

# Contents

|          |   |           |
|----------|---|-----------|
| <b>1</b> | <b>Introduction</b>   | <b>3</b>  |
| 1.0.1    | Notation . . . . .  | 3         |
| <b>2</b> | <b>Quantum Chemistry</b>                                    | <b>5</b>  |
| 2.1      | Quantum Mechanics (QM) . . . . .                            | 5         |
| 2.1.1    | The Postulates of QM . . . . .                              | 5         |
| 2.1.2    | The Schrödinger Equation (SE) . . . . .                     | 7         |
| 2.2      | Two particle system . . . . .                               | 8         |
| 2.2.1    | The Hamiltonian . . . . .                                   | 8         |
| 2.2.2    | The Wave Function . . . . .                                 | 10        |
| 2.2.3    | The energies . . . . .                                      | 12        |
| 2.3      | Many body systems . . . . .                                 | 12        |
| 2.3.1    | Born-Oppenheimer (BO) approximation . . . . .               | 12        |
| 2.3.2    | Variational Principle . . . . .                             | 13        |
| 2.3.3    | Self Consistent Field (SCF) . . . . .                       | 14        |
| <b>3</b> | <b>Multiwavelet (MW) Basis</b>                              | <b>15</b> |
| 3.1      | Multi-Resolution Analysis (MRA) . . . . .                   | 15        |
| 3.1.1    | Definition . . . . .  | 15        |
| 3.1.2    | Wavelet MRA . . . . .                                       | 16        |
| 3.1.3    | Projecting a gaussian function example . . . . .            | 17        |
| 3.2      | MW MRA . . . . .  | 18        |
| 3.2.1    | Constructing the basis functions . . . . .                  | 18        |
| 3.2.2    | Choices of Scaling functions . . . . .                      | 20        |
| 3.3      | Operators . . . . .   | 20        |
| 3.3.1    | Nonstandard (NS) form Representation of Operators . . . . . | 20        |
| 3.3.2    | Integral operators . . . . .                                | 21        |
| 3.3.3    | Differential operators . . . . .                            | 21        |
| 3.4      | Software . . . . .  | 21        |
| <b>4</b> | <b>Solvent Effect</b>                                       | <b>23</b> |
| 4.1      | Formulation of the Problem . . . . .                        | 23        |
| 4.2      | Explicit solvation models . . . . .                         | 23        |
| 4.3      | Implicit solvation models . . . . .                         | 23        |
| 4.3.1    | Polarizable Continuum Model (PCM) . . . . .                 | 23        |
| 4.4      | PCM and MW basis . . . . .                                  | 23        |
| 4.5      | Solving the Problem . . . . .                               | 23        |
| 4.5.1    | Generalized poisson equation . . . . .                      | 23        |

|          |  |           |
|----------|--|-----------|
| 4.5.2    | SCF for PCM . . . . .                                    | 23        |
| <b>5</b> | <b>Variational Implementation of the solvent effect</b>  | <b>25</b> |
| <b>6</b> | <b>Implementation</b>                                    | <b>27</b> |
| 6.1      | PCM . . . . .  | 27        |
| 6.1.1    | Dielectric function . . . . .                            | 27        |
| 6.1.2    | Differences and limitations in implementations . . . . . | 28        |
| 6.2      | Reaction potential . . . . .                             | 28        |
| 6.3      | Software used . . . . .                                  | 28        |
| <b>7</b> | <b>Results</b>   | <b>29</b> |

# Chapter 1

## Introduction

### 1.0.1 Notation

When working with quantum chemistry simplify equations or in order to give a better intuition on what is possible arithmetically. Therefore it is needed to clarify what most of the different symbols and representations mean in this subject. Following are most of the notations used through this paper. Further exceptions to the notation will be clarified where needed throughout the paper.

**Operators, scalars, vectors and matrices** In this text, we will be using objects called operators. These operators represent certain operations applied to functions. We represent as  $\hat{O}$  exchanging the letter as needed.

Scalars are constants, or coefficients without variables. They will be referred with lower case letters.

Vectors will be represented with lower case letters as  $\vec{a}$ , while matrices will be represented with upper case as  $\vec{A}$ .

**Order of operations** Operators are applied from the left onto functions. Applying the operator  $\hat{O}$  and then operator  $\hat{A}$  onto the function  $\Psi(x)$  will be written as follows

$$\hat{A}\hat{O}\Psi(x) \quad (1.1)$$

**commutation** Two operators  $\hat{O}$  and  $\hat{A}$  are said to commute if:

$$\hat{O}\hat{A} = \hat{A}\hat{O} \quad (1.2)$$

$$\hat{O}\hat{A} - \hat{A}\hat{O} = 0 \quad (1.3)$$

This operation is written with square brackets, e.g. the operation in 1.3 is written as  $[\hat{O}, \hat{A}]$ .

**Dirac notation** In this thesis we will be using Dirac notation for the most part. In this notation the quantum state described by a wave function  $\Psi$  is written as a state vector  $|Psi\rangle$  [3] called **ket**. Its complex conjugate is called a **bra** and is written as  $\langle\Psi|$ . We will interchange between this and standard

notation as needed, in order to give more clarity to the equations used. The scalar product between a bra and a ket is defined as:

$$\langle \Psi | \Psi \rangle = \int_{\mathbb{R}} \Psi^* \Psi dr \quad (1.4)$$

Where integration rules apply.

Two functions are orthonormal if:

$$\langle \Psi_i | \Psi_j \rangle = \delta_{ij} \quad (1.5)$$

Where  $\delta_{ij}$  is the Kronecker delta which equals one when  $i = j$  and zero when  $i \neq j$  [3, 6].

## Chapter 2

# Quantum Chemistry

### 2.1 QM

#### 2.1.1 The Postulates of QM

QM are based on a set rules that define operations and states. We will present these rules as six different postulates of QM (sometimes divided as 5) [3, 6].

##### First Postulate

The first postulate states that everything we can know about a physical system can be extracted from the wavefunction  $\Psi(x, t)$  of that system [3]. Additionally at a time  $t_0$  the system is defined by a state vector (or wavefunction)  $|\Psi(t_0)\rangle \in L^2$  that has a defined finite scalar product as [6]:

$$\langle \Psi | \Psi \rangle = \| |\Psi\rangle \|^2 = \int_{\mathbb{R}^3} \Psi^* \Psi d\vec{r} \quad (2.1)$$

##### Second Postulate

An generic observable  $O$  is represented by a generic operator  $\hat{O}$ . Two such observables are the position and momentum of a particle. These are represented by  $\hat{q}_i$  and  $\hat{p}_i$  respectively, where  $i = \{x, y, z\}$ . These operators fulfill the following commutation relations [3, 6]:

$$\begin{aligned} [q_i, p_j] &= i\hbar\delta_{ij} \\ [q_i, q_j] &= 0 \\ [p_i, p_j] &= 0 \end{aligned} \quad (2.2)$$

The operators that represent observables are hermitian, meaning that [6]:

$$\hat{O} = (\hat{O}^*)^T = (\hat{O}^T)^* = \hat{O}^\dagger \quad (2.3)$$

Which means that they hold the following commutation relation [6]:

$$[\hat{O}, \hat{O}^\dagger] = 0 \quad (2.4)$$

These operators are linear as well:

$$\hat{O}(f + g) = \hat{O}f + \hat{O}g \quad (2.5)$$

Where  $f$  and  $g$  are functions.

