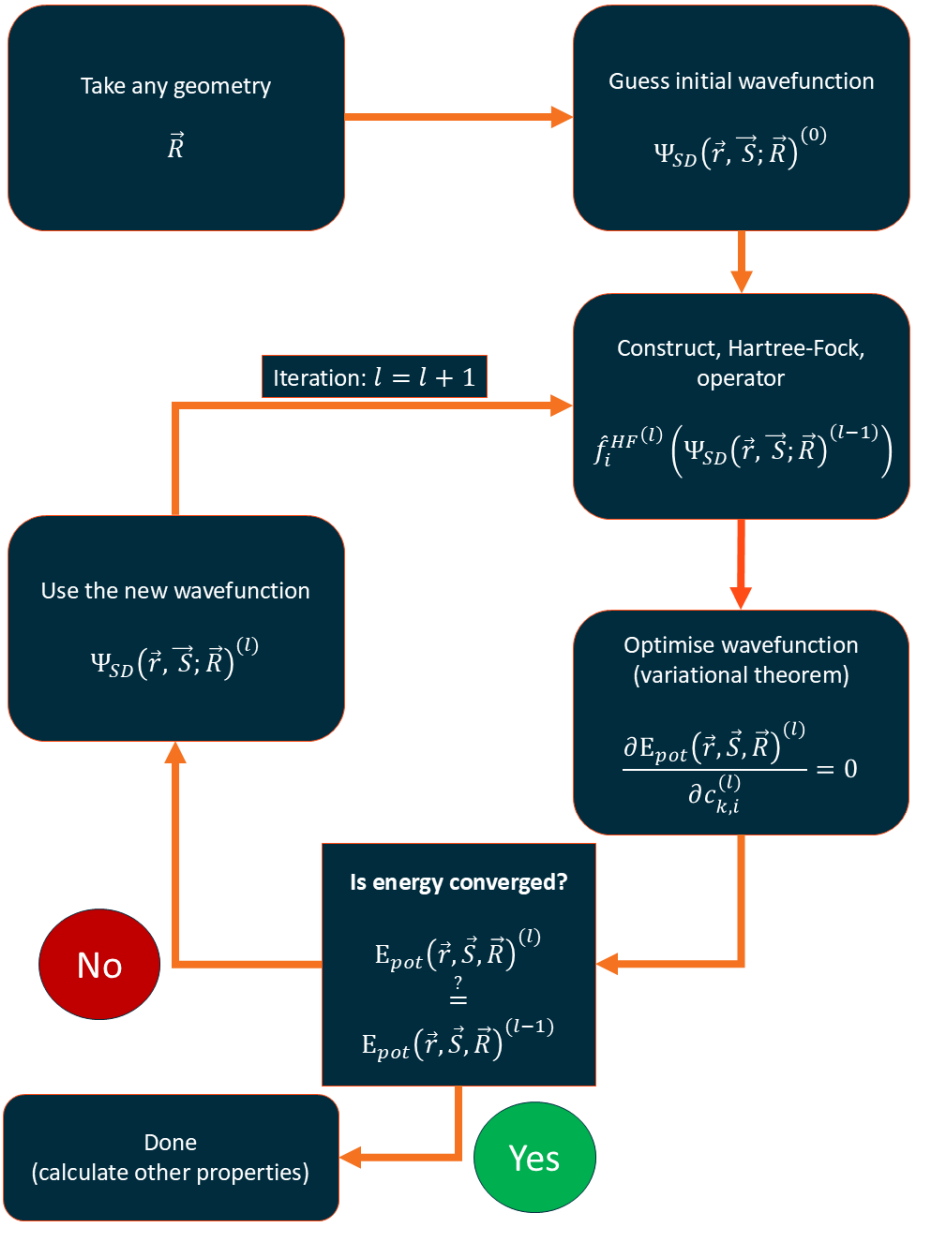

***Figure 2.1**: Simplified flow chart of the self-consistent-field method in optimising a wavefunction in the HF-theory (or other Wavefunction) method.*

2.2.4 Density functional theory, Hohenberg-Kohn and Kohn-Sham

An observant reader may have picked up on two crucial points in the previous section. First, the complexity of the wavefunction is, thus far, very dependent on the number of electrons, such that a larger chemical system with many electrons quickly becomes unmanageable. Second, the basis functions for the wavefunction are all atom-centred. This makes our solution inherently atomically localised. This is a logical approach for molecules because the electrons are only spread over certain orbitals, and even though overlapping orbitals can share electrons over many orbitals, the electron density tends to be high only in the vicinity of the atomic nuclei. However, as discussed in Chapter 1, there are two different phases to molecule-surface systems, the first is the molecule in the gas-phase and the second is the metal solid. The electronic structure of a metal is very delocalised, such that electrons are, in principle, spread over the entire metal, forming electronic bands of electrons rather than isolated electronic levels. It is not hard to imagine that using an atom-centred wavefunction method to describe such an electronic structure may not be ideal. Furthermore, the computational scaling in HF methods is not very favourable. Computational scaling is the change in the amount of time the calculation would take if the size of the chemical system is changed. In the case of "cheap" wavefunction methods like HF, the scaling nevertheless tends to be $O(N^4)$, meaning a system that has two times the number of electrons will need sixteen times more time to be solved. However, most wavefunction methods that go beyond HF, i.e., which try to improve the electronic correlation, tend to scale with $O(N^5)$ or even higher. Thus, a different approach may be needed.

It may, therefore, be fruitful to use an approach where we can describe the electronic energy with a concept that makes the calculations scale better and could possibly even amount to an observable. The concept that fits these criteria is the electronic density (see also Section 1.2.4). Such a different approach to calculating electronic structures comes in the form of density functional theory (DFT).

The density of the electrons of a system can be directly related to the total number of electrons in that system (*N*):

$$N = \int \rho(\boldsymbol{r}) d\boldsymbol{r} \tag{2.28},$$

where this integral goes over all space, and ρ is the electron density as a function of $\boldsymbol{r}$, which is a three-dimensional position vector, indicated with boldface to avoid confusion with $\vec{r}$ (which is the complete position vector of all electrons in the system). The use of electron density is intuitive, for instance, the maxima in density could indicate the likely locations of electrons. Another benefit would be that any solution would no longer be dependent on *4N* dimensions, that is the three spatial and spin dimensions, but instead, it would depend on just the three spatial coordinates of the electron density. This may, in turn, help to reduce both the complexity and the scaling of electronic structure methods.

