

# Chapter 2

## Quantum Chemistry

It is the goal of this chapter to describe the pertinent theory of quantum chemistry in order to obtain accurate physical information on the electronic and nuclear character of a molecular system: respectively, the equilibrium geometry, the electronic spectrum, excited electronic states, permanent and transition dipole moments, potential energy surfaces, as well as the vibrational eigenfunctions and eigenvalues. At the center of solving the nonrelativistic time-independent Schrödinger equation (TISE) lies the Born-Oppenheimer approximation. Its application to the TISE validates a separation of the electrons from the nuclei, leading to two eigenvalue equations: the electronic and the nuclear Schrödinger equations. In the following it will also be shown how one is able to (accurately) solve these equations for the two unknowns, i.e. the energies and wave functions.

### 2.1 Time-independent Schrödinger Equation

The nonrelativistic time-independent Schrödinger equation [41] is given as

$$\hat{H}|\Psi\rangle = E|\Psi\rangle, \quad (2.1)$$

where the total energy,  $E$ , is obtainable by operation of the time-independent molecular Hamiltonian,  $\hat{H}$ , onto the complete wave function,  $|\Psi\rangle$ . The molecular Hamiltonian is given below,

$$\begin{aligned}
\hat{H} = & - \underbrace{\sum_a \frac{\hbar^2}{2m_e} \nabla_a^2}_{\hat{T}_{\text{el}}} - \underbrace{\sum_A \frac{\hbar^2}{2m_A} \nabla_A^2}_{\hat{T}_{\text{nu}}} \\
& - \underbrace{\sum_a \sum_A \frac{Z_A e^2}{4\pi\epsilon_0 \mathbf{r}_{aA}}}_{\hat{V}_{\text{el,nu}}} + \underbrace{\sum_a \sum_{b>a} \frac{e^2}{4\pi\epsilon_0 \mathbf{r}_{ab}}}_{\hat{V}_{\text{el,el}}} + \underbrace{\sum_A \sum_{B>A} \frac{Z_A Z_B e^2}{4\pi\epsilon_0 \mathbf{R}_{AB}}}_{\hat{V}_{\text{nu,nu}}}
\end{aligned} \tag{2.2}$$

where  $\nabla^2$  is the Laplacian operator,  $m_e$  and  $m_A$  are the mass of the electron and the nucleus, respectively, all of which are used to define the two kinetic energy terms,  $\hat{T}_{\text{el}}$  and  $\hat{T}_{\text{nu}}$ . The third term  $\hat{V}_{\text{el,nu}}$  represents the Coulomb attraction between an electron and a nucleus while the remaining two terms,  $\hat{V}_{\text{el,el}}$  and  $\hat{V}_{\text{nu,nu}}$ , represent the repulsion between two electrons and two nuclei, respectively. The variable  $Z_A$  represents the atomic number of nucleus  $A$ ,  $\mathbf{r}_{ab}$  the distance between electron  $a$  and  $b$ ,  $\mathbf{r}_{aA}$  the distance between electron  $a$  and nucleus  $A$ ,  $\mathbf{R}_{AB}$  the distance between two nuclei, and  $\epsilon_0$  a constant: the permittivity of vacuum. The last three terms define the potential energy operator  $\hat{V}$ , which contains the interaction between the electrons and the nuclei, between the electrons, and between the nuclei. Relativistic effects including, spin-orbital couplings have not been considered in this work.

### 2.1.1 Born-Oppenheimer Approximation

The time-independent Schrödinger equation, eq. 2.1, is not solvable for a many-electron molecule. As a first step to circumvent this inability, the nuclear terms are separated from the electronic terms [42]. This is done by invoking the Born-Oppenheimer approximation [38]. The approximation takes into account the mass difference between the electron and the nucleus. Considering the lightest of all atoms, the hydrogen atom, the mass ratio of the nucleus to the electron is 1836, exemplifying this approximation. Furthermore, the lagging nuclei, due to this mass difference, are so slow in adapting to the change in the electronic configuration that the geometry of the nuclei can be considered fixed, when describing the electronic problem.

### 2.1.2 Electronic Schrödinger Equation

The consequence of the Born-Oppenheimer approximation is the ability to separate the motion of the electrons from that of the nuclei. Accordingly, the electronic Hamiltonian

$$\hat{H}_{\text{el}} = - \sum_a \frac{\hbar^2}{2m_e} \nabla_a^2 - \frac{1}{4\pi\epsilon_0} \left( \sum_a \sum_A \frac{Z_A e^2}{r_{aA}} + \sum_a \sum_{b>a} \frac{e^2}{r_{ab}} \right), \quad (2.3)$$

is the part of the molecular Hamiltonian given in eq. 2.2, which describes the electrons. The kinetic energy term for the nuclei as well as the nuclear repulsion, now a constant, are neglected. The electronic Schrödinger equation is then given as the following,

$$\hat{H}_{\text{el}} |\Psi_{\text{el}}(\mathbf{r}_a; \mathbf{R}_A)\rangle = E_{\text{el}}(\mathbf{R}_A) |\Psi_{\text{el}}(\mathbf{r}_a; \mathbf{R}_A)\rangle \quad (2.4)$$

where the electronic wave function,  $|\Psi_{\text{el}}(\mathbf{r}_a; \mathbf{R}_A)\rangle$ , depends directly on the electron coordinates,  $\mathbf{r}_a$ , and parametrically on the nuclear coordinates,  $\mathbf{R}_A$ , as do the electronic energies,  $E_{\text{el}}(\mathbf{R}_A)$ .

It is the intendment of quantum chemical programs to solve the stationary Schrödinger equation, eq. 2.4. In doing so, the sum of the electronic energy,  $E_{\text{el}}(\mathbf{R}_A)$  and the nuclear repulsion,  $\hat{V}_{\text{nu,nu}}(\mathbf{R}_A)$  at a specific nuclear configuration  $\mathbf{R}_A$  provides a potential energy. The potential energy for a given electronic state - a point in the potential energy surface - is defined as

$$\hat{V}_{\text{el}}(\mathbf{R}_A) = E_{\text{el}}(\mathbf{R}_A) + \hat{V}_{\text{nu,nu}}(\mathbf{R}_A). \quad (2.5)$$

A series of stationary points for different nuclear configurations will produce potential energy surfaces, which will serve as the playground for the dynamics of nuclear wave functions.

### 2.1.3 Nuclear Schrödinger Equation

Under the same approximation that was used for solving the electronic Schrödinger equation, i.e. the Born-Oppenheimer approximation, it is possible to obtain the nuclear Schrödinger equation

$$\hat{H}_{\text{el,nu}} |\Psi_{\text{el,nu}}(\mathbf{R}_A)\rangle = E_{\text{el,nu}} |\Psi_{\text{el,nu}}(\mathbf{R}_A)\rangle. \quad (2.6)$$

For the lagging motion of the nuclei it is sufficient to apply the average values of the electronic coordinates averaged over the electronic wave function. The nuclear Hamiltonian

$$\hat{H}_{\text{el,nu}} = - \sum_A \frac{\hbar^2}{2m_A} \nabla_A^2 + \sum_A \sum_{B>A} \frac{Z_A Z_B e^2}{4\pi\epsilon_0 \mathbf{R}_{AB}} + E_{\text{el}}(\mathbf{R}_A) = - \sum_A \frac{\hbar^2}{2m_A} \nabla_A^2 + \hat{V}_{\text{el}}(\mathbf{R}_A) \quad (2.7)$$

is defined by the effective energy of the electronic terms  $\hat{V}_{\text{el}}(\mathbf{R}_A)$ , along with the kinetic energy operator for the nuclei,  $\hat{T}_{\text{nu}}$  as defined in eq. 2.2. Solutions of the nuclear Schrödinger equation, eq. 2.6, describe the vibrations, rotations and translations of a molecule, whereas the nuclear energy,  $E_{\text{nu}}$ , now represents the total energy,  $E_{\text{tot}}$  in the Born-Oppenheimer approximation and accounts for the electronic and vibrational energy of a molecule.

## 2.2 Solution to the Electronic Schrödinger Equation

Solving the electronic Schrödinger equation, eq. 2.4, for different nuclear coordinates produces a series of single point energies that can be connected to form potential energy surfaces. These surfaces are where the nuclear wavepacket dynamics will take place. It is therefore essential to represent the electronic wave functions appropriately, such that the electronic energy approaches the exact value or in the case of multiple electronic states, that the relative energy between states is representative of the molecule. Of course solving this equation exactly is possible only for the simplest of molecules. So in order to solve these equations for larger molecules more approximations have to be made. The most fundamental of these approximations is the Hartree-Fock approximation.