### Third Postulate

When applying the generic operator to the state vector,  $\hat{O}|\Psi_i\rangle$ , one can only measure of the spectrum of eigenvalues  $o_i$  of the operator  $\hat{O}$  only one such value. The following equation will hold if  $|\Psi_i\rangle$  is an eigenfunction of  $\hat{O}$  [6, 2]:

$$\hat{O}|\Psi_i\rangle = o_i|\Psi_i\rangle \quad (2.6)$$

Where we multiply on the left on both sides of the equation with  $\langle\Psi_i|$  giving us

$$\langle\Psi_i|\hat{O}|\Psi_i\rangle = \langle\Psi_i|o_i|\Psi_i\rangle \quad (2.7)$$

We can take the constant  $o_i$  outside the integral, and use the fact that the wavefunctions are normalized:

$$\begin{aligned} \langle\Psi_i|\hat{O}|\Psi_i\rangle &= o_i \langle\Psi_i|\Psi_i\rangle \\ \langle\Psi_i|\hat{O}|\Psi_i\rangle &= o_i \end{aligned} \quad (2.8)$$

The Equation 2.6 is an eigenvalue equation and if the operator is the Hamiltonian  $\hat{H}$  then 2.6 becomes the SE [7].

### Fourth Postulate

The fourth postulate states the possible probabilities of getting a specific eigenvalue for a given measurement. Let  $|\Psi_i\rangle$  be an eigenfunction of  $\hat{O}$  such that:

$$\hat{O}|\Psi_i\rangle = o_i|\Psi_i\rangle \quad (2.9)$$

and

$$|\Psi\rangle = \sum_i c_i |\Psi_i\rangle \quad (2.10)$$

has no degenerate eigen-values, The probability of measuring eigen-value  $o_i$  from  $|\Psi\rangle$  is given by [6]:

$$\begin{aligned} \mathcal{P}(o_i) &= |\langle\Psi_i|\Psi\rangle|^2 \\ &= \sum_j c_i^* c_j \langle\Psi_i|\Psi_j\rangle \\ &= \sum_j c_i^* c_j \delta_{ij} \\ &= |c_i|^2 \end{aligned} \quad (2.11)$$

Following the equation 2.11 the probability of measuring the eigen-value  $o_i$  from  $|\Psi_i\rangle$  is just one. The sum of all the probabilities for each eigen-value is:

$$\sum_i \mathcal{P}(o_i) = \sum_i |c_i|^2 = 1 \quad (2.12)$$

Here we have ignored the case for degenerate eigen-values and continuous spectra of eigen-values, where the method is analogous to the one used above. The reader is invited to look them up themselves in [6, 3].

### Fifth Postulate

The fifth postulate states that immediately after a measurement where the eigenvalue was  $o_i$  the state of the system  $|\Psi\rangle$  collapses into a state where the only value one can measure is  $o_i$ , that is  $|\Psi_i\rangle$  using the conventions stated in postulate 3 and 4. This is because before measuring, the probabilities for *any* eigen-value is as stated in the fourth postulate. When the value has been measured, though, the uncertainty doesn't exist, as the state of the system must be one that gives exactly that value. The following Equation 2.13 represents the postulate.

$$|\Psi\rangle \xrightarrow{o_i} |\Psi_i\rangle \quad (2.13)$$

### Sixth Postulate

The system when undisturbed changes in a deterministic way [6]. This change is governed by the time dependent SE [6, 3]:

$$i\hbar \frac{\partial}{\partial t} |\Psi\rangle = \hat{H} |\Psi\rangle \quad (2.14)$$

Where  $\hat{H}$  is the Hamiltonian operator which has the total energy of the system as its eigen-values.

#### 2.1.2 The SE

Lets consider the following SE for a particle allowed to move in only one dimension and where its potential energy varies with position (e.g. the Harmonic oscillator model [6, 2]).

$$\hat{H}\Psi = \left( -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \hat{V}(x) \right) \Psi = i\hbar \frac{\partial}{\partial t} \Psi \quad (2.15)$$

We can substitute

$$\Psi(x, t) = \psi(x)\tau(t)$$

into 2.15 by assuming that the wavefunction can be separated into spatial and time dependent functions [3]:

$$\begin{aligned} \left( -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \hat{V}(x) \right) \psi\tau &= i\hbar \frac{\partial}{\partial t} \psi\tau \\ -\frac{\hbar^2}{2m} \tau \frac{d^2\psi}{dx^2} + \hat{V}(x)\psi\tau &= i\hbar \psi \frac{d\tau}{dt} \\ -\frac{\hbar^2}{2m} \frac{1}{\psi} \frac{d^2\psi}{dx^2} + \hat{V}(x) &= i\hbar \frac{1}{\tau} \frac{d\tau}{dt} \end{aligned} \quad (2.16)$$

In the last step of the Equation 2.16 we divided both sides with  $\frac{1}{\tau\psi}$ . This shows us that, since the left-hand side of the equation is only dependent on  $x$  and the right-hand side is only dependent on  $t$ , no matter how much we change each of the coordinates, they must always equal to a constant. This constant will be denoted by  $E$  as it is the energy of the system. This gives us the following set

of equations [3]:

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + \hat{V}(x)\psi = E\psi \quad (2.17a)$$

$$i\hbar \frac{d\tau}{dt} = E\tau \quad (2.17b)$$

Equation 2.17b can be solved by observation as [3, 6] :

$$\tau(t) = e^{-iE\frac{t}{\hbar}} \quad (2.18)$$

while the remaining Equation 2.17a can be rewritten as

$$\hat{H}\psi = E\psi \quad (2.19)$$

Which is the time-independent SE which will be used most on this text.