These possibilities seem potentially useful though a mapping to an electron density would need to be proven to be possible. For that, we have to turn to the work of Hohenberg and Kohn[121]. They were able to prove that the electron ground state density must determine the so-called "external potential", thus determine the Hamiltonian and thus determine the energy of the system. Here the external potential is defined as:

$$v_{ext}(\boldsymbol{r}) = \sum_{I=1}^{M} \frac{Z_I}{\left|\boldsymbol{r} - \vec{R}_I\right|} \tag{2.29},$$

That is, the external potential is defined as the attractive Coulomb force that the nuclei apply to the electron (density). The rest of the Hamiltonian, as seen in Equation 2.12, is governed by the number of electrons in the system (where the electrons are undistinguishable), and this is already directly related to the density via Equation 2.28. Thus, it only needs to be proven that the external potential is directly determined by the electron density.

This proof is done via *reductio ad absurdum*, i.e., the contrary results in impossibilities, and the proof is rather straightforward. Conversely, two different external potentials $v_{ext}{}^a$ and $v_{ext}{}^b$, both describe the same (nondegenerate) ground state electron density ρ_0. With both external potentials, different Hamiltonians, $\hat{H}^a$ and $\hat{H}^b$, will be associated, which both would have their

associated eigenfunctions and eigenvalues $\Psi_0{}^a$, $\Psi_0{}^b$, $E_0{}^a$, and $E_0{}^b$. Then the variational theorem(2.2.1) would say that:

$$E_0^a < \langle \Psi_0^b | \hat{H}^a | \Psi_0^b \rangle \tag{2.30}$$

This can be rewritten to:

$$E_0^a < \langle \Psi_0^b | \hat{H}^a + \hat{H}^b - \hat{H}^b | \Psi_0^b \rangle \tag{2.31}$$

$$E_0^a < \langle \Psi_0^b | v_{ext}^a - v_{ext}^b | \Psi_0^b \rangle + E_0^b \tag{2.32}$$

The external potential operators are one-electron operators thus Eq. 2.32 can be expressed as a function of the ground state density ρ_0

$$E_0^a < \int [v_{ext}^a(\boldsymbol{r}) - v_{ext}^b(\boldsymbol{r})]\rho_0(\boldsymbol{r})d\boldsymbol{r} + E_0^b \tag{2.33}$$

Then, this same procedure can be done for the ground state energy of b such that:

$$E_0^b < \int [v_{ext}^b(\boldsymbol{r}) - v_{ext}^a(\boldsymbol{r})]\rho_0(\boldsymbol{r})d\boldsymbol{r} + E_0^a \tag{2.34}$$

Now adding the two inequalities of Eqs. 2.33 and 2.34 will result in:

$$E_0^a + E_0^b < \int [v_{ext}^a(\boldsymbol{r}) - v_{ext}^b(\boldsymbol{r})]\rho_0(\boldsymbol{r})d\boldsymbol{r} + E_0^b + \int [v_{ext}^b(\boldsymbol{r}) - v_{ext}^a(\boldsymbol{r})]\rho_0(\boldsymbol{r})d\boldsymbol{r} + E_0^a \tag{2.35}$$

$$E_0^a + E_0^b < \int \left[v_{ext}^a(\boldsymbol{r}) - v_{ext}^b(\boldsymbol{r}) + v_{ext}^b(\boldsymbol{r}) - v_{ext}^a(\boldsymbol{r})\right]\rho_0(\boldsymbol{r})d\boldsymbol{r} + E_0^b + E_0^a \tag{2.36}$$

Which will result in the following impossibility:

$$E_0^a + E_0^b < E_0^b + E_0^a \tag{2.37}$$

Thus, a non-degenerate ground state density must determine a uniquely associated external potential, Hamiltonian and energy(Hohenberg-Kohn I, HK I) [121]. Further work[112,118] has even shown HK I also holds for exited electron densities. Nevertheless, for this thesis, the ground state is already sufficient.

To effectively utilise HK I to describe electronic energies we need to prove that the variational theorem also holds for the use of an electron density, as we otherwise have no way of optimising the density function. Luckily Hohenberg and Kohn have produced a second theorem that proves just that, i.e., the electron density that minimises the total energy is the exact ground state density[121]. Proving this is rather trivial keeping in mind that any density of a non-degenerate ground state will correspond to a unique wavefunction and energy

(HK I) so that for a trial density ($\tilde{\rho}$) and corresponding trial wavefunction ($\tilde{\Psi}[\tilde{\rho}]$) we have:

$$E[\tilde{\rho}] = \langle \tilde{\Psi}[\tilde{\rho}] | \hat{H}_0[\tilde{\rho}] | \tilde{\Psi}[\tilde{\rho}] \rangle \geq \langle \Psi_0[\rho_0] | \hat{H}_0[\rho_0] | \Psi_0[\rho_0] \rangle = E_0[\rho_0] \quad (2.38)$$

$$E[\tilde{\rho}] \geq E_0[\rho_0] \quad (2.39)$$

As such we can optimise the density of our system by minimising the total energy of the system (Hohenberg-Kohn II, HK II). There is a small caveat that changing certain approximations in the Hamiltonian (see Section 2.2.5.) may break with the variational theorem, but that is due to the introduction approximations in the Hamiltonian, and not because the variational theorem does not hold[112].

A major difficulty remains though. Yes, a mapping from density to Hamiltonian to wavefunction and energy must exist (HK I), however, there is no basis for what such a mapping would be as the proof for the mapping is done via *reductio ad absurdum*. So even though it is possible to map the energy to the density, we are still not able to do so exactly. Nevertheless, there are clever tricks that can be used to achieve very good approximations with such mappings, and it was the trick of Kohn and Sham[122] that resulted in the most widely used variant of DFT.

