Master thesis
Variational Monte Carlo for light atoms

Håvard Sandsdalen

April 13, 2010

Contents

Chapter 1

Introduction

INGENTING ENNÅ

Chapter 2

Quantum Physcics

In the 1920's european physicists developed quantum mechanics in order to describe the physical phenomena they had been discovering for some years. Such phenomena as the photoelectric effect and the diffraction patterns from the double-slit experiment indicated that physicists needed a new set of tools when handling systems on a very small scale, e.g. the behavior of single particles and isolated atoms.

This chapter will give an introduction to the relevant topics in quantum physics needed to describe the atomic systems in this project. Some parts will closely follow the discussions in the books [1] and [2], while other parts only contain elements from the sources listed in the bibliography.

2.1 Quantum Mechanics in one dimension

The general idea and goal of quantum mechanics is to solve the complex, time-dependent Schrödinger-equation(S.E.) for a specific physical system which cannot be described by classical mechanics. Once solved, the S.E. will give you the quantum mechanical wave function, Ψ, a mathematical function which contains all information needed about such a non-classical system. It introduces probabilities and statistical concepts which contradicts with the deterministic nature of a classical system. The full one-dimensional S.E. for an arbitrary potential, V, reads:

$$i\hbar\frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2 \Psi}{\partial x^2} + V\Psi.$$
(2.1)

The Schrödinger equation is the classical analogy to Newton's second law in classical physics, and describes the dynamics of virtually any physical system, but is only useable in small scale systems, quantum systems.

2.1.1 Probability and statistics

The wave function, Ψ, is now a function of both position, x, and time, t. Quantum mechanics uses the concept of probability and statistics via Ψ, and these solutions of the S.E. may be complex as the equation Eq. (2.1) is complex itself. To comply with the statistical interpretation we must have a function that is both real and non-negative. As described in [1], Born's statistical interpretation takes care of this problem by introducing the complex conjugate of the wave function. The product $\Psi^*\Psi = |\Psi|^2$ is interpreted as

the probability density for the system state. If the system e.g. consists of only one particle, the integral

$$\int_a^b |\Psi(x,t)|^2 \, \mathrm{d}x \tag{2.2}$$

is then interpreted as the probability of finding the particle between positions a and b at an instance t. To further have a correct correspondence with probability, we need the total probability of finding the particle anywhere in the universe to be 1. That is

$$\int_{-\infty}^{\infty} |\Psi(x,t)|^2 \, \mathrm{d}x = 1. \tag{2.3}$$

In quantum mechanics, operators represent the observables we wish to find, given a wave function, Ψ. The operator representing the position variable, $\widehat{\mathbf{x}}$, is just x itself, while the momentum operator is $\widehat{\mathbf{p}} = -i\hbar(\partial/\partial x)$. All classical dynamic variables are expressed in terms of just momentum and position, as said on p. 17 in [1]. Another important operator is the Hamilton operator. The Hamilton operator gives the time evolution of the system and is the sum of the kinetic energy operator $\widehat{\mathbf{T}}$ and the potential energy operator $\widehat{\mathbf{V}}$, $\widehat{\mathbf{H}} = \widehat{\mathbf{T}} + \widehat{\mathbf{V}}$. $\widehat{\mathbf{V}}$ is represented by the function V from Eq. (2.1), while the kinetic energy operator is

$$\widehat{\mathbf{T}} = \frac{\widehat{\mathbf{p}}^2}{2m} = \frac{(i\hbar)^2}{2m}\left(\frac{\partial}{\partial x}\right)^2 = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} \tag{2.4}$$

For an arbitrary operator, $\widehat{\mathbf{Q}}$, the expectation values, $\langle Q \rangle$, is found by the formula

$$\langle Q \rangle = \int \Psi^* \widehat{\mathbf{Q}} \Psi \mathrm{d}x. \tag{2.5}$$

The same goes for expectation values of higher moments, e.g. $\langle p^2 \rangle$:

$$\langle p^2 \rangle = \int \Psi^* \widehat{\mathbf{p}}^2 \Psi \mathrm{d}x. \tag{2.6}$$

The so-called variance of an operator or observable, σ_Q^2, can be calculated by the following formula:

$$\sigma_Q^2 = \langle Q^2 \rangle - \langle Q \rangle^2. \tag{2.7}$$

This quantity determines the standard deviation, $\sigma_Q = \sqrt{\sigma_Q^2}$. The standard deviation describes the spread around the expectation value. The smaller the standard deviation, the smaller the variation between the possible values of Q.