## 2.2 Two particle system

### 2.2.1 The Hamiltonian

Consider a one electron system (such as H or  $\text{He}^+$ ) which contains an electron and a nucleus, which are described using three dimensional coordinates  $x$ ,  $y$  and  $z$ . The Hamiltonian contains terms for the kinetic  $T$  and potential energy  $V$  contributions of both the nucleus  $N$  and the electron  $e$ . In a one electron system in vacuum the Hamiltonian for the time independent SE would be as follows [11, 7].

$$\begin{aligned} \hat{H} &= \hat{T}_N + \hat{T}_e + \hat{V} \\ \hat{T}_N &= -\frac{\hbar^2}{2m_N} \nabla_N^2 \\ \hat{T}_e &= -\frac{\hbar^2}{2m_e} \nabla_e^2 \\ \hat{V} &= -\frac{Z}{\|\vec{r}_N - \vec{r}_e\|} \end{aligned} \quad (2.20)$$

Where the operator  $\nabla^2$  is the Laplacian computing the second partial derivative  $\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$  for the coordinates of the electron  $\vec{r}_e$  and the nucleus  $\vec{r}_N$ ,  $m$  is the mass of the electron and the nucleus depending on the subscript  $N$ . The potential is the coulomb interaction between the electrons, which is calculated by dividing the nuclear charge of the atom  $Z$  with the distance between the electron and the nucleus  $\|\vec{r}_N - \vec{r}_e\|$ . Note that we will be using Atomic units in all the equations from here onwards, meaning that, although the equations presented contain constants such as  $\hbar$  in literature such as in [2], these will be presented with their value in atomic units (which is one for  $\hbar$ ).

We can see that the kinetic energy operators are separable, as they are only dependent on their respective particle coordinates. The potential energy operator, on the other hand, is not separable, as it is dependent in the coordinates of both the nucleus and the electron.



In order to solve the SE analytically one must first change into a center of mass coordinate system :

$$\begin{aligned}\mathbf{X} &= \frac{m_N x_N + m_e x_e}{m_N + m_e} & ; & \quad x = x_N - x_e \\ \mathbf{Y} &= \frac{m_N y_N + m_e y_e}{m_N + m_e} & ; & \quad y = y_N - y_e \\ \mathbf{Z} &= \frac{m_N z_N + m_e z_e}{m_N + m_e} & ; & \quad z = z_N - z_e\end{aligned}\tag{2.21}$$

Where the  $\mathbf{XYZ}$ -coordinates define a system centered in the center of mass, while the  $xyz$ -coordinates specify the relative position of the two particles [11]. Applying this coordinate system to the Hamiltonian in Equation 2.20 yields:

$$\hat{H} = -\frac{1}{2}\nabla_{\mathbf{XYZ}}^2 - \frac{1}{2\mu}\nabla_{xyz}^2 - \frac{Z}{\sqrt{x^2 + y^2 + z^2}}\tag{2.22}$$

Where the first term in Equation 2.22 describes the motion of the whole system with respect to a fixed coordinate system. The second term describes the relative motion of a pseudo-particle with reduced mass:

$$\mu = \frac{m_N m_e}{m_N + m_e} = \frac{m_e}{1 + \frac{m_e}{m_N}}\tag{2.23}$$

Given that the nucleus is more massive than the electron (the nucleus is 1800 times more massive than the electron in a Hydrogen atom [11])  $\mu$  can be approximated to the mass of the electron  $m_e$ . This lets us assume that the nucleus is stationary in relation with the electron.

The third term is the potential energy which still is dependent on the distance between the two particles. In this center of mass system the distance is just determined by the  $xyz$ -coordinates.

The electron's motion occurs at fixed distances from the nucleus and can be anywhere in a sphere around it. Therefore it is advantageous to use polar coordinates to solve the SE. In this coordinate system  $r$  describes the distance to the center,  $\theta$  describing the angle of the particle with respect to the  $z$ -axis and  $\phi$  describes the polar angle on the  $xy$ -plane. Applying this to the Hamiltonian in Equation 2.22 gives [2]:

$$\begin{aligned}\hat{H}_{r\theta\phi} &= -\frac{1}{2\mu}\nabla_{r\theta\phi}^2 - \frac{Z}{r} \\ \nabla_{r\theta\phi}^2 &= \frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + \frac{1}{r^2}\Lambda^2 \\ \Lambda^2 &= \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\end{aligned}\tag{2.24}$$

The operator  $\Lambda^2$  is the Legendrian operator [2].

### 2.2.2 The Wave Function

#### Separation of variables

We Substitute the Equations in 2.24 into Equation 2.19 in the following Equation 2.25.

$$\begin{aligned} \hat{H}_{r\theta\phi}\Psi &= E\Psi \\ -\frac{1}{2\mu}\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}\Psi + \frac{1}{2\mu}\frac{1}{r^2}\Lambda^2\Psi - \frac{Z}{r}\Psi &= E\Psi \end{aligned} \quad (2.25)$$

we can easily see that we can separate the wavefunction into two parts; a Radial function  $R(r)$  and an angular function  $Y(\theta, \phi)$ :

$$\Psi(r, \theta, \phi) = R(r)Y(\theta, \phi)$$

which we substitute into Equation 2.25:

$$\begin{aligned} \left(-\frac{1}{r^2}\frac{1}{2\mu}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + \frac{1}{2r^2}\Lambda^2 - \frac{Z}{r}\right)RY &= ERY \\ -\frac{1}{r^2}Y\frac{1}{2\mu}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}R + \frac{1}{2r^2}R\Lambda^2Y - \frac{Z}{r}RY &= ERY \\ -\frac{1}{r^2}\frac{1}{R}\frac{1}{2\mu R}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}R + \frac{1}{2r^2}\frac{1}{Y}\Lambda^2Y - \frac{Z}{r} &= E \end{aligned} \quad (2.26)$$

Here we assumed that  $\mu \approx m_e = 1A.U.$  This is separable into a radial equation and an angular equation:

$$-\frac{1}{2r^2}\frac{1}{R}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}R = \varepsilon_r \quad (2.27a)$$

$$\frac{1}{2r^2}\frac{1}{Y}\Lambda^2Y = \varepsilon_{\theta\phi} \quad (2.27b)$$

$$E = \varepsilon_{\theta\phi} + \varepsilon_r - \frac{Z}{r} \quad (2.27c)$$

We can assume the  $\frac{1}{r^2}$  to be a constant on the angular partial differential equation as we are solving for an electron orbiting on a sphere around the nucleus. This means that the radius behaves like a parameter and we can write

$$2r^2\varepsilon_{\theta\phi} = \varepsilon_{\theta\phi r}$$

. We can further separate the variables of Equation 2.27b by substituting  $\Lambda^2$  from 2.24 and  $Y(\theta, \phi) = \Theta(\theta)\Phi(\phi)$  into it:

$$\begin{aligned} \varepsilon_{\theta\phi r} &= \frac{1}{Y}\Lambda^2Y \\ \varepsilon_{\theta\phi r} &= \frac{1}{\Theta\Phi} \left( \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} \right) \Theta\Phi \\ \varepsilon_{\theta\phi r} &= \frac{1}{\Theta\Phi} \left( \Phi\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\Theta + \Theta\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\Phi \right) \\ \varepsilon_{\theta\phi r} &= \frac{1}{\Theta}\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\Theta + \frac{1}{\Phi}\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\Phi \\ -\frac{1}{\Phi}\frac{\partial^2}{\partial\phi^2}\Phi &= \frac{1}{\Theta}\sin\theta\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\Theta - \varepsilon_{\theta\phi r}\sin^2\theta \end{aligned} \quad (2.28)$$