Kohn-Sham (KS) DFT is constructed by initially taking a fictitious system of *N* non-interacting electrons that has the same ground-state electronic density as the real system, where the *N* electrons do interact. Kohn and Sham proposed that this is possible because electron density mapping is defined by the number of electrons and the external potential (HK I), which are taken the same for both systems. Here KS used that the exact eigenvalue problems for N non-interacting electrons can be computed exactly (see also 2.2.2). In reality, electrons do interact with each other but this can, in the Kohn-Sham framework, be corrected by adding a correction term to the total energy of the non-interacting electrons. As such, the total energy is no more than the sum of the energy of the non-interacting electrons and the addition of a correction such that the energy functional (i.e., a function that is a function of another function) will be described in full by[112,118,122]:

$$E[\rho(\boldsymbol{r})] = T_{non-i}[\rho(\boldsymbol{r})] + V_{nuc}[\rho(\boldsymbol{r})] + V_{Cee}[\rho(\boldsymbol{r})] + \underbrace{\Delta T_i[\rho(\boldsymbol{r})] + \Delta V_{Qee}[\rho(\boldsymbol{r})]}_{E_{xc}[\rho(\boldsymbol{r})]} \quad (2.40).$$

Here the terms are, in order of appearance: the non-interacting electronic kinetic energy, the nuclear-electron attractive Coulombic force, i.e., the external potential; the classical electron-electron Coulomb interaction; the correction on the kinetic energy term including electronic correlation; and the quantum correction to the electronic interaction including the electron exchange energy. The last two terms are generally combined into one collection of unknowns that is referred to as the exchange-correlation functional ($E_{xc}[\rho(\boldsymbol{r})]$)[122]. This term may also include other corrections to the non-interacting electron system, like a self-interaction correction[112].

For the non-interacting electrons, the exact eigenfunction is the Slater determinant (see Equation 2.23) but now built up using the one-electron KS orbitals. The corresponding electron density is

$$\rho(\boldsymbol{r}) = \sum_{i=1}^{N} \langle \chi_i | \chi_i \rangle \tag{2.41}$$

Here χ_i are the KS-orbitals, which are similar, but not equal, to the AOs used in Equation 2.23. We can now represent the energy functional in atomic units as[112]:

$$E[\rho(\boldsymbol{r})] = \sum_{i=1}^{N} \left(\left(\left\langle \chi_i \right| -\frac{1}{2}\nabla_i^2 \left| \chi_i \right\rangle \right) - \left\langle \chi_i \left| \sum_{I=1}^{M} \left(\frac{Z_I}{|\boldsymbol{r}_i - \vec{R}_I|} \right) \right| \chi_i \right\rangle \right) + \sum_{i=1}^{N} \left(\left\langle \chi_i \left| \frac{1}{2} \int \frac{\rho(\boldsymbol{r}')}{|\boldsymbol{r}_i - \boldsymbol{r}'|} d\boldsymbol{r}' \right| \chi_i \right\rangle \right) + E_{xc}[\rho(\boldsymbol{r})] \tag{2.42}$$

This will mean it is now possible to start solving, and also optimising, a set of N number of one-electron non-interacting eigenvalue equations of the form:

$$\hat{h}_i^{KS} \chi_i = \varepsilon_i \chi_i \tag{2.43}$$

where the one-electron Kohn Sham Hamiltonian is given by:

$$\hat{h}_i^{KS} = -\frac{1}{2}\nabla_i^2 - \sum_{I=1}^{M} \left(\frac{Z_I}{|\boldsymbol{r}_i - \vec{R}_I|} \right) + \int \frac{\rho(\boldsymbol{r}')}{|\boldsymbol{r}_i - \boldsymbol{r}'|} d\boldsymbol{r}' + V_{xc}[\rho(\boldsymbol{r})] \tag{2.44}$$

and in which

$$V_{xc}[\rho(\boldsymbol{r})] = \frac{\delta E_{xc}[\rho(\boldsymbol{r})]}{\delta \rho(\boldsymbol{r})} \tag{2.45}$$

is the functional derivative of the exchange-correlation energy as presented in 2.42[112].

From this point on, solving the known parts of the KS equations is very similar to the wavefunction approach as discussed in 2.2.2 and 2.2.3, and from Equation 2.42 it is obvious that yet another self-consistent field-based approach will be required. To reiterate, the Hamiltonian determines the density but requires a density to be determined first. Thus, one has to: guess, improve, and reuse the density until it no longer changes. Solving the unknown exchange-correlation part (V_{xc}) of the energy functional (hereafter referred to as density functional, or DF) is, however, still far from trivial. Luckily, in the KS approach, the unknowns are reduced to a smaller fraction of the total value and any error made there will influence the final result less than trying to come up with one whole new answer for a density energy mapping. The majority of research and studies done to improve the quality of DFT are all to try and find a better approximation to this V_{xc}. Some of the more common approaches will be discussed in the next section.

2.2.5 Exchange-correlation functional approximations

The exact form of the E_{xc} is not known, but it stands to reason that this term will, just like the one-electron potential, depend on the electron density. Thus, E_{xc} is often expressed as an integral over a product of the density and the so-called "energy-density" ε_{xc}(this is not required but is a common notational method)[112]. In this frame, E_{xc} is described by:

$$E_{xc}[\rho(\boldsymbol{r})] = \int \rho(\boldsymbol{r})\varepsilon_{xc}[\rho(\boldsymbol{r})]d\boldsymbol{r} \tag{2.46}$$

Here the energy density functional is often split up into contributions from exchange and correlation[112,118]:

$$\varepsilon_{xc}[\rho(\boldsymbol{r})] = \varepsilon_x[\rho(\boldsymbol{r})] + \varepsilon_c[\rho(\boldsymbol{r})] \tag{2.47}$$

However, again this is not always the case[112], and it should be reiterated that the E_{xc} DF is meant to compensate for more than just exchange and correlation energy, for instance for an error due to electrons interacting with themselves (which occurs in the construction of the density). Additionally, splitting up the exchange-correlation functional also does not mean that the actual contributions are necessarily properly split, as the exact form of the E_{xc} DF is not known[112,118,173].

Nevertheless, there now is a starting point for approximating the E_{xc} DF. The simplest and most logical starting point is to let the exchange-correlation be

dependent on a single value of the electron density at a given location, i.e., to let there be a *local* dependency on the density in Eqs. 2.46 and 2.47. This is referred to as the local density approximation (LDA). An example of local density exchange energy is the Slater exchange based on the uniform electron gas[112,178,179]:

$$\varepsilon_x[\rho(\boldsymbol{r})] = -\frac{9\alpha}{8}\left(\frac{3}{\pi}\right)^{\frac{1}{3}}\rho(\boldsymbol{r})^{\frac{1}{3}} \tag{2.48},$$

where α can take either the value 1 or 2/3[180,181], depending on the underlying derivation (see Ref. [112] for more information). Setting up the correlation contribution has generally always been a far more arduous task, and quickly goes beyond the scope of this work and the reader is referred to the works of [182–187] for detailed derivations on that end.