### 2.2.1 Hartree-Fock

The Hartree-Fock (HF) method [43, 44, 45] is an approximation which determines the ground state energy and wave function for an  $N$ -electron system. It approximates the exact wave function as a single antisymmetrized determinant that is optimized by solving the Hartree-Fock equation iteratively, in a process known as the self-consistent field (SCF) method. The antisymmetrized determinant is termed a Slater determinant and from this point the theory will be expanded.

### Slater Determinant

A Slater determinant is the simplest antisymmetrized wave function that can be used to describe the ground state of an  $N$ -electron system. The Slater determinant in its complete form,

$$\Psi_0(\mathbf{x}) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(\mathbf{x}_1) & \chi_2(\mathbf{x}_1) & \cdots & \chi_N(\mathbf{x}_1) \\ \chi_1(\mathbf{x}_2) & \chi_2(\mathbf{x}_2) & \cdots & \chi_N(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(\mathbf{x}_N) & \chi_2(\mathbf{x}_N) & \cdots & \chi_N(\mathbf{x}_N) \end{vmatrix} \quad (2.8)$$

is described by single particle functions,  $\chi(\mathbf{x})$ , also known as spin orbitals, and the index from eq. 2.4 is dropped for clarity. A spin orbital is formed from the product of a spatial orbital,  $\psi(\mathbf{r})$ , which depends on the position of the electron, with a spin function, either an  $\alpha(\omega)$  or a  $\beta(\omega)$  spin

$$\chi_a(\mathbf{x}_a) = \chi_a(\mathbf{r}, \omega) = \psi(\mathbf{r}) \cdot \begin{cases} \alpha(\omega) \\ \beta(\omega) \end{cases} \quad (2.9)$$

and is assumed to be orthonormal

$$\langle \chi_a | \chi_b \rangle = \delta_{ab}. \quad (2.10)$$

According to the variational principle, the best wave function  $\Psi_0(\mathbf{x})$  is the one that gives the lowest energy

$$E_0 = \langle \Psi_0(\mathbf{x}) | \hat{\mathbf{H}}_{\text{el}} | \Psi_0(\mathbf{x}) \rangle. \quad (2.11)$$

The minimization of the energy leads to the Hartree-Fock equations.

### Hartree-Fock Equations

The minimization of the energy in eq. 2.11 is attainable by varying the spin orbitals. The Hartree-Fock equation

$$\hat{\mathbf{f}}(\mathbf{x}_a) |\chi(\mathbf{x}_a)\rangle = \varepsilon_a |\chi(\mathbf{x}_a)\rangle \quad (2.12)$$

is an eigenvalue equation whose solution provides the minimum energy,  $E_0$  and consequently the optimal spin orbitals,  $\chi(\mathbf{x})_a$ . The Fock operator

$$\hat{\mathbf{f}}(\mathbf{x}_a) = \underbrace{-\frac{\hbar^2}{2m_e} \nabla_a^2 - \sum_A \frac{Z_A e^2}{4\pi\epsilon_0 \mathbf{r}_{aA}}}_{\hat{\mathbf{h}}(\mathbf{x}_a)} + \underbrace{\sum_b^N \left[ \hat{\mathbf{J}}_b(\mathbf{x}_a) - \hat{\mathbf{K}}_b(\mathbf{x}_a) \right]}_{\hat{\mathbf{v}}^{\text{HF}}(\mathbf{x}_a)} \quad (2.13)$$

is defined by the single electron Hamiltonian or core Hamiltonian, denoted as  $\hat{h}(\mathbf{x}_a)$ , and the effective Hartree-Fock potential operator  $\hat{v}^{\text{HF}}(\mathbf{x}_a)$ . The effective Hartree-Fock potential is defined by two terms that result from the electron-electron repulsion term  $\hat{V}_{\text{el,el}}$  of eq. 2.2. The first term is the Coulomb operator

$$\hat{J}_b(\mathbf{x}_1)|\chi_a(\mathbf{x}_1)\rangle = \left[ \int d\mathbf{x}_2 \chi_b^*(\mathbf{x}_2) \frac{e^2}{4\pi\epsilon_0\hat{r}_{12}} \chi_b(\mathbf{x}_2) \right] |\chi_a(\mathbf{x}_1)\rangle \quad (2.14)$$

and is described classically as the interaction of one electron, in this case electron  $a$ , with the remaining  $N - 1$  electrons. The exchange operator

$$\hat{K}_b(\mathbf{x}_1)|\chi_a(\mathbf{x}_1)\rangle = \left[ \int d\mathbf{x}_2 \chi_b^*(\mathbf{x}_2) \frac{e^2}{4\pi\epsilon_0\hat{r}_{12}} \chi_a(\mathbf{x}_2) \right] |\chi_b(\mathbf{x}_1)\rangle \quad (2.15)$$

is of purely quantum mechanical nature, i.e. it does not have a classical counterpart. The two-electron potential operator  $\frac{1}{\hat{r}_{12}}$  describes the interaction of electron 1 with electron 2. It is termed the exchange operator, as can be seen from eq. 2.15, where upon its application, the position and spin of electron  $a$  has been exchanged with that of electron  $b$ . The exchange of position and spin between two electrons can also be induced by the permutation operator,  $\mathcal{P}_{12}$ , and a succinct form of the Fock operator can be written as

$$\hat{f}(\mathbf{x}_1) = \hat{h}(\mathbf{x}_1) + \sum_{b \neq a}^{N/2} \int d\mathbf{x}_2 \chi_b^*(\mathbf{x}_2) \frac{e^2}{4\pi\epsilon_0\hat{r}_{12}} (1 - \mathcal{P}_{12}) \chi_b(\mathbf{x}_2). \quad (2.16)$$

### Restricted Closed-Shell Hartree-Fock

To solve the Hartree-Fock equation, eq. 2.12, it is necessary to evaluate the form of the spin orbitals. A spin orbital can be restricted or unrestricted in its spatial orbital. In the restricted case, for a closed-shell system, the pair of spin orbitals are defined to have the same spatial function, given below,

$$\chi_{2i}(\mathbf{x}) = \begin{cases} \psi_i(\mathbf{r})\alpha(\omega) \\ \psi_i(\mathbf{r})\beta(\omega) \end{cases} \quad i = 1, 2, \dots, K \quad (2.17)$$

where the index runs from 1 to the maximum number of spatial orbitals  $K$ . Inserting this equation into the Hartree-Fock eq. 2.12 results in two separate Hartree-Fock equations,

$$\hat{f}(\mathbf{x}_1)|\psi_i(\mathbf{r}_1)\alpha(\omega_1)\rangle = \varepsilon_i|\psi_i(\mathbf{r}_1)\alpha(\omega_1)\rangle \quad (2.18)$$

$$\hat{f}(\mathbf{x}_1)|\psi_i(\mathbf{r}_1)\beta(\omega_1)\rangle = \varepsilon_i|\psi_i(\mathbf{r}_1)\beta(\omega_1)\rangle \quad (2.19)$$

defined in terms of their spin functions,  $\alpha(\omega_a)$  and  $\beta(\omega_a)$ , and results in the orbital energy,  $\varepsilon_i$ . In order to obtain an expression exclusively in terms of the spatial orbitals, it is necessary to purge the Fock operator of the spin function. This is done by first replacing the spin orbital by its spatial orbital and spin functions.