Once again we have an equation where each side is dependent on a different variable, which tells us that both terms must equal a constant, which we will call  $m_l^2$ , giving us the three different sets of differential equations needed to be solved for the wavefunction [2, 15, 3].

$$-\frac{1}{R} \frac{1}{2r^2} \frac{d}{dr} r^2 \frac{d}{dr} R = \varepsilon_r \quad (2.29a)$$

$$-\frac{1}{\Phi} \frac{d^2}{d\phi^2} \Phi = m_l^2 \quad (2.29b)$$

$$\frac{1}{\Theta} \sin \theta \frac{d}{d\theta} \sin \theta \frac{d}{d\theta} \Theta - \varepsilon_{\theta\phi r} \sin^2 \theta = m_l^2 \quad (2.29c)$$

$$\varepsilon_r + \frac{1}{2r^2} \varepsilon_{\theta\phi r} - \frac{Z}{r} = E \quad (2.29d)$$

### Solutions to the differential equations

We will start by solving the Equation 2.29b. Shifting terms around one can see that it is a second order linear differential equation

$$\frac{d^2}{d\phi} \Phi + m_l^2 \Phi = 0$$

which has general solution as follows [8, 15, 3]:

$$\Phi(\phi) = Ae^{im_l\phi} + Be^{-im_l\phi} \quad (2.30)$$

We limit ourselves to the form of Equation 2.30 where  $B = 0$  to simplify notation. Two requirements need to be met by this solution in order for it to be a valid solution to the SE.

The first requirement is that it needs to be single valued, that means it has a cyclic boundary condition [15, 3] where  $\Phi(\phi) = \Phi(\phi + 2\pi)$ . Which means the following must hold:

$$Ae^{im_l\phi} (1 - e^{im_l 2\pi}) = 0 \quad (2.31)$$

$$1 - e^{im_l 2\pi} = 0 \quad (2.32)$$

$$1 = e^{im_l 2\pi} \quad (2.33)$$

which hold true only for  $m_l = 0, \pm 1, \pm 2, \dots$

The second restriction is that it has to be normalized, that is

$$\langle \Phi | \Phi \rangle = 1$$

Using the definition from Equation 1.4. We find out that the form of the function is

$$\Phi(\phi) = \frac{1}{\sqrt{2\pi}} e^{im_l\phi} ; m_l = 0, \pm 1, \pm 2, \dots \quad (2.34)$$

The second equation we will solve is 2.29c. We rearrange its terms and substitute  $z = \cos \theta$  and  $P(z) = \Theta(\theta)$  to get the following

$$\frac{1}{\sin \theta} \frac{d}{d\theta} \sin \theta \frac{d}{d\theta} \Theta - \Theta \frac{m_l^2}{\sin^2 \theta} = \Theta \varepsilon_{\theta\phi r} \quad (2.35)$$

$$(2.36)$$

### 2.2.3 The energies

Applying the hamiltonian in Equation 2.24 to the wavefunction in

$$H_{r\theta\phi}R(r)Y(\theta, \phi) = ER(r)Y(\theta, \phi) \quad (2.37)$$

## 2.3 Many body systems

For bigger systems, there is no practical way to analytically solve the SE. For one, for each particle, the amount of dimensions that need to be evaluated increases by three, that is, one can expect the wave function dimension to increase by a factor of  $3N$  for each particle  $N$  [7].

Additionally, the potential energy operator becomes more complicated, as it would not just have the attractive forces between electron-nucleus, but also the repulsive forces between all the electrons. Both of these problems add more terms per particle and thus would be impossible to be solved in a realistic timeframe [11].

### 2.3.1 BO approximation

The Hamiltonian for many electron systems contains terms for the correlated motion of the particles [7, 11]. This includes the repulsion and attraction of all the particles to each other. This means that no particle is moving independently of the other particles. Trying to solve a SE analytically with a Hamiltonian such as this is not possible. In order to simplify the problem we use the BO approximation [7, 11].

In the BO approximation one assumes that the motion of the nucleus is negligible in comparison to the motion of the electrons [7, 11]. This is because the electrons are 1800 times less massive than the protons and electrons and the kinetic energy operator is inversely proportional to the mass of the particle. This way we can imagine the system as having stationary nucleus and electrons in motion around the nucleus.

By using this assumption we can separate the problem of a SE for the whole system (electron and nuclei) into two separate problems, first solving for the electron motion, attraction and repulsion energies and second solving for the kinetic energy of the molecule [7]. By this line of thought one can write the following set of equations in 2.38 based on Equation 2.20 adding the nucleus-nucleus and electron-electron repulsion potentials,  $V_{NN}$  and  $V_{ee}$  respectively.

$$\begin{aligned} H_{tot}\Psi_{tot}(\vec{R}, \vec{r}) &= E_{tot}\Psi_{tot}(\vec{R}, \vec{r}) \\ H_{tot} &= H_e + H_N \\ H_e &= T_e + V_{Ne} + V_{ee} ; H_N = T_N + V_{NN} \\ \Psi_{tot}(\vec{R}, \vec{r}) &= \Psi_N(\vec{R})\Psi_e(\vec{r}; \vec{R}) \\ (H_e + V_{NN})\Psi_e(\vec{r}; \vec{R}) &= E_e(\vec{R})\Psi_e(\vec{r}; \vec{R}) \\ (T_N + E_e(\vec{R}))\Psi_N(\vec{R}) &= E_{tot}\Psi_N(\vec{R}) \end{aligned} \quad (2.38)$$

In the equations above, both the total Hamiltonian  $H_{tot}$  and total wave function  $\Psi_{tot}$  are divided into electronic and nucleic contributions ( $\Psi_e$  and  $\Psi_N$

respectively). This separation is not complete, as there still is the nucleus-electron attraction which must be included in the electronic Hamiltonian  $H_e$ . Additionally, when solving the electronic problem we need to take into account the nucleus-nucleus repulsion potential  $V_N N$ . For these reasons the electronic wave function  $\Psi_e$  is dependent on both the electron coordinates  $\vec{r}$  and nucleus coordinates  $\vec{R}$ . The electronic wave function is dependent on the electronic coordinates as variables, but depends on the nuclei coordinates parametrically [11]. This means that for each molecule geometry the electronic problem is solved as if the nucleus was motionless. This leads to the nucleus-nucleus potential to be a constant for each molecule geometry.