The wave functions, Ψ, exist in the so-called *Hilbert space*, a mathematical vector space of square-integrable functions.

2.1.2   The time-independent Schrödinger Equation

However, in any cases, we are only interested in a time-independent version of Eq. (2.1). A crucial point is then to demand the potential, V, to be a time-independent potential as well, viz. $V = V(x)$(in one spatial dimension). This equation can be obtained by the well-known method of **separation of variables**. The trick is to write our wave function, $\Psi(x,t)$, as a product of a purely spatial function, $\psi(x)$, and another function,

$\phi(t)$, depending only of time. That is, we assume: $\Psi(x,t) = \psi(x)\phi(t)$. By inserting Ψ into the full S.E., Eq. 2.1, remembering that ψ and ϕ only depend on one variable each, then dividing by $\Psi = \psi\phi$, we get

$$i\hbar\frac{1}{\phi}\frac{\mathrm{d}\phi}{\mathrm{d}t} = -\frac{\hbar^2}{2m}\frac{1}{\psi}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + V(x). \tag{2.8}$$

By inspecting Eq. (2.8), we see that the left side of the equation depends on t alone, while the right side depends only on x. This means that both sides must be **constant** and of course equal. By varying t and changing the left side, the right side would change without ever varying x, which says it must a constant. We call this separation constant E, giving us the two equations

$$\frac{\mathrm{d}\phi}{\mathrm{d}t} = -\frac{iE}{\hbar}\phi, \tag{2.9}$$

and

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + V\psi = E\psi. \tag{2.10}$$

Eq. (2.9) can be solved quite easily, and will give an exponential form of the time-dependent part.

$$\phi(t) = e^{-iEt/\hbar}. \tag{2.11}$$

The second equation, Eq. (2.10), is called the **time-independent Schrödinger equation**. By inspecting Eq. (2.11), we see that expectation values will be constant in time because the time-dependent part from Ψ, $\phi(t)$, will only give a factor 1 when it is multiplied with its complex conjugate from Ψ^*. That is:

$$e^{-iEt/\hbar}e^{+iEt/\hbar} = 1. \tag{2.12}$$

The expectation values depend solely on the spatial parts, ϕ. We call these separable solutions **stationary states**.

Stationary states and expectation values

Another point about the stationary solutions is the close relation to classical mechanics. The Hamilton function determines the total energy of the system, and is the sum of the kinetic and potential energy. The classical Hamiltonian function for any system with a time-independent potential is

$$H(x,p) = \frac{p^2}{2m} + V(x). \tag{2.13}$$

By using the canonical substitution $p \to (\hbar/i)(\mathrm{d}/\mathrm{d}x)$ for the quantum mechanical momentum operator, we get

$$\widehat{\mathbf{H}} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x). \tag{2.14}$$

This is identical to the time-independent Schrödinger equation, Eq. (2.10), and we can then obtain a much simplified Schrödinger equation:

$$\widehat{\mathbf{H}}\psi = E\psi. \tag{2.15}$$

The expectation value of the Hamilton operator, the total energy, is now given as

$$\langle H \rangle = \int \psi^* \widehat{\mathbf{H}} \psi \mathrm{d}x = E \int |\psi|^2 \, \mathrm{d}x = E \int |\Psi|^2 \, \mathrm{d}x = E. \tag{2.16}$$

Calculating $\langle H^2 \rangle$ gives

$$\langle H^2 \rangle = \int \psi^* \widehat{\mathbf{H}}^2 \psi \mathrm{d}x = E \int \psi^* \widehat{\mathbf{H}} \psi \mathrm{d}x = E^2 \int |\psi|^2 \, \mathrm{d}x = E^2 \int |\Psi|^2 \, \mathrm{d}x = E^2. \tag{2.17}$$

And so the variance and standard deviation are both zero

$$\sigma_H^2 = \langle H^2 \rangle - \langle H \rangle^2 = E^2 - E^2 = 0. \tag{2.18}$$

For these separable solutions, every measurement of the total energy will return the same value, E. Thus the spread around the expectation value is exactly zero.