Recognizing that in a closed-shell scenario, the results from the  $\alpha$  terms are identical to those for  $\beta$ , it is sufficient to multiply eq. 2.18 from the left by  $\alpha^*(\omega_a)$  and integrate over its spin

$$\left[ \int d\omega_1 \alpha^*(\omega_1) \hat{\mathbf{f}}(\mathbf{x}_1) \alpha(\omega_1) \right] |\psi_i(\mathbf{r}_1)\rangle = \varepsilon_i |\psi_i(\mathbf{r}_1)\rangle. \quad (2.20)$$

The closed-shell Fock operator has the following form

$$\hat{\mathbf{f}}(\mathbf{r}_1) = \hat{\mathbf{h}}(\mathbf{r}_1) + \sum_{a=1}^{N/2} \left( 2\hat{\mathbf{J}}_a(\mathbf{r}_1) - \hat{\mathbf{K}}_a(\mathbf{r}_1) \right), \quad (2.21)$$

where the sum over  $N$  is replaced by  $N/2$ , i.e. the number of  $\alpha$  or  $\beta$  electrons. The Fock operator can be written in terms of the permutation operator and the spatial orbitals as

$$\hat{\mathbf{f}}(\mathbf{r}_1) = \hat{\mathbf{h}}(\mathbf{r}_1) + \sum_{a=1}^{N/2} \int d\mathbf{r}_2 \psi_a^*(\mathbf{r}_2) \frac{e^2}{4\pi\epsilon_0 \hat{\mathbf{r}}_{12}} (2 - \mathcal{P}_{12}) \psi_a(\mathbf{r}_2). \quad (2.22)$$

The Coulomb and exchange operators are now defined with respect to the spatial orbitals and are analogous to equations 2.14 and 2.15, specifically

$$\hat{\mathbf{J}}_a(\mathbf{r}_1) |\psi_i(\mathbf{r}_1)\rangle = \left[ \int d\mathbf{r}_2 \psi_a^*(\mathbf{r}_2) \frac{e^2}{4\pi\epsilon_0 \hat{\mathbf{r}}_{12}} \psi_a(\mathbf{r}_2) \right] |\psi_i(\mathbf{r}_1)\rangle \quad (2.23)$$

$$\hat{\mathbf{K}}_a(\mathbf{r}_1) |\psi_i(\mathbf{r}_1)\rangle = \left[ \int d\mathbf{r}_2 \psi_b^*(\mathbf{r}_2) \frac{e^2}{4\pi\epsilon_0 \hat{\mathbf{r}}_{12}} \psi_i(\mathbf{r}_2) \right] |\psi_b(\mathbf{r}_1)\rangle. \quad (2.24)$$

Now that the Fock operator has been defined in terms of the spatial orbitals, the Roothaan-Hall equations, which provide an algebraic method that aids in solving the Hartree-Fock equations, will be discussed.

### Roothaan-Hall Equations

As seen from the previous section, the spatial orbitals were obtained by integrating out the spin functions. The Hartree-Fock eq. 2.12 can be rewritten in terms of these spatial orbitals,

$$\hat{\mathbf{f}}(\mathbf{r}_1) |\psi_i(\mathbf{r}_1)\rangle = \varepsilon_i |\psi_i(\mathbf{r}_1)\rangle. \quad (2.25)$$

where the wave function  $|\psi_i(\mathbf{r}_1)\rangle$  is a molecular orbital, and  $\varepsilon_i$  is the corresponding energy. For molecular systems, eq. 2.25 can not be solved analytically, but instead is converted into a set of algebraic equations by first introducing a set of known spatial functions, as introduced by Roothaan and Hall [46, 47].

The premise for the Roothaan-Hall equations is that the molecular orbitals can be expanded as a linear combination of known  $K$  one-electron functions,

$$|\psi_i\rangle = \sum_{\mu=1}^K C_{\mu i} |\phi_\mu\rangle \quad (2.26)$$

where the basis functions are denoted by the Greek indices and the molecular orbitals with Latin indices. Equation 2.26 can be inserted into eq. 2.25 and by multiplying from the left with  $\phi_\nu^*$  and integrating results in the following matrix equation

$$\sum_{\mu}^K C_{\mu i} \underbrace{\int d\mathbf{r}_1 \phi_\nu^*(\mathbf{r}_1) \hat{\mathbf{f}}(\mathbf{r}_1) \phi_\mu(\mathbf{r}_1)}_{F_{\nu\mu}} = \varepsilon_i \sum_{\mu}^K C_{\mu i} \underbrace{\int d\mathbf{r}_1 \phi_\nu^*(\mathbf{r}_1) \phi_\mu(\mathbf{r}_1)}_{S_{\nu\mu}}. \quad (2.27)$$

The one-electron basis functions  $\phi_\mu$  are not necessarily orthogonal and therefore the matrix elements  $S_{\nu\mu}$  describe the overlap between two functions,  $\nu$  and  $\mu$ , and form the  $K \times K$  overlap matrix  $\mathbf{S}$ . The Fock matrix  $\mathbf{F}$ , also  $K \times K$ , is formed from the matrix elements  $F_{\nu\mu}$ . Both matrices are Hermitian, for real orbitals, they are real and symmetric. This allows for the diagonalization of  $S_{\nu\mu}$  via a unitary transformation. Equation 2.27 can be compactly written as

$$\mathbf{FC} = \mathbf{SC}\boldsymbol{\varepsilon}, \quad (2.28)$$

where the matrix  $\mathbf{C}$  contains the coefficients for the molecular orbitals  $\psi_i$  in a column wise fashion, i.e. the first column gives the coefficients for  $\psi_1$ , the second column those for  $\psi_2$ , and the  $K^{\text{th}}$  column those for  $\psi_K$ . The energies of each molecular orbital are found in the diagonalized matrix  $\boldsymbol{\varepsilon}$ .

Analyzing the one-electron Fock operator in eq. 2.22 by applying the expansion from eq. 2.26, it becomes apparent that the Fock matrix  $\mathbf{F}$  depends on the coefficients,  $\mathbf{C}$ . This deems the Roothaan-Hall equations nonlinear and in order to solve a nonlinear system an iterative approach is used: the self-consistent field procedure. However, before discussing the SCF procedure, it is informative to review the theory of open-shell Hartree-Fock.

### Unrestricted Open-shell Hartree-Fock

In the previous section the spatial orbitals were restricted to having the same value for both the  $\alpha$  and the  $\beta$  spins. In an open-shell case it is not correct to describe the spatial orbitals as restricted, but rather as unrestricted, which means that the spatial orbitals are different for differing spin functions. The spin orbitals, which are formed from the unrestricted spatial orbitals, are also unrestricted and are defined as,

$$\chi_{2i}(\mathbf{x}) = \begin{cases} \psi_i^\alpha(\mathbf{r}_1)\alpha(\omega) & i = 1, 2, \dots, K \\ \psi_i^\beta(\mathbf{r}_1)\beta(\omega) & \end{cases} \quad (2.29)$$

where the index,  $i$  runs from 1 to the maximum number of spatial orbitals  $K$ . Inserting this equation into the Hartree-Fock equation, eq. 2.12, results in two separate equations,

$$\hat{\mathbf{f}}(\mathbf{x}_1)|\psi_i^\alpha(\mathbf{r}_1)\alpha(\omega_1)\rangle = \varepsilon_i^\alpha|\psi_i^\alpha(\mathbf{r}_1)\alpha(\omega_1)\rangle \quad (2.30)$$

$$\hat{\mathbf{f}}(\mathbf{x}_1)|\psi_i^\beta(\mathbf{r}_1)\beta(\omega_1)\rangle = \varepsilon_i^\beta|\psi_i^\beta(\mathbf{r}_1)\beta(\omega_1)\rangle \quad (2.31)$$

defined in terms of the spin functions,  $\alpha(\omega_1)$  and  $\beta(\omega_1)$ . An unrestricted open-shell description is considered and therefore eqs. 2.30 and 2.31 must be handled individually. Following the same general procedure as was done for the restricted closed-shell case the subsequent eigenvalue equations are obtained,

$$\left[ \int d\omega_1 \alpha^*(\omega_1) \hat{\mathbf{f}}(\mathbf{x}_1) \alpha(\omega_1) \right] |\psi_i^\alpha(\mathbf{r}_1)\rangle = \varepsilon_i^\alpha |\psi_i^\alpha(\mathbf{r}_1)\rangle \quad (2.32)$$

$$\left[ \int d\omega_1 \beta^*(\omega_1) \hat{\mathbf{f}}(\mathbf{x}_1) \beta(\omega_1) \right] |\psi_i^\beta(\mathbf{r}_1)\rangle = \varepsilon_i^\beta |\psi_i^\beta(\mathbf{r}_1)\rangle. \quad (2.33)$$