It is at this time a good moment to discuss that the LDA can also work for calculations where the electrons have to be spin polarised, i.e., when there are unpaired electrons in the mix. The electron spin density is simply given by the normalised spin polarization factor[112]:

$$\zeta(\boldsymbol{r}) = \frac{\rho^{\alpha}(\boldsymbol{r}) - \rho^{\beta}(\boldsymbol{r})}{\rho^{\alpha}(\boldsymbol{r}) + \rho^{\beta}(\boldsymbol{r})} = \frac{\rho^{\alpha}(\boldsymbol{r}) - \rho^{\beta}(\boldsymbol{r})}{\rho(\boldsymbol{r})} \tag{2.49},$$

where ρ^{α} is the α-spin density and ρ^{β} is the β-spin density. At this point, the exchange-correlation energy density can be expressed as a function of the total electron density and the spin polarisation such that[112]:

$$\begin{aligned}\varepsilon_{xc}[\rho(\boldsymbol{r}), \zeta(\boldsymbol{r})] \\ = \varepsilon_{xc}[\rho(\boldsymbol{r})] + \left(\varepsilon_{xc}^{Spin}[\rho(\boldsymbol{r})]\right. \\ \left. - \varepsilon_{xc}[\rho(\boldsymbol{r})]\right)\left(\frac{(1+\zeta(\boldsymbol{r}))^{\frac{4}{3}} + (1-\zeta(\boldsymbol{r}))^{\frac{4}{3}} - 2}{2(2^{\frac{1}{3}} - 1)}\right)\end{aligned} \tag{2.50},$$

where $\varepsilon_{xc}^{Spin}[\rho(\boldsymbol{r})]$ is the energy density functional based on the uniform electron gas of electrons with all uniform spin, and $\varepsilon_{xc}[\rho(\boldsymbol{r})]$ is the regular ground state energy density. Equations 2.49 and 2.50 show that the addition of spin into DFT will make the formulation more complicated. Because it requires the evaluation of the uniform spin exchange-correlation energy functional it also slightly increased computational demands, though not by much. For the sake of clarity in formulation, the spin density terms will from now on not be discussed

in detail, but it is good to have noted that using spin densities is possible and will be used in Chapters 3-5.

The LDA is a local approximation to E_{xc}. When locally approximating any function, a Taylor expansion may quickly come to mind. As such, a common next step in improving the exchange-correlation energy is to go beyond the dependence on the local value of the density and to also include a dependence on the local first-order derivative, i.e., gradient, of the density. This brings us to the generalised gradient approximation (GGA) to the exchange-correlation DF. E_{xc} can now be expressed as:

$$E_{xc}[\rho(\boldsymbol{r}), \nabla\rho(\boldsymbol{r})] = \int \rho(\boldsymbol{r}) f[\rho(\boldsymbol{r}), \nabla\rho(\boldsymbol{r})] d\boldsymbol{r} \quad (2.51),$$

where the function *f* can take some different forms but is often[112] set as:

$$f[\rho(\boldsymbol{r}), \nabla\rho(\boldsymbol{r})] = \varepsilon_{xc}^{LDA}[\rho(\boldsymbol{r})] + \Delta\varepsilon_{xc}\left[\frac{|\nabla\rho(\boldsymbol{r})|}{\rho(\boldsymbol{r})^{\frac{4}{3}}}\right] \quad (2.52).$$

However, it should be noted that the precise implementations of GGA DFs vary greatly. It is not uncommon for semi-empirical parameters to be introduced into the exchange-correlation DF to improve the description for certain systems. For an example of a GGA DF without the use of such parameters, the reader is strongly encouraged to read the work behind the PW91[188] and/or PBE[154] DF, which are some of the most commonly applied DFs, and the PBE DF is also used further in Chapters 3-5. Going even beyond the GGA, it is possible to take the Taylor expansion further, with limited returns, to start using the second-order derivative of the density as well. These types of DFs are then referred to as meta-GGA (mGGA) DFs[112]. These types of DFs are moving beyond the scope of this thesis.

A quite different approach to improving the exchange-correlation description is to use the fact that we have a potentially more precise description for the exchange energy based on the HF wavefunction method (Equation 2.25, Section 2.2.2). Since the density in KS-DFT is often based on Slater-like eigenfunctions, computing the exact exchange using the $\hat{K}(\vec{r}_i, S_i; \vec{R})$ operator (see Eq. 2.25 and 2.26) is possible. Mixing this associated exact exchange with the semi-local exchange-correlation energy amounts to the use of a so-called hybrid functional. Note that this will increase computational demands moving from the worst-case

DFT scenario of $O(N^3)$[112,118] to a worst-case of $O(N^4)$ scaling[112,118]. Additionally, the exchange-correlation energy is not just a correction for the exchange energy and cannot be cleanly split into two separate contributions[112]. Thus, replacing the entire semi-local exchange contribution with exact exchange does not necessarily yield any improvement over GGA DFs. As such, the exact exchange is mixed into the (usually GGA) DFT exchange with a certain fraction(α)[112]:

$$E_{xc}^{Hybrid} = \alpha E_x^{HF} + (1-\alpha)E_x^{DFT} + E_c^{DFT} \quad (2.53).$$

One of the most straightforward global hybrid DFs, which uses PBE as the GGA backbone, is the PBE0 DF where α is set to a value of $1/4$[152,153]. Finally, it should be noted that the global description of exact exchange is not accurate for larger-range Coulombic systems like metals where the interaction between electrons needs to be screened at long range[156,189–194]. To accommodate this range-separated, or screened exchange, hybrids have been developed where the exact exchange energy is only active at short range and is fully replaced with semi-local exchange at long range, see also Chapters 3, 4 and 5.

Analogously to hybrid DFs, it is also possible to replace the correlation contribution with better approximations of non-local correlation energies. Specific non-local correlation functionals are capable of approximately describing the long-range like Van der Waals (VdW) dispersion interaction[182]. However, such improvements again come with additional computational demands. Furthermore, it is possible to combine the two concepts of exact exchange and long-range correlation interaction into a single DF. In Chapters 4 and 5 we have done exactly that with a screened hybrid DF, HSE[156,189,190] and the VdW-DF2 correlation DF[183,195]. These two chapters go into more detail about the implementation and the DF so there is no need to repeat that here, though it should be noted that the combination of these different DFs is not necessarily internally consistent. Only recently, work has been done to try and build an internally consistent combination of exact exchange and non-local correlation, and an example of such a DF is VdW-DF-ahcx[194].