General solutions

The general solution for these systems is a linear combination of different separable solutions. Different solutions with different separation constants, e.g.

$$\Psi_1(x,t) = \psi_1(x)e^{-iE_1 t/\hbar}, \quad \Psi_2(x,t) = \psi_2(x)e^{-iE_2 t/\hbar} \tag{2.19}$$

which both are solutions of Eq. (2.10), can be used to construct the general solution

$$\Psi(x,t) = \sum_{n=1}^{\infty} c_n \psi_n(x)e^{-iE_n t/\hbar} = \sum_{n=1}^{\infty} c_n \Psi_n(x,t), \tag{2.20}$$

where the factors c_n are probability weights for its corresponding stationary state.

Spin

An important, but difficult consept in quantum physics is spin. Spin is an intrinsic property of every elementary particle. Also composite systems will have a certain value of spin when imposing addition rules on the single particles that make up such a system. In this project we will deal with fermions, i.e. half integer spin particles(see section 2.3.1).

A particle will either have *spin up* or *spin down*. This is denoted by tacking on a factor to the wave function itself, namely the factors

$$\chi_+ = \uparrow \tag{2.21}$$

and

$$\chi_+ = \downarrow . \tag{2.22}$$

These functions, χ, are mutually orthogonal, but exist in another Hilbert space than the spatial wave functions, Ψ, and will not interfere with the integration $\int dx$.

This presentation of spin is very short due to the fact that we don't need that much information about spin in this project. As shown later, the Hamiltonian will not depend on spin values, so the functions χ will only be used as a label to indicate which states are occupied or not. This will become more apparent in the discussion of many particle systems.

2.2 Quantum Mechanics in three dimensions

While discussing quantum mechanics in one dimension is useful for getting in the basics, most real life systems occur in three dimensions. This section closely follows the discussion in [1].

In three dimensions the one-dimensional Hamiltonian, $H(x, p_x) = p_x^2/2m_e + V(x)$ is replaced by

$$H(x, y, z, p_x, p_y, p_z) = \frac{1}{2m_e} \left(p_x^2 + p_y^2 + p_z^2 \right) + V(x, y, z). \tag{2.23}$$

with m_e being the electron mass. For quantum mechanical systems the momentum operators are substituted by

$$p_x \to \frac{\hbar}{i} \frac{\partial}{\partial x}, \quad p_y \to \frac{\hbar}{i} \frac{\partial}{\partial y}, \quad p_z \to \frac{\hbar}{i} \frac{\partial}{\partial z}. \tag{2.24}$$

We could also write this more compact in vector form

$$\mathbf{p} = \frac{\hbar}{i} \nabla. \tag{2.25}$$

Introducing the **Laplacian** in Cartesian coordinates, $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$, we can write the full Hamiltonian as

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m_e} \nabla^2 \Psi + V\Psi. \tag{2.26}$$

The normalization integral in three dimensions changes using the infinitesimal volume element $d^3\mathbf{r} = dx \, dy \, dz$. We now have

$$\int |\Psi(x, y, z, t)|^2 \, dx \, dy \, dz = \int |\Psi(\mathbf{r}, t)|^2 \, d^3\mathbf{r} = 1. \tag{2.27}$$

The general solutions in three dimensions can be expressed as

$$\Psi(\mathbf{r}, t) = \sum c_n \psi_n(\mathbf{r}) e^{-iE_n t/\hbar}. \tag{2.28}$$