Solving the electronic problem over different geometries gives rise to a Potential Energy Surface (PES) on which the molecule exists [7]. This parametric dependency on the geometry of the molecule means that the electronic energy is as well dependent on it. This way we can attempt to find a minimum (the method used for this can vary) for the electronic energy by iteratively solving the electronic problem with different geometries. This is important to measure how good our trial wave function is as according to the variational principle.

Once a minimum has been reached on the PES one can go on to solve for the total energy of the system by doing solving the final equation on 2.38. This, as according to the variational principle, can also be iterated over in order to minimize the energy.

### 2.3.2 Variational Principle

Consider a complete set of orthonormal eigenfunctions  $\Psi_i$  of the Hamiltonian  $H$ . From Equation 2.10 we build an arbitrary wave function  $\Phi$  with a linear combination of the eigenfunctions with coefficients  $c_i$ .

$$\Phi = \sum_i c_i \Psi_i \quad (2.39)$$

We also know from Equation 2.11 that the probability of  $\Phi$  can be calculated as shown below;

$$\langle \Phi | \Phi \rangle = \sum_i^n c_i^2 \quad (2.40)$$

We also know that the wave function  $\Phi$  is normalized, so the sum above should equal to one. Additionally, the expectation value of the Hamiltonian can be calculated as in Equation 2.8 to give us this:

$$\langle \Phi | H | \Phi \rangle = \sum_i^n c_i^2 E_i \quad (2.41)$$

This tells us the the energy of the wave function  $\Phi$  can be determined by knowing the energies  $E_i$  of each eigenfunction  $\psi_i$  and the coefficients  $c_i$  associated with the linear combination that describes  $\Phi$  [7].

We know that for this to be a quantum mechanical system there must be a lowest energy among all energies  $E_i$ . We choose to call this lowest energy  $E_0$ . Subtracting  $E_0$  from Equation 2.41 to find out the difference between the calculated energy of the arbitrary wave function  $\Phi$  with respect to the ground state energy gives us:

$$\sum_i^n c_i^2 (E_i - E_0) = \langle \Phi | H | \Phi \rangle - E_0 \langle \Phi | \Phi \rangle \quad (2.42)$$

We know that each term  $c_i$  must be greater or equal to zero (non-trivial) and that the term  $(E_i - E_0)$  must be greater or equal to zero as well [7], because each individual  $E_i$  may add more energy to the ground state. This leads to the following set of inequalities.

$$\begin{aligned} \langle \Phi | H | \Phi \rangle - E_0 \langle \Phi | \Phi \rangle &\geq 0 \\ \frac{\langle \Phi | H | \Phi \rangle}{\langle \Phi | \Phi \rangle} &\geq E_0 \end{aligned} \quad (2.43)$$

We know from Equation 2.6 that the inequality in the last term in 2.43 shows that the energy calculated as an Eigenvalue of  $\Phi$  is always greater or equal to zero. This lets us construct our trial wave functions for the ground state of a system with any basis set. We can assess the quality of the guess by their associated energies, attempting to reach as low a value as possible [7].

### 2.3.3 SCF

## Chapter 3

# MW Basis

As stated on the previous chapter, the main goal of computational chemistry is to approximate systems in order to calculate their energy through the SE. These systems are completely described by wave functions [6]. This means that to approximate a solution to the system is to approximate its wave function.

In order to construct a solution (wave function) to the SE of a given system one uses sets of orthogonal functions with differing properties. These sets of functions construct a basis for the space on which the wave functions are projected into. These sets are thus called basis sets [7] and they are essential to solving many body systems. In this text we will be focusing in the MW basis from MRA methods.

### 3.1 MRA

#### 3.1.1 Definition

Consider that we have a function  $\varphi \in L^2(\mathbb{R})$  where its translations and dilations are described as [14]

$$\varphi_k^j(x) = 2^{\frac{j}{2}} \varphi(2^j x - k), \quad j, k \in \mathbb{Z} \quad (3.1)$$

. Where  $j$  is the scale of the function and  $k$  is the translation of the function [13] A space  $V_n$  is spanned by translations of  $\varphi_{nk}$ . This space forms a hierarchical chain of Linear subspaces [4]:

$$V_0 \subset V_1 \subset \dots \subset V_j \subset \dots \subset L^2(\mathbb{R}) \quad (3.2)$$

Where  $V_0$  is spanned only by  $\varphi_{0,0}(x) = \varphi(x)$  [13]. The function  $\varphi(x)$  satisfies the two-scale difference relations [4, 14, 13]:

$$\begin{aligned} \varphi(x) &= \varphi(2x) + \varphi(2x - 1) \\ \varphi_k^j(x) &= \varphi_{2k}^{j+1}(2^{j+1}x - 2k) + \varphi_{2k+1}^{j+1}(2^{j+1}x - 2k - 1) \end{aligned} \quad (3.3)$$

If relation 3.2 and the following refinement equation holds for  $\varphi_{j,k}(x)$  one can call the subspaces  $V_n$  or the functions  $\varphi_{j,k}(x)$  build a MRA of  $L_2(\mathbb{R})$ .

$$\varphi_k^j(x) = \sum_{k \in \mathbb{Z}} h_k^{j+1} \varphi_k^{j+1}(x) \quad (3.4)$$

Where  $h$  is a coefficient characteristic to the transformation between scales.

### 3.1.2 Wavelet MRA

Following from now we will work with the Haar wavelet basis for simplicity [4]. Lets define the Haar function [14] as

$$\varphi_0^0 = \varphi(x) = \begin{cases} 1 & \text{for } x \in [0, 1) \\ 0 & \text{elsewhere} \end{cases} \quad (3.5)$$

Lets now define a second set of subspaces  $W_n$ . These are the orthogonal complements of  $V_n$  [1], also called difference subspaces, defined as [4, 13, 1].

$$W_n \oplus V_n = V_{n+1} \quad (3.6)$$

The subspaces  $W_n$  are then spanned by a set of functions defined by the translations and dilations of  $\psi(x)$ :

$$\psi_k^j(x) = 2^{\frac{j}{2}} \psi(2^j x - k), \quad j, k \in \mathbb{Z} \quad (3.7)$$

Where  $\psi(x)$  is called the Haar wavelet [14] and is defined as:

$$\psi_0^0 = \psi(x) = \begin{cases} 1 & \text{for } x \in [0, \frac{1}{2}) \\ -1 & \text{for } x \in [\frac{1}{2}, 1) \\ 0 & \text{elsewhere} \end{cases} \quad (3.8)$$

And  $\varphi$  is related to  $\psi$  by the following two-scale difference relation [4, 14, 13]:

$$\begin{aligned} \psi(x) &= \varphi(2x) - \varphi(2x - 1) \\ \psi_k^j(x) &= \psi_{2k}^{j+1}(2^{j+1}x - 2k) + \psi_{2k+1}^{j+1}(2^{j+1}x - 2k - 1) \end{aligned} \quad (3.9)$$

The functions  $\varphi_k^j$  and  $\psi_k^j$  are orthonormal and dense [4, 13, 12] in  $L^2(\mathbb{R})$ .