2.2.6 Periodic boundary conditions, plane waves, Bloch's theorem, and pseudopotentials

A proper description of metal surfaces will require a large number of atoms. Smaller clusters of atoms will inevitably exhibit nanoparticle behaviour. This type of behaviour, though interesting, is not what we want when describing a macroscopic metal surface. A clever way to resolve this is by imposing so-called periodic boundary conditions (PBC). In a PBC environment, a given unit cell is constructed and images of that unit cell are repeated infinite times in two or all three dimensions. This means that only the atoms in the cell need to be simulated but the images of the cell do ensure that atoms on the edges of the cell still "feel" like they are part of an infinite ensemble[112]. In mathematical terms, PBC in three dimensions means that for any potential:

$$V(\vec{\mathrm{X}}) = V(\vec{\mathrm{X}} + \vec{A}) \tag{2.54}$$

$$\vec{A} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3 \tag{2.55},$$

where $\vec{\mathrm{X}}$ are Cartesian coordinates within the cell, the n_i integers and the a_i cell-vectors in 3D Cartesian space with a given orthogonal component spanning the repeating unit cell (the three lattice vectors do not need to be fully orthogonal). A downside is that the atoms in the cell interact with the periodic images of themselves, which if the cell is not large enough may cause artefacts in the results[112].

Most solid compounds, except for amorphous solids, can inherently be described by a given repeating cell. For simple non-alloy metals such unit cells can be constructed from a single atom placed inside a box spanned by three distinctly sized vectors spanning three-dimensional space. For a (metal) surface, this becomes more difficult as the periodicity will be broken in at least one direction. The interface between the bulk metal and the vacuum creates a discontinuity that needs to be dealt with. The simplest solution is to create PBC only in the direction of the surface-plane (See **Figure 2.2A** for an FCC(111) surface example, the surface-plane is indicated by the *U, V*-plane), excluding the surface normal (i.e., the *Z*-axis). This does require the resulting surface "slab" to be thick enough to properly simulate the underlying metal bulk, and it also means that the slab has two surfaces, one on the top side (higher *Z*) and one on the bottom side of the slab. If an electronic structure code will allow for this,

then this type of setup will work well enough for atomic orbital-based approaches. If the code does not allow for axis selective PBC (like two-dimensional PBC) then the other option is to include a large vacuum along the *Z*-axis such that the slab cannot interact, or hardly interacts with its periodic images. An example of such a setup can be found in **Figure 2.2B**. For this thesis, a computer program was used that imposed PBC in all three dimensions, for reasons that will be discussed below. Thus, in this thesis, all metal slabs will be separated with a minimum of *10 Å* vacuum. Further slab-specific details can be found in the method sections of the relevant chapters.

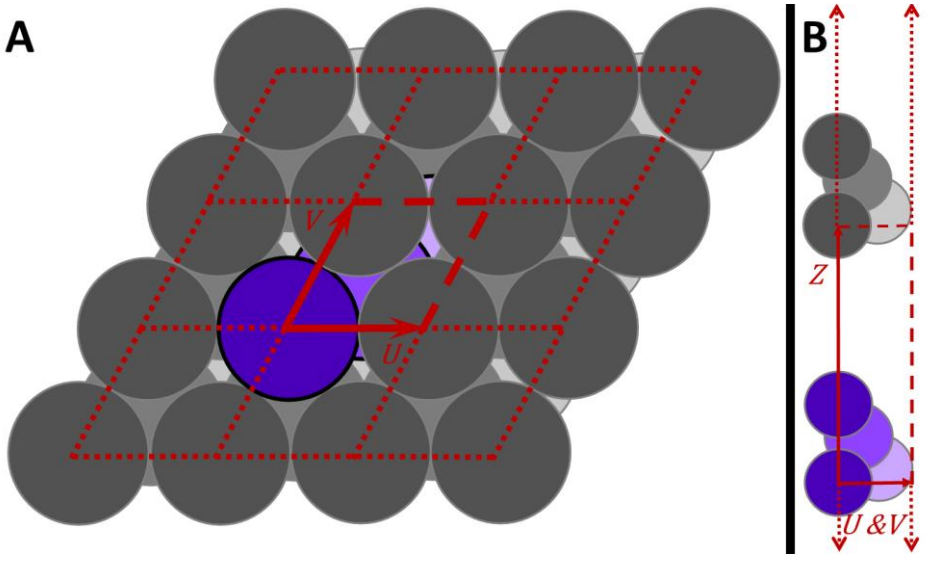

***Figure 2.2**: Schematic description of a periodic metal FCC(111) surface. Purple shades indicate the original atoms in the repeating cell, grey depicts periodic images and red arrows indicate the relevant axes where the red dashed lines close the repeating unit, red dots show the periodic images of the cell translated to different locations; **A**: periodicity in the surface (U,V-) plane; **B**: periodicity along the surface normal (Z axis) for a 4 layer surface slab, including the layer of vacuum in-between surfaces.*

PBC allow for an elegant trick to ease the description of the electrons in a periodic potential (like that of metals) via Bloch's theorem[181]. This theorem states that any eigenfunction of the Schrödinger equation in a periodic potential can be expressed as a plane wave such that:

$$\psi_{\vec{k}}(\boldsymbol{r}) = \mu_{\vec{k}}(\boldsymbol{r})e^{i\vec{k}\boldsymbol{r}} \qquad (2.56).$$

In Equation 2.56 $\mu_{\vec{k}}(\boldsymbol{r})$ is a periodic function that obeys the periodicity of the lattice, i.e., the potential as defined in Equation 2.54, and $\vec{k}$ is a wave vector in

the first Brillouin zone. The Brillouin zone is the reciprocal version of the periodic unit cell.

Using Bloch's theorem the KS-orbitals, as defined in Equations 2.41 and 2.42, and for a given sample point in k-space, the KS-orbital can be expanded as a Fourier-series, i.e., plane wave basis set, such that:

$$\chi_{i,\vec{k}}(\boldsymbol{r}) = N \sum_{\vec{G}} c_{i,k}(\vec{G}) e^{i(\vec{k}+\vec{G})\boldsymbol{r}} \tag{2.57}.$$

Here *N* is the normalisation constant $c_{i,k}$ are the expansion coefficients, and $\vec{G}$ are reciprocal lattice vectors. For an infinite sampling of the reciprocal lattice this series is exact, however, computationally the series is limited by a discretisation over a k-space grid and a "cut-off" energy such that:

$$\frac{1}{2}\left|\vec{k}+\vec{G}\right|^2 \leq E_{cut-off} \tag{2.58}.$$

In practice, this means that the k-point grid and cut-off energy need to be chosen wisely to ensure proper sampling of the periodic electronic state and thereby ensure convergence of the total energy. Put simply, more k-points mean more plane waves and a higher cut-off energy also means more plane waves. More plane waves mean that the basis set further approaches the limit of the exact solution, but at a greater computational cost.