The spatial wave functions, ψ_n, satisfy the time-independent Schrödinger equation:

$$-\frac{\hbar^2}{2m_e} \nabla^2 \psi + V\psi = E\psi. \tag{2.29}$$

2.2.1 Separation of variables - quantum numbers l and m

For a central symmetrical potential where the function V only depends on the distance, $V = V(|\mathbf{r}|) = V(r)$, it is common to introduce **spherical coordinates**, (r, θ, φ)(see figure 2.1), and try the approach of separation of variables. That means solutions of the form

$$\psi(r, \theta, \varphi) = R(r)Y(\theta, \varphi). \tag{2.30}$$

In spherical coordinates the time-independent Schrödinger equation, Eq. (2.29), is

$$-\frac{\hbar^2}{2m_e} \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \left(\frac{\partial^2 \psi}{\partial \varphi^2} \right) \right] + V\psi = E\psi. \tag{2.31}$$

By performing the same exercise as in section 2.1.2, calling the separation constant $l(l+1)$, this will give rise to the radial and angular equations for a single particle in a three dimensional central symmetrical potential:

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{2m_e r^2}{\hbar^2}\left[V(r) - E\right] = l(l+1);$$
(2.32)

$$\frac{1}{Y}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\varphi^2}\right] = -l(l+1).$$
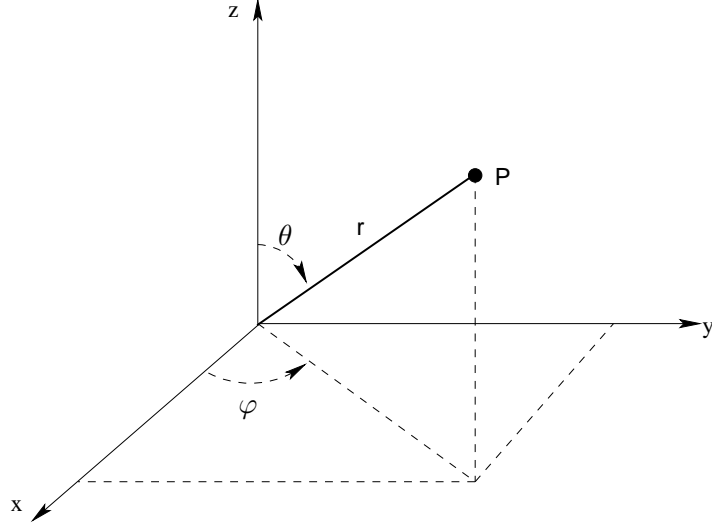(2.33)

Figure 2.1: Visualizing the spherical coordinates of some point P; radius r, polar angle θ and azimuthal angle φ.

2.2.2   The Angular equation

If we multiply Eq. (2.33) by $Y\sin^2\theta$, again using separation of variables, with $Y(\theta,\varphi) = T(\theta)F(\varphi)$, and divide by $Y = TF$, we get

$$\frac{1}{T}\left[\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{dT}{d\theta}\right)\right] + l(l+1)\sin^2\theta = -\frac{1}{F}\frac{d^2 F}{d\varphi^2}.$$
(2.34)

This time we call the separation constant m^2.

The φ equation

The equation for φ is calculated quite easily, with

$$\frac{d^2 F}{d\varphi^2} = -m^2 F \Rightarrow F(\varphi) = e^{im\varphi}$$
(2.35)

letting the value m take both positive and negative values. Because the angle φ represents a direction in space, we must require that

$$F(\varphi + 2\pi) = F(\varphi).$$
(2.36)

It then follows that

$$e^{im(\varphi+2\pi)} = e^{im\varphi} \quad \rightarrow \quad e^{2\pi im} = 1. \tag{2.37}$$

For this to be fulfilled, m has to be an integer. Viz., $m = 0, \pm 1, \pm 2, \ldots$.

The θ equation

The differential equation for the polar angle, θ, reads

$$\sin\theta \frac{d}{d\theta} \left(\sin\theta \frac{dT}{d\theta} \right) + [l(l+1)\sin^2\theta - m^2]T = 0. \tag{2.38}$$

This equation is more diffcult to solve by standard mathematics. In short, the solution is given by

$$T(\theta) = AP_l^m(\cos\theta), \tag{2.39}$$

where A is a constant, and P_l^m is the **associated Legendre function**

$$P_l^m(x) = (1-x^2)^{|m|/2} \left(\frac{d}{dx} \right)^{|m|} P_l(x). \tag{2.40}$$

$P_l(x)$ is the lth degree **Legendre polynomial**, defined by the so-called **Rodrigues formula**:

$$P_l(x) = \frac{1}{2^l l!} \left(\frac{d}{dx} \right)^l (x^2-1)^l. \tag{2.41}$$

We see that l must be a positive integer for the differentiations to make sense, and furthermore, $|m|$ must be smaller or equal to l for $P_l^m(x)$ to be non-zero.