The Fock operators defined in terms of the spatial coordinates are

$$\hat{\mathbf{f}}(\mathbf{r}_1)|\psi_i^\alpha(\mathbf{r}_1)\rangle = \int d\omega_1 \alpha^*(\omega_1) \hat{\mathbf{f}}(\mathbf{x}_1) \alpha(\omega_1) \psi_i^\alpha(\mathbf{r}_1) = \varepsilon_i^\alpha |\psi_i^\alpha(\mathbf{r}_1)\rangle \quad (2.34)$$

$$\hat{\mathbf{f}}(\mathbf{r}_1)|\psi_i^\beta(\mathbf{r}_1)\rangle = \int d\omega_1 \beta^*(\omega_1) \hat{\mathbf{f}}(\mathbf{x}_1) \beta(\omega_1) \psi_i^\beta(\mathbf{r}_1) = \varepsilon_i^\beta |\psi_i^\beta(\mathbf{r}_1)\rangle \quad (2.35)$$

and depend on the Fock operator given in eq. 2.16 which includes the spin function variable. The Fock operator defined only in terms of the spatial orbitals is obtained by following the same steps that were used for the restricted case, the only difference being that the sum runs over an unequal number of  $\alpha$  and  $\beta$  spins and is denoted in the following

equations

$$\hat{\mathbf{f}}^\alpha(\mathbf{r}_1) = \hat{\mathbf{h}}(\mathbf{r}_1) + \sum_a^{N_\alpha} \left( \hat{\mathbf{J}}_a^\alpha(\mathbf{r}_1) - \hat{\mathbf{K}}_a^\alpha(\mathbf{r}_1) \right) + \sum_a^{N_\beta} \hat{\mathbf{J}}_a^\beta(\mathbf{r}_1) \quad (2.36)$$

$$\hat{\mathbf{f}}^\beta(\mathbf{r}_1) = \hat{\mathbf{h}}(\mathbf{r}_1) + \sum_a^{N_\beta} \left( \hat{\mathbf{J}}_a^\beta(\mathbf{r}_1) - \hat{\mathbf{K}}_a^\beta(\mathbf{r}_1) \right) + \sum_a^{N_\alpha} \hat{\mathbf{J}}_a^\alpha(\mathbf{r}_1). \quad (2.37)$$

The Coulomb and exchange operators maintain their form in equations 2.23 and 2.24, only now the spatial functions are differentiated according to the spin type.

Solving the eigenvalue equations, eqs. 2.30 and 2.31, for the spatial orbitals and hence the energy, remains the central goal of this section. The solution to the unrestricted Hartree-Fock eigenvalue equation is obtained by solving the Pople-Nesbet equations [48]. These equations are analogous to the Roothaan-Hall equations and will be described in the succeeding subsection.

### Pople-Nesbet Equations

In the previous section, the Hartree-Fock equations for the unrestricted open-shell spatial functions were described, and the energy expressions were given in terms of their expectation values. Accurate energies are completely dependent on an accurate set of spatial functions, and by replacing the unknown spatial orbital with an expansion of known one-electron functions one is able to obtain matrix equations that are solvable through algebraic methods, as is seen below. The unrestricted eigenvalue equations are given again for consistency

$$\hat{\mathbf{f}}^\alpha(\mathbf{r}_1)|\psi_i^\alpha(\mathbf{r}_1)\rangle = \varepsilon_i^\alpha|\psi_i^\alpha(\mathbf{r}_1)\rangle \quad (2.38)$$

$$\hat{\mathbf{f}}^\beta(\mathbf{r}_1)|\psi_i^\beta(\mathbf{r}_1)\rangle = \varepsilon_i^\beta|\psi_i^\beta(\mathbf{r}_1)\rangle. \quad (2.39)$$

The molecular orbitals  $\psi_i(\mathbf{r}_1)$  are expanded as a linear combination of known  $K$  one-electron functions,

$$|\psi_i^\alpha\rangle = \sum_{\mu=1}^K C_{\mu i}^\alpha |\phi_\mu\rangle \quad (2.40)$$

$$|\psi_i^\beta\rangle = \sum_{\mu=1}^K C_{\mu i}^\beta |\phi_\mu\rangle \quad (2.41)$$

where the basis functions are denoted by the Greek indices and the molecular orbitals with Latin indices. Equations 2.40 and 2.41 can be inserted into eqs. 2.38 and 2.39 respectively and then multiplied from the left with  $\phi_\nu^*$ , and integrating results in the following matrix equations

$$\sum_{\mu}^K C_{\mu i}^{\alpha} \underbrace{\int d\mathbf{r}_1 \phi_{\nu}^*(\mathbf{r}_1) \hat{\mathbf{f}}^{\alpha}(\mathbf{r}_1) \phi_{\mu}(\mathbf{r}_1)}_{F_{\nu\mu}^{\alpha}} = \varepsilon_i^{\alpha} \sum_{\mu}^K C_{\mu i}^{\alpha} \underbrace{\int d\mathbf{r}_1 \phi_{\nu}^*(\mathbf{r}_1) \phi_{\mu}(\mathbf{r}_1)}_{S_{\nu\mu}^{\alpha}} \quad (2.42)$$

$$\sum_{\mu}^K C_{\mu i}^{\beta} \underbrace{\int d\mathbf{r}_1 \phi_{\nu}^*(\mathbf{r}_1) \hat{\mathbf{f}}^{\beta}(\mathbf{r}_1) \phi_{\mu}(\mathbf{r}_1)}_{F_{\nu\mu}^{\beta}} = \varepsilon_i^{\beta} \sum_{\mu}^K C_{\mu i}^{\beta} \underbrace{\int d\mathbf{r}_1 \phi_{\nu}^*(\mathbf{r}_1) \phi_{\mu}(\mathbf{r}_1)}_{S_{\nu\mu}^{\beta}}. \quad (2.43)$$

The one-electron basis functions  $\phi_{\mu}$  are generally not orthogonal and therefore the matrix elements  $S_{\nu\mu}^{\alpha}$  and  $S_{\nu\mu}^{\beta}$  describe the overlap between two functions,  $\nu$  and  $\mu$ , for their respective  $\alpha$  and  $\beta$  spatial orbitals and form the  $K \times K$  overlap matrix  $\mathbf{S}^{\sigma}$ , where  $\sigma$  represents the spin  $\alpha$  or  $\beta$ . The Fock matrix  $\mathbf{F}^{\sigma}$ , also  $K \times K$ , is formed from the matrix elements  $F_{\nu\mu}^{\alpha}$  and  $F_{\nu\mu}^{\beta}$ . Both matrices are Hermitian, so  $\mathbf{S}^{\sigma}$  can be diagonalized via a unitary transformation. The Pople-Nesbet eqs. 2.42 and 2.43 can be compactly written as

$$\mathbf{F}^{\sigma} \mathbf{C}^{\sigma} = \mathbf{S} \mathbf{C}^{\sigma} \boldsymbol{\varepsilon}^{\sigma}, \quad (2.44)$$

where  $\sigma$  can be either the  $\alpha$  or the  $\beta$  spin function and the matrices  $\mathbf{C}^{\alpha}$  and  $\mathbf{C}^{\beta}$  contain the coefficients for the molecular orbitals  $\psi^{\alpha}$  and  $\psi^{\beta}$  respectively, and the energies are found along the diagonal of the matrices  $\boldsymbol{\varepsilon}^{\alpha}$  and  $\boldsymbol{\varepsilon}^{\beta}$ , which have been diagonalized.

The nonlinearity of these equations is due to the Fock matrix, which depends on the expansion coefficients of eq. 2.26 and therefore the matrix eq. 2.44 is solved iteratively. The iterative method is termed the Self-consistent Field method which will be described in the next section.

### Self-consistent Field

The Self-consistent Field method was introduced by Hartree in 1928. It is used to solve the nonlinear Hartree-Fock equations iteratively [43] and has been applied to the nonlinear equations of Roothaan-Hall and Pople-Nesbet. This method begins by solving the nonlinear equations with a guessed set of molecular orbital coefficients. Because the Fock

operator also depends on these coefficients a new set of coefficients will be produced along with new energies. After each iteration the coefficients are compared to the previous values and if they have not changed within a specified criterion then the procedure has reached self-consistency, and the iterative process is stopped.

The Hartree-Fock energy for the ground electronic state is then given as

$$E_{\text{HF}} = \langle \Psi_0(\mathbf{x}) | \hat{\mathbf{H}}_{\text{el}} | \Psi_0(\mathbf{x}) \rangle. \quad (2.45)$$

The accuracy of the Hartree-Fock energy lies in the size and quality of the basis set expansion of eqs. 2.26 or 2.40, and 2.41. The larger the basis set, of a particular quality, the more accurate are the energies. If the basis set is consistently increased until the energy values do not change it is said that the Hartree-Fock limit has been reached.