The plane wave basis set is quite useful for efficiently describing the periodic nature of metals and for describing the highly delocalised electrons in the metals. However, it comes with a certain computational cost. For one, the plane wave approach means periodicity needs to be ensured in all three dimensions and that the size of the vacuum separating the slabs (see above) will increase the periodic unit cell size thus increasing the number of plane waves required. That is, in a plane-wave electronic structure method we "pay" computational costs for the size of the vacuum. An additional downside is the large costs associated with hybrid DFs as solving the exact exchange operator (Eq. 2.25) using plane waves can be a rather demanding task. Lastly, the description of larger atoms, that is atoms with many electrons, and thus many nodes in the wavefunction of valence electrons (because of orthogonality demands) can quickly require very large basis sets to properly describe the highly oscillatory behaviour of such wavefunctions.

The complexity of the basis set for many-electron atoms can be reduced by the use of pseudopotentials[196,197]. The idea is that the electrons close to the nuclei of heavy, many-electron atoms, also referred to as the “core-electrons”, are not chemically relevant. Therefore a more simplistic description of those electrons and the resulting effective potential can be used to limit the size of the basis set for the valence electrons. Pseudopotentials additionally allow for the inclusion of relativistic effects of the core-electrons. Thus far, relativistic effects have not been discussed in this thesis, and the reader is referred to Ref. [198] for more information. Briefly, electrons close to the nuclei move fast enough that such effects will start to influence the electronic structure. The use of pseudopotentials incorporating such effects is a way to approximately include these effects without altering the electronic structure method.

A principal idea behind pseudopotentials is that the chemically relevant valence electrons do not interact with the full charge of the nuclei as the electrons in between the nuclei and the valence electrons shield, or screen, the charges of the nuclei and the core-electrons. Also, the core-electrons do not affect the chemistry much. As such we can describe the nuclei and core electrons by one, different, effective potential with a given ‘core’ radius r_c. The nuclei and the core-electrons within this core radius are no longer distinctly described but are described by a pseudo-potential. This will simplify the calculation with the wavefunction describing the valence electrons, as it no longer needs to be made orthogonal to wavefunctions describing the core-electron wavefunctions. (see **Figure 2.3** for a schematic drawing).

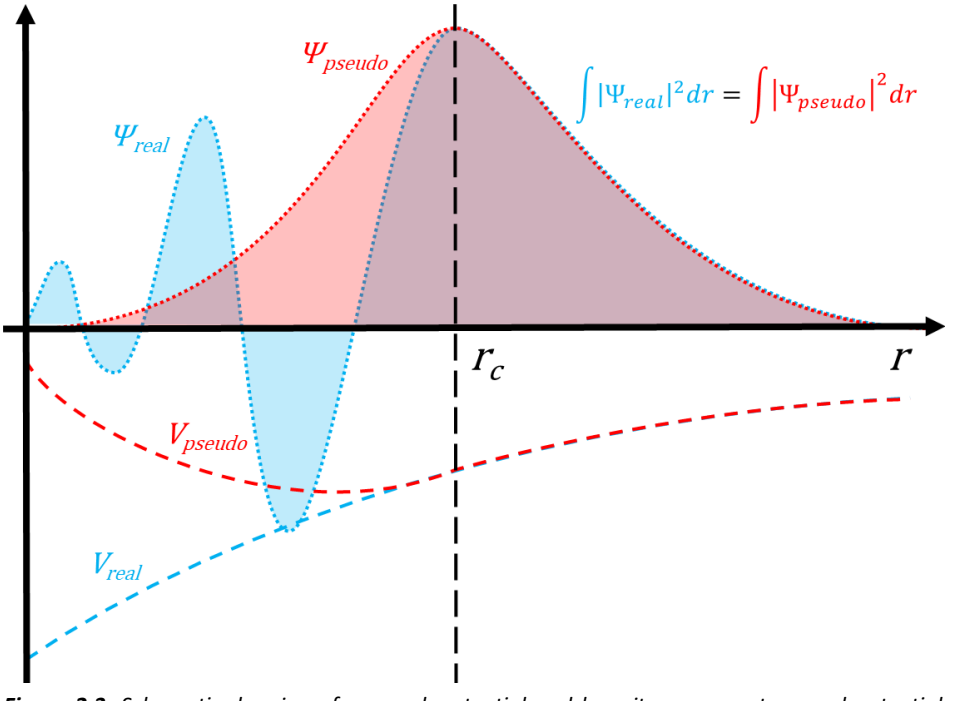

***Figure 2.3**: Schematic drawing of a pseudopotential and how it compares to a real potential. Pseudo potential and wavefunction in red, real potential and wavefunction in light blue. The horizontal axis measures the distance of the electron to the nucleus. The shading serves as a guide to the eye.*

To ensure that the chemical state of the atom is not altered pseudopotentials are usually constrained such that the wavefunction and potential outside of r_c is described the same as the real wavefunction and potential. Furthermore, the pseudopotentials are often norm-conserving, meaning that the norm of the pseudo-wavefunction is kept the same as that of its real counterpart, i.e.,

$$\int |\Psi_{real}|^2 dr = \int |\Psi_{pseudo}|^2 dr \qquad (2.59).$$

However, to further reduce the basis set size this last constraint is not always adhered to. The electronic structure calculations in the following chapters have all used a slightly different approach with the same aim, namely the Projector Augmented Wave (PAW)[199] method to describe the core-electrons. In this method, a linear transformation is used to transform the rapidly oscillating (KS)-wavefunction near the core of the atom to a smooth function. This is done in such a way that the wavefunction is only transformed within the cutoff radius, similar to other pseudopotentials. However, in the PAW method, there is no

norm-conserving. Furthermore, all-electron observables can still be computed with the PAW method by simply reversing the linear transformation. The finer details of PAW pseudopotentials are outside the scope of this thesis but further reading is available at Refs. [199,200].

2.2.7 From electronic structure to potential energy surface

All of the last six sub-sections put together mean that it is possible to calculate accurate electronic energies (within the DF approximation) for a given geometry of the nuclei. This still leaves two possible classes of methods to use this electronic structure to compute any motion of the nuclei, i.e., to simulate the chemistry that occurs. The first and maybe the most straightforward class of methods is *ab initio* or Born-Oppenheimer molecular dynamics (AIMD/BOMD). In this approach, the forces on the nuclei are calculated from the electronic structure "on-the-fly". Whenever the nuclei are at a given position the electronic structure is computed, which will, in turn, govern the potential and forces on the nuclei (see Section 2.3). The AIMD/BOMD approach may at face value seem logical but it comes with large computational demands when thousands of molecular trajectories need to be simulated because each trajectory then requires hundreds of electronic structure calculations in sequence. As such, for lower dimensional systems, i.e., smaller molecules, there is a more efficient class of methods.