The Definition on Equation 3.6 can be applied recursively in order to get any space  $V_n$  as long as one knows the first subspace  $V_0$  and one has a method for constructing the subspace  $W_m$  from  $V_0$  and  $W_{m-1}$ .

$$V_0 \oplus W_0 \oplus W_1 \oplus \dots \oplus W_{n-1} = V_n \quad (3.10)$$

Projecting a function  $f(x)$  unto this basis would be then a weighted linear combination of the Haar functions, but taking into account the definition on Equation 3.10 one arrives at [13].

$$f(x) \approx \sum_k^{2^j-1} \sum_j^N s_k^j \varphi_k^j = s_0^0 \varphi_0^0 + \sum_k^{2^j-1} \sum_j^{N-1} d_k^j \psi_k^j \quad (3.11)$$

where  $d$  are the difference coefficients and  $s$  are the scaled averages of dyadic intervals of the function  $f(x)$

The scaling coefficients  $s_k^j$  are computed by the projection  $\langle \varphi_k^j(x) | f(x) \rangle$ . Likewise the difference coefficients  $d_k^j(x)$  are computed by the projection  $\langle \psi_k^j(x) | f(x) \rangle$ . Because of the way the Haar function is defined, we can define of the scaling coefficients as scaled averages of  $f(x)$  at intervals  $2^{-j}$  [13, 4]

$$s_k^j = \int_{\mathbb{R}} \varphi_k^j(x) f(x) dx = \int_{2^{-j}k}^{2^{-j}(k+1)} f(x) dx \quad (3.12)$$



We can then obtain the difference coefficients by using Equations 3.12, 3.7 and 3.9:

$$\begin{aligned}
d_k^{j-1} &= \int_{\mathbb{R}} \psi_k^{j-1}(x) dx \\
d_k^{j-1} &= 2^{\frac{j-1}{2}} \int_{\mathbb{R}} \psi(2^{j-1}x - k) f(x) dx \\
d_k^{j-1} &= 2^{\frac{j-1}{2}} \left( \int_{\mathbb{R}} \varphi(2^j x - 2k) f(x) dx - \int_{\mathbb{R}} \varphi(2^j x - 2k - 1) f(x) dx \right) \\
d_k^{j-1} &= 2^{\frac{j-1}{2}} \left( \int_{2^{-j}2k}^{2^{-j}(2k+1)} f(x) dx - \int_{2^{-j}(2k+1)}^{2^{-j}(2k+2)} f(x) dx \right) \\
d_k^{j-1} &= \frac{1}{\sqrt{2}} (s_{2k}^j - s_{2k+1}^j)
\end{aligned} \tag{3.13}$$

The scaling coefficients can be obtained in the same manner:

$$\begin{aligned}
s_k^{j-1} &= \int_{\mathbb{R}} \varphi_k^{j-1}(x) dx \\
s_k^{j-1} &= 2^{\frac{j-1}{2}} \int_{\mathbb{R}} \varphi(2^{j-1}x - k) f(x) dx \\
s_k^{j-1} &= 2^{\frac{j-1}{2}} \left( \int_{\mathbb{R}} \varphi(2^j x - 2k) f(x) dx + \int_{\mathbb{R}} \varphi(2^j x - 2k - 1) f(x) dx \right) \\
s_k^{j-1} &= 2^{\frac{j-1}{2}} \left( \int_{2^{-j}2k}^{2^{-j}(2k+1)} f(x) dx + \int_{2^{-j}(2k+1)}^{2^{-j}(2k+2)} f(x) dx \right) \\
s_k^{j-1} &= \frac{1}{\sqrt{2}} (s_{2k}^j + s_{2k+1}^j)
\end{aligned} \tag{3.14}$$

The result of Equations 3.13 and 3.14 show us that we can represent the projection of coefficients unto a coarser scale as an orthogonal matrix [13, 4]:

$$\begin{pmatrix} d_k^j \\ s_k^j \end{pmatrix} = \begin{pmatrix} \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \end{pmatrix} \begin{pmatrix} s_{2k}^{j+1} \\ s_{2k+1}^{j+1} \end{pmatrix} \tag{3.15}$$

Projecting the coefficients into a more refined scale is just a transpose of the above matrix:

$$\begin{pmatrix} s_{2k}^{j+1} \\ s_{2k+1}^{j+1} \end{pmatrix} = \begin{pmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \end{pmatrix} \begin{pmatrix} d_k^j \\ s_k^j \end{pmatrix} \tag{3.16}$$

### 3.1.3 Projecting a gaussian function example

As an example, lets approximate the function  $f(x) = \frac{10}{\sqrt{\pi}} e^{-100(x-0.5)^2}$  in  $L^2(\mathbb{R})$  with Haar basis up to scale 5 using 3.11. Gives us the following figures.

## 3.2 MW MRA

### 3.2.1 Constructing the basis functions

Following the same basics as in the Haar basis from the previous section we can define a hierarchical set of multiresolution spaces  $V_j^l$  where [10]:

$$V_j^l \stackrel{\text{def}}{=} \{f : \text{all polynomials of degree } \leq l \\ \text{on } (2^{-j}k, 2^{-j}(k+1)) \text{ for } 0 \leq k < 2^n, \\ f \text{ vanishes elsewhere}\} \quad (3.17)$$

and

$$V_0^l \subset V_1^l \subset \dots \subset V_j^l \subset \dots \subset L^2(\mathbb{R}) \quad (3.18)$$

We again define subspaces  $W_j^l$  as the orthogonal complements of  $V_j^l$  [1] defined as:

$$V_j^l \oplus W_j^l = V_{j+1}^l \quad (3.19)$$

with orthogonal basis functions  $h_{ik}^j$  which are translations and dilations of functions  $h_l$ :

$$h_{ik}^j(x) = 2^{\frac{j}{2}} h_i(2^j x - k), \quad i = 1, \dots, l; \quad k \in \mathbb{Z} \quad (3.20)$$