### Basis Sets and Natural Orbitals

The basis set used to expand the Hartree-Fock spatial orbitals ( $\psi_i$  see eq. 2.9) are typically a set of atomic functions, in a linear combination of atomic orbitals (LCAO), recall eq. 2.26

$$|\psi_i\rangle = \sum_{\mu=1}^K C_{\mu i} |\phi_{\mu}\rangle. \quad (2.46)$$

The coefficients  $C_{\mu i}$  are varied in order to minimize the energy and are known as molecular orbital expansion coefficients. The atomic orbitals  $\phi_{\mu}$  were initially introduced as a set of Slater-type orbitals (STO) which are proportional to  $e^{-\zeta r}$ . When evaluating the two electron integrals, see eqs. 2.14 and 2.15, STO orbitals are very cumbersome. Gaussian-type orbitals (GTO) are proportional to  $e^{-\alpha r^2}$ , and due to the property that the multiplication of two 1s Gaussian orbitals produces another 1s Gaussian orbital their use as a basis simplifies the evaluation of the two electron integrals. Boys proposed to use a linear combination of Gaussian-type functions to represent the STO [49]. Since that time, there has been a wide development of different types of basis sets, and for a comprehensive overview the reader is referred to [50, 51]. The calculations performed in this work were performed using the *MOLCAS* [52] package. The basis sets employed are the natural atomic orbitals [53, 54], chosen for their accuracy and compactness which tends to reduce the computational time [55, 56].

### 2.2.2 Configuration Interaction (CI)

The Hartree-Fock method accounts for some correlation of electrons with parallel spins but does not account for electrons with antiparallel spins. The correlation energy  $E_{\text{corr}}$

$$E_{\text{corr}} = E_{\text{exact}} - E_{\text{HF}} \quad (2.47)$$

is defined as the energy difference between the exact energy  $E_{\text{exact}}$  ( $\equiv E_{\text{el}}$  from eq. 2.4), within the bounds of the Born-Oppenheimer approximation, and the Hartree-Fock energy  $E_{\text{HF}}$ . This "missing" energy is negative due to the Hartree-Fock energy defining an upper bound to the energy. One way to account for the correlation energy is to expand the exact electronic wave function in terms of a linear combination of Slater Determinants.

From the Hartree-Fock description, a set of  $2K$  spin orbitals can be produced that describe a single determinant ground-state wave function for the  $N$  electrons.

$$|\Psi_0\rangle = |\chi_1\chi_2 \dots \chi_a\chi_b \dots \chi_N\rangle \quad (2.48)$$

The configuration of the  $N$  electrons is such that the lower energy spin orbitals are occupied and the higher energized  $2K-N$  virtual orbitals are not, following a basic Aufbau principle. It is clear however, that many other determinants can be formed from the many different possible excitations of the electrons.

Excited determinants can be described with respect to the HF determinant. Didactically, a singly excited determinant

$$|\Psi_a^\tau\rangle = |\chi_1\chi_2 \dots \chi_\tau\chi_b \dots \chi_N\rangle \quad (2.49)$$

is one in which a single electron is relocated from its occupied spin orbital  $a$  to one of the virtual spin orbitals  $\tau$ . And in the same manner a doubly excited determinant can be formed

$$|\Psi_{ab}^{\tau\mathfrak{s}}\rangle = |\chi_1\chi_2 \dots \chi_\tau\chi_{\mathfrak{s}} \dots \chi_N\rangle \quad (2.50)$$

where two electrons have been relocated from their original positions,  $a$  and  $b$ , to two virtual spin orbitals,  $\tau$  or  $\mathfrak{s}$ . This procedure continues until all  $N$  electrons have been promoted to various virtual states. The number of possible determinants is defined by the binomial coefficient  $\binom{2K}{N}$  and are termed accordingly to the number of electrons that have been promoted to virtual orbitals: Hartree-Fock ground state, singly, doubly,

triply, ...  $N$ -tuply excited states. The full-CI expansion of the ground-state wave function

$$|\Phi_0\rangle = |\Psi_0\rangle + \sum_{a\tau} c_a^\tau |\Psi_a^\tau\rangle + \sum_{\substack{a>b \\ \tau>s}} c_{ab}^{rs} |\Psi_{ab}^{rs}\rangle + \sum_{\substack{a>b>c \\ \tau>s>t}} c_{abc}^{rst} |\Psi_{abc}^{rst}\rangle + \dots \quad (2.51)$$

is a sum of the unique possible configurations, organized above in terms of the  $N$ -electron determinants, and is exact for a given basis.

The full CI wave function can be reduced in size based on symmetry properties. If the state that is being calculated is a singlet state of gerade symmetry, then only the configurations that share those same properties are used. In order for the configurations to be eigenfunctions of the spin and angular momentum operators, a new configuration can be generated from a linear combination of the original configurations. These configurations are termed configuration state functions (CSF). A CI calculation that is based on these considerations is still termed a full-CI, and is the best calculation one can do to recover the correlation energy.

Even if the CI wave function is represented by symmetry adapted CSFs, for larger molecules a full CI calculation is computationally impossible. It is for this reason that the CI calculation is truncated. The most common truncation is one of singles and doubles, a CISD calculation. The single configurations play an insignificant role in the determination of the correlation energy [57] but are significant in the determination of the dipole moments [58] and the double configurations tend to account for the major part of the correlation energy but are highly dependent on the basis size [41]. For larger molecules a CISD calculation is not sufficient in describing the correlation energy and the calculations can incorporate further triplet and quadruplet excitations, again at the cost of computational effort. Another shortcoming of this method is that once the CI expansion has been truncated the method is no longer size consistent nor size extensive.

Size extensive and size consistent are two problems that arise from a truncated CI calculation. A system is said to be size extensive when the energy for  $N$  noninteracting molecules equals the sum of  $N$  times the energy of the single molecule. Size consistent is a problem that refers to the dissociation of a molecule, where the energy of the molecule at bond lengths of dissociation should be equal to the sum of energies of each part.

A truncated CI calculation optimizes the CI expansion coefficients  $c$ , see eq. 2.51. An extra flexibility in the quest to retrieve the correlation energy is obtained by allowing for the optimization of the molecular orbital coefficients, eq. 2.26, and accounts for what is

termed static correlation. This is the essence of the multi-configurational self-consistent field (MCSCF) method.

### 2.2.3 Multi-configurational Self-consistent Field

The MCSCF method is also based on the variational principle, in which the minimization of the energy,

$$E = \frac{\langle \Psi^{\text{MCSCF}} | \hat{\mathbf{H}} | \Psi^{\text{MCSCF}} \rangle}{\langle \Psi^{\text{MCSCF}} | \Psi^{\text{MCSCF}} \rangle} \quad (2.52)$$

is found by varying the orbital coefficients - an optimization of the MCSCF wave function. The MCSCF wave function is a truncated CI expansion and is given equationally as

$$|\Psi^{\text{MCSCF}}\rangle = \sum_A c_A |\Phi_A\rangle \quad (2.53)$$

where the index A runs over the configuration state functions  $\Phi_A = |\psi_a \bar{\psi}_a \psi_b \bar{\psi}_b \dots\rangle$ . Each state function is composed of a set of molecular orbitals that are occupied by an  $\alpha$  spin electron  $\psi_i$  or by a  $\beta$  spin electron  $\bar{\psi}_i$ . These MOs can also be expanded in a basis of atomic orbitals as

$$|\psi_i\rangle = \sum_{\mu} C_{\mu i} |\phi_{\mu}\rangle \quad (2.54)$$

giving rise to another set of coefficients  $C_{\mu i}$ . It is the task of MCSCF to optimize all the CI expansion coefficients  $c_A$ , as well as the molecular orbital coefficients  $C_{\mu i}$  for the atomic orbitals simultaneously.

Aside from the optimization of two sets of coefficients, another difficulty that remains in the MCSCF method is the choice of the CSFs that should be used to describe the wave function. It is imperative to include the CSFs that are most important to the wanted molecular properties. The daunting task of choosing the appropriate CSFs to be included in the MCSCF wave function has been alleviated to some extent by employing the complete active space self-consistent field approach.