When dealing with a limited number of degrees of freedom (DOF) it may be more efficient to pre-compute the electronic structure for a large grid of molecular geometries as a function of the DOFs of the system and use interpolative techniques or fitting to form a continuous energy representation. Put differently, a potential energy surface (PES) is computed in advance, after which, this PES is used to solve the equations of motion efficiently. Note that with more degrees of freedom, this approach may quickly become less efficient, as the initial sampling of geometries to form the PES will grow fast with the number of degrees of freedom.

In the following chapters, all molecular dynamics (MD) calculations are limited to that of diatomic molecules whilst the metal surface is kept static. Thus, the

calculations are limited to six dimensions, see Chapters 3, 4, and 5 for the relevant breakdown of the DOF. For such a setup the construction of a PES is most efficient. In this thesis, the discreet electronic structure energies are turned into a continuous PES description based on the corrugation-reducing procedure (CRP)[201,202]. In the CRP the six-dimensional (6D) molecule-metal potential energy (V^{6D}) is set up such that:

$$V^{6D}(\vec{\Gamma}) = I^{6D}(\vec{\Gamma}) + \sum_{l=1}^{2} V_l^{3D}(\vec{\gamma}_l) \tag{2.60}$$

$$V_l^{3D}(\vec{\gamma}_l) = I^{3D}(\vec{\gamma}_l) + \sum_{m=1}^{M} V_{l,m}^{1D}(d_{lm}) \tag{2.61}.$$

Here $\vec{\Gamma}$ are the six coordinates of the molecule, $\vec{\gamma}_l$ the three coordinates of the atom *l (which can be calculated from* $\vec{\Gamma}$*)*, d_{lm} is the distance between the atom *l* of the diatomic molecule and a surface atom *m*, the total number of metal surface atoms taken into account is *M*, I^{6D} is the molecular six-dimensional interpolation function, I^{3D} is the atomic three-dimensional interpolation function, and V^{1D} is the one-dimensional corrugation reduction function. V^{1D} is fitted to the atom-surface interaction of a geometry in which atom *l* is put above a top surface atom and its distance to the surface atom is varied. This procedure is set up to ease the interpolation procedure, produce a six-dimensional function (I^{6D}) that contains less corrugation than V^{6D} and is, therefore, easier to interpolate, and thereby limit the number of electronic structure calculations needed to construct a smooth PES. Put differently it reduces the number of oscillations that will occur in the interpolation functions when only a limited amount of electronic structure data is available. This procedure has been developed previously and in this thesis it is only further applied, thus the procedure is described in more detail in the following Refs. [201–204].

2.3 The nuclear motion and initial conditions

The potential energy surface that results from the electronic structure calculations as discussed in Section 2.2 can be used directly to influence the movement of the nuclei via Newtonian physics. It is generally assumed that the atomic nuclei, with the possible exception of the nuclei of hydrogen or helium, tend to be too heavy for the quantum mechanical effects associated with their

motion to be relevant. Moreover, the mass difference between the electrons and the nuclei is so large that the motion of the nuclei can be approximated by the motion of the atom as a whole. Therefore, the acceleration of any atom, i.e., atomic nucleus, *I* with atomic mass M_I will be given by:

$$\vec{a}_I\left(\vec{R}_I(t)\right) = \frac{-\nabla_I V_I^{Elec}\left[\vec{R}(t)\right]}{M_I} = \frac{d^2\vec{R}_I(t)}{dt^2} \quad (2.62).$$

The acceleration at a given time *t* can be used to update the positions of the atoms with a given time step *Δt* via a simple Taylor expansion truncated at the second order in the position:

$$\vec{R}_I(t+\Delta t) = \vec{R}_I(t) + \frac{d\vec{R}_I(t)}{dt}\Delta t + \frac{1}{2!}\frac{d^2\vec{R}_I(t)}{dt^2}\Delta t^2 \quad (2.63).$$

This can be rewritten as

$$\vec{R}_I(t+\Delta t) = \vec{R}_I(t) + \vec{v}_I(t)\Delta t + \frac{-\nabla_I V_I^{Elec}\left[\vec{R}(t)\right]}{2M_I}\Delta t^2 \quad (2.64).$$

Here $\vec{v}_I(t)$ is the velocity of an atom *I* and the potential energy determining the force working on the atom at a given time *t* is dependent on the positions of all other atoms in the system at that same time *t*. There are several methods to effectively solve the time propagation in nuclear dynamics, the most famous perhaps being the velocity-Verlet algorithm[205]. In this thesis however, a more complicated algorithm, the Burlisch–Stoer algorithm[206], is used to improve numerical stability as one needs to be careful with selecting the size of the timestep (*Δt*) when the gradient of the PES changes fast with the change of positions of the atoms, i.e., when the gradient of the acceleration is far away from zero. The algorithm used for this thesis is discussed in some more depth in Section 2.3.1 below. After that, Section 2.3.2 will discuss the sampling of the initial molecular conditions used to start the MD trajectories.

2.3.1 Burlisch–Stoer algorithm

In this thesis, the time propagation for the MD trajectories is all done using the Burlisch–Stoer algorithm (BuSA)[206]. The exact functionality of this algorithm is out of the scope of this work, and the reader is referred to [207] for a detailed overview. However, below a few key points will be briefly discussed to give an inkling of the procedure and its benefits. The BuSA works by implementing

Hamiltonian mechanics for propagating nuclear motion. This means that de change of position of an atom in time will be governed by:

$$\frac{d\vec{R}}{dt} = \frac{\partial \hat{H}(\vec{R},\vec{P})}{\partial \vec{P}} \quad (2.65),$$

while its change of momentum is determined by

$$\frac{d\vec{P}}{dt} = -\frac{\partial \hat{H}(\vec{R},\vec{P})}{\partial \vec{R}} \quad (2.66),$$

in which

$$\hat{H}(\vec{R},\vec{P}) = \underbrace{\frac{\vec{P}^2}{2M}}_{\hat{T}} + \hat{V}(\vec{R}) \quad (2.67).$$

Here $\vec{P}$ is the momentum vector of all atoms in the system, $\hat{V}$ is the potential as defined by the electronic structure and *M* is the mass of the respective atom. From 2.65-2.67, it follows that[206,207]:

$$\frac{d\vec{R}}{dt} = \frac{\partial \hat{T}(\vec{P})}{\partial \vec{P}} = \frac{\vec{P}}{M} = \vec{v} \quad (2.68),$$

$$\frac{d\vec{P}}{dt} = -\frac{\partial \hat{V}(\vec{R})}{\partial \vec{R}} \quad (2.69).$$

In the end, Hamiltonian mechanics is a reformulation of the previously mentioned Newtonian mechanics but for the BuSA it is the more useful formalism. Additionally, it turns one second-order differential equation into two separate first-order differential equations.