The functions  $h_1, \dots, h_l$  are piecewise polynomial, orthogonal to lower order polynomials and vanish outside  $[0, 1]$  [1]

$$\int_0^1 h_i(x) x^m dx = 0, \quad m = 0, 1, \dots, l-1 \quad (3.21)$$

Our aim is to find a set of functions  $f_i$  on the interval  $[-1, 1]$  that can be used in the construction of  $h_1, \dots, h_l$  with the following restrictions [1, 4]:

1. functions  $f_i$  on the interval  $(0, 1)$  are polynomials of degree  $l-1$ .
2. functions  $f_i$  extend to the interval  $(-1, 0)$  as even or odd functions dependent to the parity  $i+l-1$ .
3. functions  $f_1, \dots, f_l$  satisfy :

$$\int_{-1}^1 f_i(x) f_j(x) dx \equiv \langle f_i | f_j \rangle = \delta_{ij}, \quad i, j = 1, \dots, l.$$

4. functions  $f_j$  have vanishing moments,

$$\int_{-1}^1 f_j(x) x^i dx = 0, \quad i = 0, 1, \dots, j+l-2.$$

The functions  $f_1^{(1)}, f_2^{(1)}, \dots, f_l^{(1)}$  are defined by [1]:

$$f_j^{(1)}(x) = \begin{cases} x^{j-1} & \text{for } x \in (0, 1) \\ -x^{j-1} & \text{for } x \in (-1, 0) \\ 0 & \text{elsewhere.} \end{cases} \quad (3.22)$$

The  $2l$  functions  $1, x, \dots, x^{l-1}$  and  $f_1^{(1)}, f_2^{(1)}, \dots, f_l^{(1)}$  are linearly independent, thus they span the space of polynomial functions of degree  $< l$  on the intervals  $(0, 1)$  and  $(-1, 0)$  [1, 4]. We do the following process to find the functions  $f_i$  [1]:

1. Using the Gram-Schmidt process we orthogonalize  $f_j^{(1)}$  with respect to  $1, x, \dots, x^{l-1}$  giving us the functions  $f_j^{(2)}$  for  $j = 1, \dots, l$ .
2. We try to find at least one  $f_j^{(2)}$  which is not orthogonal to  $x^l$  and reorder the functions so that  $\langle f_1^{(2)} | x^l \rangle \neq 0$ . We now need to find an  $a_j$  for the equation  $f_j^{(3)} = f_j^{(2)} - a_j \cdot f_0^{(2)}$  such that  $\langle f_j^{(3)} | x^l \rangle = 0$  for  $l = 2, \dots, l$ . We repeat this process orthogonalizing to  $x^{k+1}, \dots, x^{2k-2}$ , each turn yielding  $f_1^{(2)}, f_2^{(3)}, f_3^{(4)}, \dots, f_k^{(k+1)}$  such that  $\langle f_j^{(j+1)} | x^i \rangle = 0$  for  $i \leq j + l - 2$ .
3. Lastly we perform the Gram-Schmidt orthogonalization process on  $f_l^{l+1}, f_{l-1}^l, f_{l-2}^{l-1}, \dots, f_2^1$  in that order to get  $f_l, f_{l-1}, \dots, f_1$ .

We now construct the functions  $h_l$  [1]:

$$h_i(x) = \sqrt{2} f_i(2x - 1), \quad i = 1, \dots, l \quad (3.23)$$

which they themselves build the functions in Equation 3.20 defining a basis for scaling subspace  $W_j^l$ .

From the definition of these subspaces we know that we need to define a basis for the subspace  $V_0^l$  which is the orthogonal complement of  $W_0^l$  in  $V_1^l$  [1]. The basis functions  $u_i(x)$  of the subspace  $V_0^l$  can be defined using the following two-scale difference equations [5], which are analogous to the two-scale difference equations in 3.9.

$$h_i(x) = \sqrt{2} \sum_{j=0}^{l-1} \left( \bar{H}_{ij}^{(0)} h_j(2x) + \bar{H}_{ij}^{(1)} h_j(2x - 1) \right), \quad i = 0, \dots, l - 1 \quad (3.24)$$

$$u_i(x) = \sqrt{2} \sum_{j=0}^{l-1} \left( \bar{G}_{ij}^{(0)} h_j(2x) + \bar{G}_{ij}^{(1)} h_j(2x - 1) \right), \quad i = 0, \dots, l - 1 \quad (3.25)$$

Where  $\bar{H}$  and  $\bar{G}$  are quadrature mirror filter matrices [5] which have the following properties:

$$\bar{H}^{(0)} \bar{H}^{(0)T} + \bar{H}^{(1)} \bar{H}^{(1)T} = \bar{I} \quad (3.26)$$

$$\bar{G}^{(0)} \bar{G}^{(0)T} + \bar{G}^{(1)} \bar{G}^{(1)T} = \bar{I} \quad (3.27)$$

$$\bar{H}^{(0)} \bar{G}^{(0)T} + \bar{H}^{(1)} \bar{G}^{(1)T} = \bar{0} \quad (3.28)$$

Which can be summarized in the orthogonal block matrix  $\bar{U}$  [5]

$$\bar{U} = \begin{pmatrix} \bar{H}^{(0)} & \bar{H}^{(1)} \\ \bar{G}^{(0)} & \bar{G}^{(1)} \end{pmatrix} \quad (3.29)$$

Which lets us put the two two-scale difference equations in the following way [13]

$$\begin{pmatrix} \vec{h}(x) \\ \vec{u}(x) \end{pmatrix} = \sqrt{2} \begin{pmatrix} \bar{H}^{(0)} & \bar{H}^{(1)} \\ \bar{G}^{(0)} & \bar{G}^{(1)} \end{pmatrix} \begin{pmatrix} \vec{h}(2x) \\ \vec{h}(2x - 1) \end{pmatrix} \quad (3.30)$$

and subsequently

$$\begin{pmatrix} \vec{h}(2x) \\ \vec{h}(2x - 1) \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} \bar{H}^{(0)} & \bar{G}^{(0)} \\ \bar{H}^{(1)} & \bar{G}^{(1)} \end{pmatrix} \begin{pmatrix} \vec{h}(x) \\ \vec{u}(x) \end{pmatrix} \quad (3.31)$$

### 3.2.2 Choices of Scaling functions

Now that we have stated how to build the scaling and wavelet basis functions we need to make a choice of functions  $f$  to build said basis. Here we will briefly show two examples of polynomial functions used to create the basis. These two are the Legendre polynomials and the Lagrange interpolating polynomials [4, 5]

**Legendre basis** The Legendre scaling function is defined as follows

$$\phi_j(x) \begin{cases} \sqrt{2j+1}P_j(2x-1), & x \in [0, 1) \\ 0, & x \notin (0, 1) \end{cases} \quad (3.32)$$

Where  $P_j$  are the Legendre polynomials of order  $j$  defined in  $[-1, 1]$  [4] Following are some examples of the polynomials together with figures of the first few terms of the functions. These functions have the advantage of being simple to compute, since each incremental polynomial order only adds a single term to the function.