#### Complete Active Space Self-consistent Field (CASSCF)

The complete active space self-consistent field method is a descendant of MCSCF and has been developed by Roos *et al.* [59]. The method prevents the manual picking of every

configuration state function which should be included in the optimization of the wave function. Instead, the molecular orbitals are partitioned into two groups: the primary and secondary orbitals, as can be seen in fig. 2.1. The primary orbitals are further partitioned into two subgroups; the inactive and the active orbitals. The inactive orbitals are frozen and remain doubly occupied throughout the calculation and can be considered the core orbitals. Contrary to the primary inactive orbitals, the orbitals in the secondary space remain unoccupied. However, the active orbitals consist of a combination of occupied and unoccupied orbitals where every possible configuration, with consideration of symmetry and spatial constraints, within this space is allowed. CASSCF therefore constitutes a full-CI calculation within the restricted complete active space.

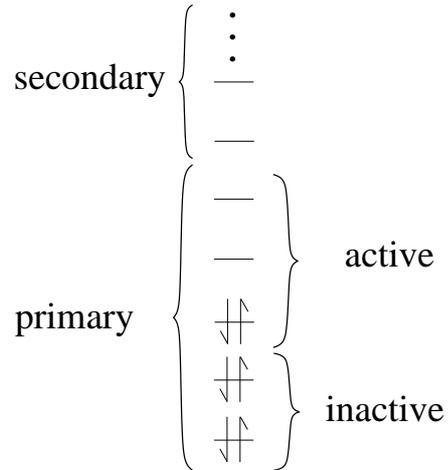
In this way, an active space defines the realm in which the electrons can form all configurations. Although this method reduces the effort of picking the CSFs, it is still not a black box. The proper orbitals that represent the molecular system and its properties must be selected by hand. A state average CASSCF (SA-CASSCF) formulation is used to calculate electronic excited states for a given symmetry and spin, by minimizing the weighted sum of their energies. The result of the minimization is the procurement of the CASSCF wave function  $|\Psi_i^{\text{CASSCF}}\rangle$  as well as the energy  $E^{\text{CASSCF}}$  for each electronic state  $i$  [59]. The method is good at obtaining the static correlation by allowing for partially occupied orbitals and describes well values at dissociation but it has difficulties in recovering the dynamic correlation, i.e. the correlation of electron motion. The dynamic correlation can be accounted for either perturbationally via a CASPT2 calculation or variationally via a multireference configuration interaction (MRCI), where the former is used in this work.

### Complete Active Space and the 2nd Order Perturbation Theory (CASPT2)

A standard approach used to recover at least part of the dynamical correlation energy is the Møller and Plesset [60] method, which is size extensive and size consistent [61]. The method is based on perturbation theory where the Hamiltonian operator  $\hat{H}$  is split into two parts: a part that is solvable  $\hat{H}_0$ , the zeroth-order Hamiltonian and a part which is not  $\lambda\hat{V}$ , the perturbation.

$$\hat{H}|\Psi_i\rangle = (\hat{H}_0 + \lambda\hat{V})|\Psi_i\rangle = E_i|\Psi_i\rangle \quad (2.55)$$

**Figure 2.1:** Within the scope of complete active space, the molecular orbitals are partitioned into two sets of orbitals; primary and secondary. The primary orbitals are further partitioned into a set of active and inactive orbitals.



The eigenenergies and eigenfunctions can be expanded as a Taylor series for small perturbations to the system  $\lambda \ll 1$ ,

$$|\Psi_i\rangle = |\Psi_i^{(0)}\rangle + \lambda|\Psi_i^{(1)}\rangle + \lambda^2|\Psi_i^{(2)}\rangle \dots \quad (2.56)$$

$$E_i = E_i^{(0)} + \lambda E_i^{(1)} + \lambda^2 E_i^{(2)} \dots \quad (2.57)$$

where  $\lambda$  is an ordering parameter. Once the eqs. 2.56, 2.57 are inserted into the eigenvalue equation, eq. 2.55, the terms can be ordered according to  $\lambda$  and the following energies expressions are retrieved.

$$E_i^{(0)} = \langle \Psi_i^{(0)} | \hat{\mathbf{H}}_0 | \Psi_i^{(0)} \rangle \quad (2.58)$$

$$E_i^{(1)} = \langle \Psi_i^{(0)} | \hat{\mathbf{V}} | \Psi_i^{(0)} \rangle \quad (2.59)$$

$$E_i^{(2)} = \langle \Psi_i^{(0)} | \hat{\mathbf{V}} | \Psi_i^{(1)} \rangle \quad (2.60)$$

If the unperturbed Hamiltonian is replaced by a sum of one-electron Fock operators, as suggested by Møller and Plesset [60], it can be shown that the first energy correction term is already included in the Hartree-Fock energy. Therefore, it is the second order energy term in eq. 2.57 that accounts for the dynamical correlation that is missing from the Hartree-Fock; this is termed second order perturbation theory (PT2).

Analogously, the dynamical correlation energy that is missing from a CASSCF calculation can be retrieved in part by applying perturbation theory [62]. The reference wave function is taken as the SA-CASSCF wave function  $|\Psi_i^{\text{CASSCF}}\rangle$  for a particular electronic state  $i$ . The CASPT2 wave function,  $|\Psi^{\text{CASPT2}}\rangle$ , is a sum of the reference wave function,  $|\Psi^{\text{CASSCF}}\rangle$ , with the first order perturbative wave function,  $|\Psi^{\text{pert}}\rangle$

$$|\Psi_i^{\text{CASPT2}}\rangle = |\Psi_i^{\text{CASSCF}}\rangle + |\Psi_i^{\text{pert}}\rangle. \quad (2.61)$$

As was seen in eq. 2.60, the second order energy correction depends on the first order wave function. For this purpose, the second order perturbation to the effective energy matrix elements,  $\mathcal{E}_{ij}$ , can be defined as

$$\mathcal{E}_{ij} = \langle \Psi_i^{\text{CASSCF}} | \hat{V} | \Psi_j^{\text{pert}} \rangle \quad (2.62)$$

and the complete CASPT2 energy for the electronic state  $i$

$$E_i^{\text{SS-CASPT2}} = E_i^{\text{CASSCF}} + \mathcal{E}_{ii} \quad (2.63)$$

is then given as a sum of the reference energy,  $E_i^{\text{CASSCF}}$  with the second order energy correction,  $\mathcal{E}_{ii}$ . This single state (SS) CASPT2 energy,  $E_i^{\text{SS-CASPT2}}$ , refers to each electronic state  $i$ . The SS-CASPT2 calculation also has its limitations. The CASSCF wave function is inadequate in describing the states around avoided crossings and where erroneous valence-Rydberg mixing occur, and therefore the multi-state CASPT2 (MS-CASPT2) was developed [63].

The MS-CASPT2 method [63] is able to describe well the near degenerate electronic states and is also able to differentiate the valence from the Rydberg states, see e.g. refs. [63, 64, 65]. Instead of using a single reference wave function, the method uses a "Perturbation Modified CASSCF" wave function  $|\Psi_i^{\text{PMCAS}}\rangle$  as the reference function: a linear combination of the CASSCF reference wave functions. The MS-CASPT2 wave function is then given below

$$|\Psi_i^{\text{MS-CASPT2}}\rangle = \underbrace{\sum_t \hat{C}_{ia} |\Psi_a^{\text{CASSCF}}\rangle}_{\Psi_i^{\text{PMCAS}}} + |\Psi_i^{\text{pert}}\rangle. \quad (2.64)$$

The Hamiltonian is reformulated with the addition of reference states and is termed the effective Hamiltonian

$$H_{ij}^{\text{eff}} = E_i^{\text{CASSCF}} \delta_{ij} + \frac{1}{2}(\mathcal{E}_{ij} + \mathcal{E}_{ji}) \quad (2.65)$$

where the diagonal elements are the SS-CASPT2 energies and the off-diagonal elements are the couplings between CASSCF electronic states  $i$  and  $j$ . This allows for the simultaneous treatment of all the electronic states being calculated and can account for a substantial amount of dynamic correlation energy. The final energies are obtained by diagonalizing the effective Hamiltonian  $H_{ij}^{\text{eff}}$ .

### 2.2.4 Density Functional Theory (DFT)

Density Functional Theory (DFT) is another method used to calculate the electronic energy of a molecular system and is based on the theorems presented by Hohenberg and Kohn [66]; therein it was shown that the ground electronic state energy can be determined by the charge density  $\rho(\mathbf{r})$ . This method differs from the HF method and its descendants by replacing the many-body electronic wave function, which depends on  $4N$  coordinates ( $3N$  spatial coordinates and the  $1N$  spin coordinate), with the electronic density, which depends only on the three cartesian coordinates  $\mathbf{r} = x, y, \text{ and } z$ .