The BuSA uses the above equations to propagate the atoms in time via a predictor-corrector method. In such an integration method there are always two distinct steps, the first is to use an arbitrary fit to previous function values and derivatives to extrapolate the value of the next function value. The second step will use an interpolative method, often based on the predicted value, to improve the initial fit approximation.

In the BuSA this procedure is along the following lines[206]. First, an initial large time step *S* is chosen such that a new position for $t + S$ is extrapolated (updating velocities where required with Equation 2.68) by subdividing *S* into *N* smaller sub-steps s_n and using Richardson extrapolation[208] to find

$$\vec{R}(t_2) = \vec{R}(t_1 + S) \quad (2.70),$$

by extrapolating N_{max} times:

$$\vec{R}(t_{i+n}) = \vec{R}(t_i + s_n) \quad (2.71).$$

These results can then be fitted to a rational function to estimate an error of the Richardson extrapolation. If the error is not yet sufficiently small the number of substeps N_{max} is increased such that over time:

$$s_n \to 0 \wedge N_{max} \to \infty \quad (2.72).$$

The more steps used in the Richardson extrapolation the more accurate it will be[208]. In practise the extrapolation error will eventually fall below a preset threshold for a given amount of substeps and the approximation is stopped there, or a maximum number of iterations ($iter_{max} = 9$)[209] is reached. In this last scenario, the initial timestep S may have been too large and is halved after which the process is repeated. If the first scenario is encountered the solution to the differential equations (Eqs. 2.65 and 2.66) will have been found for the next point in time, and a new step size S for the next step will be chosen based on[209]:

$$S_{new} = \begin{cases} 1.5S; & if: iter \leq 6 \\ 0.6^{iter-0.6} * 1.5S; & if: iter > 6 \end{cases} \quad (2.73).$$

This way the step size of the time integration will always adapt to the gradient of the potential, i.e., if the potential is very steep or, more generally, shows many oscillations, the timestep will be reduced until accurate results are obtained, or a minimum size threshold is reached resulting in an error message. If the potential is, however, shallow and "stable" then the timestep can be increased in size again. This algorithm allows us to mitigate the risks associated with the choice of a poor, constant, timestep for the MD.

2.3.2 Initial conditions of diatomic molecules

Equation 2.63 has two parameters that define the starting location and velocity, or kinetic energy of the atoms, which can be derived from known or chosen initial conditions of the atoms. All dynamics calculations in this thesis are quasi-classical trajectory (QCT) calculations[210,211]. This means that the molecule is propagated through time classically but the initial conditions of the molecule are defined according to the quantisation of the rovibrational states of the molecule. As a result of this, the initial condition of the molecule will include zero point energy (ZPE)[173]. The translational kinetic energy of the entire molecule is not

quantised and can be selected according to a few different methods depending on the type of experiment that is being simulated or the experimental data that is available, see the respective chapters for more details.

Rovibrational initial conditions, however, are defined via three quantum numbers *v*, *j*, and m_j. The population distribution of these states is governed by model simulations of the diatomic molecules, and the states are populated according to input settings like rotational and/or vibrational temperatures. The population of a given *v, j* state is given by:

$$F_{v,j} = \frac{2j+1}{Z(T_{vib}, T_{rot})} e^{-\frac{E_{v,j=0}-E_{v=0,j=0}}{k_B T_{vib}}} e^{-\frac{E_{v,j}-E_{v,j=0}}{k_B T_{rot}}} \quad (2.74).$$

Here $Z(T_{vib}, T_{rot})$ is the partition function for given vibrational and rotational temperatures, $E_{v,j}$ is the energy of a given (*v, j*) state, and T_{vib} and T_{rot} are the vibrational and rotational temperatures. In molecular beam experiments (see Section 1.2.4) these temperatures are related to the nozzle temperature. Initial intramolecular distances and momenta are computed from a quasi-classical full-cycle vibrational simulation of the molecule in the gas-phase. The rotational state is selected according to the rotational population of the initial angular momentum which is defined by

$$L = \hbar\sqrt{j(j+1)} \quad (2.75),$$

and the orientation of *L* is randomly sampled with the constraint that

$$\cos(\theta_L) = \frac{m_j}{\sqrt{j(j+1)}} \quad (2.76).$$

Here θ_L is the angle between *L* and the surface normal. The m_j states are all sampled with equal probability as these states are degenerate for homonuclear diatomic molecules in the absence of a magnetic field. It must be noted that, depending on the nuclear spin statistics of the diatomic molecule in question, not all *j* states are allowed, e.g., even *j* states are not permitted for O_2[173]. Put very briefly this is due to the combination of the Pauli principle, as also briefly discussed in Section 2.2.2, and the fact that undistinguishable nuclei may get interchanged in the rotation of a molecule. That is, nuclei have their own spin, which depending on the number of protons and neutrons in the nuclei can be either integral or fractional, i.e., the nucleus will behave like a fermion or a boson. This means the sign of the wavefunction has to either change sign (like with electrons, i.e. fermions) or remain the same (for bosons) when two nuclei

are interchanged by the rotation. This means that certain types of rotational transitions and rotation states may be less occupied (for H_2) or completely forbidden (for O_2). The details of this are beyond the scope of this thesis and the reader is referred to Ref. [173] for a more detailed explanation. Chapter 3 includes a table in Section 3.2.5 with the rovibrational occupations for an O_2 beam of $T_{vib} = 300\ K$ and $T_{rot} = 9\ K$. The temperature conditions, i.e., T_{vib} and T_{rot}, are consistent in all three further chapters of this thesis. Further details of the initial conditions of the molecules in QCT dynamics are given in the respective chapters.

Lastly, although in the initial conditions of the molecule, quantisation is taken into account in QCT, the classical time propagation means that quantisation may be lost and energy may leak from states where this would normally not be allowed. This generally does not happen in the QCT for a diatomic molecule in isolation but this may occur when the molecule is interacting with other molecules or with a metal surface.