**Lagrange interpolating basis**

$$\varphi = \frac{1}{\sqrt{w_i}} l_i(x), \quad i = 0, \dots, M-1 \quad (3.33)$$

$$l_i(x) = \prod_{k=0, k \neq i}^{M-1} \frac{x - x_k}{x_i - x_k} \quad (3.34)$$

$$w_i = \frac{1}{MP'_M(2x_i - 1)P_{M-1}(2x_i - 1)} \quad (3.35)$$

Where  $M$  is the scale of the subspace, the  $P$  functions are the Legendre polynomials and  $x_0, \dots, x_{M-1}$  are the roots of  $P_M(2x-1)$  [4]. These scaling functions have the characteristic of  $l_i(x_j) = \delta_{ij}$  simplifying integrals and thus projections of the basis.

## 3.3 Operators

### 3.3.1 NS form Representation of Operators

Lets us define two projection operators  $P_n^k$  and  $Q_n^k$  and their relation as:

$$P_n^k : L^2([0, 1]) \rightarrow V_n^k \quad (3.36)$$

$$Q_n^k : L^2([0, 1]) \rightarrow W_n^k \quad (3.37)$$

$$Q_n^k = P_{n+1}^k - P_n^k \quad (3.38)$$

A function  $f$  would then be projected into a scale  $n$  by  $f_n^k = P_n^k f$ . Its projection unto a more refined scale would then be  $f_{n+1}^k = f_n^k + df_n^k$  where  $df_n^k = Q_n^k f$  [10].

We expand a linear operator  $T : L^2([0, 1]) \rightarrow L^2([0, 1])$  as

$$\begin{aligned}
T &= P_0^k T P_0^k + \sum_{n=0}^{\infty} (P_{n+1}^k T P_{n+1}^k - P_n^k T P_n^k) \\
&= P_0^k T P_0^k + \sum_{n=0}^{\infty} ((P_n^k + Q_n^k) T (P_n^k + Q_n^k) - P_n^k T P_n^k) \\
&= P_0^k T P_0^k + \sum_{n=0}^{\infty} (P_n^k T Q_n^k + Q_n^k T P_n^k + Q_n^k T Q_n^k)
\end{aligned} \tag{3.39}$$

We represent the operator  $T$  as

$$A_n^k \stackrel{\text{def}}{=} Q_n^k T Q_n^k : W_n^k \rightarrow W_n^k \tag{3.40}$$

$$B_n^k \stackrel{\text{def}}{=} Q_n^k T P_n^k : V_n^k \rightarrow W_n^k \tag{3.41}$$

$$C_n^k \stackrel{\text{def}}{=} P_n^k T Q_n^k : W_n^k \rightarrow V_n^k \tag{3.42}$$

$$T_n^k \stackrel{\text{def}}{=} P_0^k T P_0^k : V_n^k \rightarrow V_n^k \tag{3.43}$$

so we can write the NS form of the operator  $T$  as [10, 5]

$$T = T_0^k + \sum_{n=0}^{\infty} (A_n^k + B_n^k + C_n^k) \tag{3.44}$$

We can then apply  $T$  on  $f$  and get, by using the definitions above, the following result:

$$\begin{aligned}
Tf &= g = \hat{g}_0^k + \sum_{n=0}^{\infty} (\tilde{g}_n^k + d\tilde{g}_n^k) \\
&= T_0^k f_0^k + \sum_{n=0}^{\infty} ((A_n^k + C_n^k) d f_n^k + B_n^k f_n^k) \\
\hat{g}_n^k &\stackrel{\text{def}}{=} T_n^k f = T_n^k f_n^k \\
\tilde{g}_n^k &\stackrel{\text{def}}{=} C_n^k f = C_n^k f_n^k \\
d\tilde{g}_n^k &\stackrel{\text{def}}{=} (A_n^k + B_n^k) f = A_n^k f_n^k + B_n^k f_n^k
\end{aligned} \tag{3.45}$$

In practice we truncate this to the fines scale  $N + 1$  where the following is assumed to be true [10]:

$$\hat{g}_{N+1}^k \simeq g_{N+1}^k \stackrel{\text{def}}{=} (Tf)_{N+1}^k \tag{3.46}$$

### 3.3.2 Integral operators

### 3.3.3 Differential operators

## 3.4 Software



## Chapter 4

# Solvent Effect

### 4.1 Formulation of the Problem

### 4.2 Explicit solvation models

### 4.3 Implicit solvation models

#### 4.3.1 PCM

Interlocking spheres

### 4.4 PCM and MW basis

### 4.5 Solving the Problem

#### 4.5.1 Generalized poisson equation

#### 4.5.2 SCF for PCM





## Chapter 5

# Variational Implementation of the solvent effect



## Chapter 6

# Implementation

### 6.1 PCM

#### 6.1.1 Dielectric function

From [9] the cavity was implemented as follows

```
Cavity = C;  
ri = position of the center of the sphere;  
Ri = radius of sphere;  
s(r) =  $|r - r_i| - R_i$ ;  
 $\sigma$  = width of slope ;  
for each sphere Ci at point r do  
|  $C_i = \frac{1}{2}(1 - \text{erf}(\frac{s(r)}{\sigma}))$ ;  
|  $C = C \cdot C_i$ ;  
end
```

This would give us 1 on the inside of the Cavity and zero everywhere else. We construct the dielectric function as a combination of the permittivity of free space  $\varepsilon_0 = 1.0$ , the dielectric constant of the dielectric continuum  $\varepsilon_\infty$ , and the Cavity in either a linear or exponential way [9] (Equations 6.1 and 6.2 respectively). The linear dielectric function is as follows:

$$\varepsilon(r) = \varepsilon_0 C(r) + \varepsilon_\infty (1 - C(r)) \quad (6.1)$$

The exponential dielectric function is as follows:

$$\varepsilon(r) = \varepsilon_0 \exp\left(\log\left(\frac{\varepsilon_\infty}{\varepsilon_0}\right)(1 - C(r))\right) \quad (6.2)$$

They were simply added to the end of the implementation of C so as to change the output of the cavity.

### 6.1.2 Differences and limitations in implementations

## 6.2 Reaction potential

## 6.3 Software used

The problem was first implemented in Vampyr which is a python Then it was implemented in C++ using MRchem Both implementations are identical, except for slight changes for performance improvement, such as a KAIN accelerator, iterating through  $V_r$  instead of  $V_{tot}$  and keeping the potential from cycle to cycle in the c++ version of the model.

## Chapter 7

# Results



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