The first theorem demonstrates the one-to-one mapping of the ground state electron density to the ground state electronic energy

$$\rho \Leftrightarrow E_0, \quad (2.66)$$

but does not provide the means to solve for the energy. The second theorem proves that the exact ground state density minimizes the total electronic energy of the molecular system. However, because the exact charge density is typically not known it is approximated by the sum of the squared one-electron wave functions:

$$\rho(\mathbf{r}) = \sum_i |\psi_i(\mathbf{r})|^2. \quad (2.67)$$

The ground state electronic energy calculated from the trial charge density  $\rho(\mathbf{r})$  represents an upper-bound to the true ground electronic state energy

$$E[\rho] \geq E_0^{\text{exact}} \quad (2.68)$$

which would be obtained if the exact electron density was known: the variational theorem.

The electronic energy functional is given below,

$$E[\rho] = T[\rho] + E_{\text{ne}}[\rho] + J[\rho] + E_{\text{xc}}[\rho] \quad (2.69)$$

and is composed as the sum of several functionals:  $T[\rho]$ , which denotes the kinetic energy;  $E_{\text{ne}}[\rho]$ , which denotes the attraction between the nuclei and the electrons;  $J[\rho]$ , which represents the Coulomb repulsion between electrons; and  $E_{\text{xc}}[\rho]$ , the exchange term which has no classical counterpart. From the list of functionals, only the calculation of  $J[\rho]$  is known.

The Kohn-Sham approach [67] introduces orbitals back into DFT in order to calculate exactly the non-interacting kinetic energy. Minimizing the energy produces a set of equations known as the Kohn-Sham equations

$$\left[ -\frac{\hbar^2}{2m} \nabla^2 + \mathbf{V}_{\text{eff}}(\mathbf{r}) \right] |\psi_{\text{KS}}(\mathbf{r})\rangle = E_{\text{el}} |\psi_{\text{KS}}(\mathbf{r})\rangle, \quad (2.70)$$

which are solved iteratively. The main difference between Kohn-Sham and the HF equations is the form of the effective potential, which for the DFT method is defined as

$$\mathbf{V}_{\text{eff}}(\mathbf{r}) = \mathbf{V}(\mathbf{r}) + \int \frac{e^2 \rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \mathbf{V}_{\text{xc}}(\mathbf{r}) \quad (2.71)$$

where the second term denotes the classical electrostatic Hartree term and the final term  $\mathbf{V}_{\text{xc}}$  is the exchange correlation potential, which accounts for the many-particle interactions. The exchange potential is defined as the partial derivative of the exchange energy functional with respect to the charge density:

$$\mathbf{V}_{\text{xc}}(\mathbf{r}) = \frac{\delta E_{\text{xc}}[\rho]}{\delta \rho(\mathbf{r})}. \quad (2.72)$$

If the exact form of the exchange energy,  $E_{\text{xc}}$  were known, then DFT would solve for the exact total energy of the system. Because it is not known, the art of a DFT calculation is to find a functional that describes this energy well. For the extension of the stationary DFT to time-dependent situations, the reader is referred to ref. [68].

## 2.3 Solution to the Nuclear Schrödinger Equation

In the previous section 2.2, the methods for solving the electronic Schrödinger equation were discussed. In this section the focus is turned to the solution of the nuclear Schrödinger equation, eq. 2.6. The nuclear motion can be divided up into translational, vibrational and rotational modes. The nuclear wave functions and energies can be written approximately as a product and as a sum of the individual components, respectively.

$$|\Psi_{\text{el,nu}}\rangle = |\Psi_{\text{nu}}^{\text{tran}}\rangle |\Psi_{\text{el,nu}}^{\text{rot}}\rangle |\Psi_{\text{el,nu}}^{\text{vib}}\rangle \quad (2.73)$$

$$E_{\text{el,nu}} = E_{\text{nu}}^{\text{tran}} + E_{\text{el,nu}}^{\text{rot}} + E_{\text{el,nu}}^{\text{vib}} \quad (2.74)$$

The constant energy from the translational motion is solved by using the particle in the box method [42] within the space-fixed coordinates, in contrast to the internal energy, which

involves rotational and vibrational energy. In this work, the rotational motion has not been considered, and therefore the following section will describe solving the vibrational eigenvalue equations using the Fourier Grid Hamiltonian (FGH) method within the body-fixed frame, a frame that nicely describes the vibrations of the nuclei with respect to one another.

### 2.3.1 Fourier Grid Hamiltonian Method

The bound state eigenvalues and eigenfunctions can be calculated numerically by implementing the Fourier Grid Hamiltonian (FGH) method [69, 70]. The advantages of the FGH method are first its simplicity and second its capability of generating accurate eigenvalues and eigenfunctions. Calculation of the eigenvalues and eigenfunctions depends significantly on the dimensionality of the problem, and is therefore restricted to a few, depending on the grid size and the computer's capacities. Here the development of the theory is given in one-dimension but can be extended to multi-dimensions. Let us consider a single particle of mass  $m$  or molecular fragments with reduced mass  $m$  moving along one direction, the  $x$  direction. The Hamiltonian operator for such a case can be written as

$$\hat{\mathbf{H}} = \hat{\mathbf{T}} + \mathbf{V}_{\text{el}}(\hat{\mathbf{x}}) = \frac{\hat{\mathbf{p}}^2}{2m} + \mathbf{V}_{\text{el}}(\hat{\mathbf{x}}), \quad (2.75)$$

where the kinetic term  $\hat{\mathbf{T}}$  depends on the momentum operator  $\hat{\mathbf{p}}$ , and the potential term  $\mathbf{V}_{\text{el}}$  depends on the position operator  $\hat{\mathbf{x}}$ . Because the wave functions of the Hamiltonian operator are calculated directly as the amplitudes of the wave function at its position on the grid, it is necessary to discretize the space.

#### Space Discretization

In this case a grid is built up from a series of uniformly spaced intervals. In the coordinate representation, by defining the total number of points  $N$  and the spacing  $\Delta x$ , the definite value of the position along the grid is given as

$$x_i = x_{\text{min}} + i\Delta x, \quad (2.76)$$

where  $i$  is a value between 0 and  $N - 1$ . The length of the grid is simply the product of the number of points times the spacing,  $L = (N - 1) \cdot \Delta x$ , and the maximum value of the coordinate is  $x_{\text{max}} = x_{\text{min}} + L$ .

The momentum spacing  $\Delta k$  on a grid of  $N$  points is inversely proportional to the uniform spacing of the position  $\Delta x$  and is given as

$$\Delta k = 2\pi/N\Delta x. \quad (2.77)$$

In momentum space, the values of  $k$  are equally distributed around the central point  $k = 0$ , when considering an odd number of grid points  $N$  (for an even number of grid points, see ref. [70]). The number  $n$  of positive and negative momentum values is then equal to

$$n = \frac{N - 1}{2}. \quad (2.78)$$

The  $i^{\text{th}}$  discrete value of  $k$  along the grid can be defined as

$$k_i = i\Delta k + k_{\min}, \quad (2.79)$$

where  $k_{\min} = -n\Delta k$  and the index  $i$  runs from 0 to  $N - 1$ . Because the momentum is evenly distributed along the grid around the zero central point, with an equal number of positive values and negative values, it may be more convenient to give the discrete value of  $k$  in terms of another index  $l$  which runs from  $-n$  to  $+n$ :

$$k_l = l\Delta k. \quad (2.80)$$

## Position and Momentum Operators

The discretization of the momentum and coordinate space also affects the position and momentum operators which in turn alters respectively the potential and kinetic operators, therefore the position and momentum operators will also be discretized. The position operator  $\hat{x}$  acting on a basis vector  $|x_i\rangle$  has the following solution

$$\hat{x}|x_i\rangle = x_i|x_i\rangle. \quad (2.81)$$

The orthogonal and completeness relations for the infinite space are

$$\hat{I}_x = \int_{-\infty}^{\infty} |x\rangle\langle x|dx \quad \text{and} \quad \langle x_i|x_j\rangle = \delta(x_i - x_j) \quad (2.82)$$

as well as for the discretized space

$$\hat{I}_x = \sum_{i=0}^{N-1} |x_i\rangle\Delta x\langle x_i| \quad \text{and} \quad \Delta x\langle x_i|x_j\rangle = \delta_{ij}. \quad (2.83)$$

The potential, which depends on the position operator, is diagonal, as exemplified by the delta function  $\delta_{ij}$ , in the coordinate representation

$$\langle x_j | \mathbf{V}_{el}(\hat{\mathbf{x}}) | x_i \rangle = \frac{V_{el}(x_i) \delta_{ij}}{\Delta x}. \quad (2.84)$$

The eigenfunctions of the momentum operator can be written in the same fashion as for the position operator

$$\hat{\mathbf{p}} | k_l \rangle = k_l \hbar | k_l \rangle, \quad (2.85)$$

where the orthogonal and completeness relations for the infinite space are

$$\hat{I}_k = \int_{-\infty}^{\infty} |k\rangle \langle k| dk \quad \text{and} \quad \langle k_m | k_n \rangle = \delta(k_m - k_n) \quad (2.86)$$

as well as for the discretized space

$$\hat{I}_k = \sum_{-n}^n |k_l\rangle \Delta k \langle k_l| dk \quad \text{and} \quad \Delta k \langle k_m | k_n \rangle = \delta_{mn}. \quad (2.87)$$

The kinetic operator is nonlocal in the coordinate representation but is diagonal in the momentum and is represented equationally as

$$\langle k_m | \hat{\mathbf{T}} | k_n \rangle = \frac{(l\Delta k)^2}{2m} \delta_{mn}. \quad (2.88)$$

Finally the transformation matrix elements between the momentum  $k$  and the coordinate space  $x$  can be written as

$$\langle k_l | x_i \rangle = \frac{1}{\sqrt{2\pi}} e^{-il\Delta k x_j} \quad (2.89)$$

which lends itself for Fourier transformation (FT) [71].

## Wave Function

The kinetic operator is easily solvable in momentum space, and consequently the wave function too must be represented in the same space. Keeping with the grid representation, the wave function in coordinate space can be transformed to the momentum space via a discrete Fourier transform. Starting with the definition of the wave function in coordinate space, and inserting the identity operator for the momentum space one can make the

following derivation:

$$\begin{aligned}
|\Psi_{\text{el}}(x)\rangle &= \hat{I}_x |\Psi_{\text{el}}(x)\rangle = \sum_{i=0}^{N-1} |x_i\rangle \Delta x \langle x_i | \Psi_{\text{el}}(x)\rangle & (2.90) \\
&= \sum_{i=0}^{N-1} |x_i\rangle \Delta x \langle x_i | \hat{I}_k \Psi_{\text{el}}(x)\rangle \\
&= \sum_{i=0}^{N-1} |x_i\rangle \Delta x \sum_{l=-n}^n \langle x_i | k_l \rangle \Delta k \langle k_l | \Psi_{\text{el}}(x)\rangle \\
&= \frac{\sqrt{2\pi}}{N} \sum_{i=0}^{N-1} |x_i\rangle \sum_{l=-n}^n e^{il\Delta k x_j} |\Psi_{\text{el}}(k_l)\rangle \\
\langle x_i | \Psi_{\text{el}}(x)\rangle &= \frac{\sqrt{2\pi}}{N} \sum_{i=0}^{N-1} \langle x_i | x_i \rangle \sum_{l=-n}^n e^{il\Delta k x_j} |\Psi_{\text{el}}(k_l)\rangle & (2.91)
\end{aligned}$$

Multiplication from the left with  $\langle x_i |$  was carried out above in order to define the wave function at a specific point  $x_i$ . In doing so, one obtains the following equation

$$|\Psi_{\text{el}}(x_i)\rangle = \frac{\sqrt{2\pi}}{N} \sum_{l=-n}^n e^{il\Delta k x_j} |\Psi_{\text{el}}(k_l)\rangle \quad (2.92)$$

which is the Fourier transformation from  $k$  space to  $x$  space. Following the same procedure, the back Fourier transform, that is from the  $x$  space to the  $k$  space, can be shown to have the following form for a discretized space

$$|\Psi_{\text{el}}(k_l)\rangle = \frac{\sqrt{2\pi}}{N} \sum_{i=0}^{N-1} e^{-il\Delta k x_j} |\Psi_{\text{el}}(x_i)\rangle. \quad (2.93)$$

## Discretization of the Hamiltonian

It is the goal of the FGH to solve the matrix elements of the discretized Hamiltonian in coordinate space. Starting from eq. 2.75, we can consider the matrix elements of the Hamiltonian

$$H_{\text{el},ij} = \langle x_i | \hat{\mathbf{H}} | x_j \rangle = \langle x_i | \hat{\mathbf{T}} | x_j \rangle + \langle x_i | \mathbf{V}_{\text{el}}(\hat{\mathbf{x}}) | x_j \rangle \quad (2.94)$$

as the sum of the kinetic and potential terms. The kinetic term should be represented in the momentum space where it is diagonal, therefore the unitary operator  $I_k$  is inserted into eq. 2.94.

$$H_{\text{el},ij} = \sum_{l=-n}^n \langle x_i | k_l \rangle T_l \Delta k \langle k_l | x_j \rangle + \langle x_i | \mathbf{V}_{\text{el}}(\hat{\mathbf{x}}) | x_j \rangle \quad (2.95)$$

The matrix elements for each term above have been discussed, and by inserting the space transformation eq. 2.89 as well as the matrix elements for the potential term, eq. 2.84, the Hamiltonian can be rewritten in terms of a discrete grid

$$H_{\text{el},ij} = \frac{1}{N\Delta x} \sum_{l=-n}^n e^{il\Delta k(x_i-x_j)} T_l \Delta k + \frac{V_{\text{el}}(x_i)\delta_{ij}}{\Delta x} \quad (2.96)$$

where the kinetic term has the following form

$$T_l = \frac{\hbar^2(l\Delta k)^2}{2m}. \quad (2.97)$$

The method for calculating the effect of the kinetic operator is an efficient approach of applying the FT method in which the wave function is transformed to the momentum space via a forward Fourier transformation. In this representation the kinetic term (equation 2.97) is applied by multiplication to the wave function. The wave function is then back Fourier transformed for the contribution from the potential term, which is simply the value of the potential  $V(x_i)$  at the point  $x_i$  on the grid. The Fourier transform method used in this work uses a fast Fourier transform algorithm that computes as  $N\log_2 N$  in comparison to FT which computes as  $N^2$  [72], which saves a significant amount of computation time.

The discretized Hamiltonian can be further simplified by combining the positive and negative  $l$  terms

$$H_{\text{el},ij} = \frac{1}{\Delta x} \left\{ \frac{2}{N} \sum_{l=1}^n \cos\left(\frac{l2\pi(i-j)}{N}\right) T_l + V_{\text{el}}(x_i)\delta_{ij} \right\} \quad (2.98)$$

and the expectation value of the energy can be written as

$$E_{\text{el}}^v = \frac{\langle \Psi_{\text{el}} | \hat{\mathbf{H}} | \Psi_{\text{el}} \rangle}{\langle \Psi_{\text{el}} | \Psi_{\text{el}} \rangle} = \frac{\sum_{ij} \Psi_{\text{el},i}^* \Delta x H_{\text{el},ij} \Delta x \Psi_{\text{el},j}}{\Delta x \sum_i |\Psi_{\text{el},i}|^2} \quad (2.99)$$

where the variational method seeks to minimize the energy. Once the  $H_{\text{el},ij}$  are obtained, the vibrational states  $v$  in the electronic states el can be obtained from the secular equations

$$\sum_j [H_{\text{el},ij} - E_{\text{el}}^v \delta_{ij}] |\Psi_{\text{el},j}^v\rangle = 0 \quad (2.100)$$

where the bound-state vibrational eigenvalues are given as  $E_{\text{el}}^v$  and the eigenvectors as  $|\Psi_{\text{el},j}^v\rangle$ .

The dynamic simulations that were done in this work start from the vibrational ground state wave function in the electronic ground state,  $|\Psi_0^0\rangle$ , calculated from the FGH method.

The ground electronic state eigenvalues,  $E_0^v$ , used to determine the vibrational frequencies were also obtained from this method. Now that both the electronic and nuclear terms have been solved for, and we are equipped with the ingredients needed for dynamic simulations, attention is turned to quantum dynamics and solving the time-dependent Schrödinger equation.