These solutions are the physically acceptable ones from the differential equation Eq. (2.33). Another set of non-physical solutions also exist, but these are not interesting for us.

Taking into account the normalization of the angular wave functions, a quite general expression for the functions, Y_l^m is then

$$Y_l^m(\theta, \varphi) = \epsilon \sqrt{\frac{(2l+1)}{4\pi} \frac{(l-|m|)!}{(l+|m|)!}} e^{im\varphi} P_l^m(\cos\theta). \tag{2.42}$$

These are also called the **spherical harmonics**. Here $\epsilon = (-1)^m$ for $m \geq 0$ and $\epsilon = 1$ for $m \leq 0$. Examples of these are:

$$Y_0^0 = \left(\frac{1}{4\pi} \right)^{1/2}, \tag{2.43}$$

$$Y_1^0 = \left(\frac{3}{4\pi} \right)^{1/2} \cos\theta \tag{2.44}$$

and

$$Y_1^{\pm 1} = \pm \left(\frac{3}{8\pi} \right)^{1/2} \sin\theta e^{\pm i\varphi}. \tag{2.45}$$

The quantum number l is commonly called the **azimuthal quantum number**, while m is called the **magnetic quantum number**. We observe that the spherical harmonics do not depend on the potential V, other than it being a spherically symmetric potential.

2.2.3 The Radial equation and solution for the hydrogen atom

The radial equation reads

$$\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{2m_e r^2}{\hbar^2}[V(r) - E]R = l(l+1)R. \tag{2.46}$$

The first simple step is to change variables by using

$$u(r) = rR(r) \tag{2.47}$$

this will give the radial part of the Schrödinger equation on a much simpler form

$$-\frac{\hbar^2}{2m_e}\frac{d^2u}{dr^2} + \left[V + \frac{\hbar^2}{2m_e}\frac{l(l+1)}{r^2}\right]u = Eu. \tag{2.48}$$

The only difference between this Eq. (2.48) and the one dimensional Schrödinger equation, Eq. (2.10), is the potential. Here we have an effective potential

$$V_{eff} = V + \frac{\hbar^2}{2m_e}\frac{l(l+1)}{r^2} \tag{2.49}$$

as opposed to the simple V in Eq. (2.10). The extra term in V_{eff}

$$\frac{\hbar^2}{2m_e}\frac{l(l+1)}{r^2}, \tag{2.50}$$

is called the centrifugal term.

The Hydrogen atom and the principal quantum number - n

An important quantum mechanical system is the hydrogen atom. It consists of an electron, charged $-e$, and a motionless proton, charged e. The proton is only seen as motionless due to the Born-Oppenheimer approximation. More on the Born-Oppenheimer approximation in section 2.3.4.
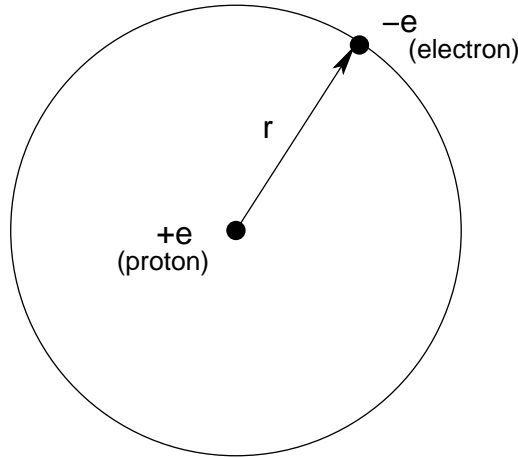

Figure 2.2: A shell model of the hydrogen atom.

For the hydrogen atom, the potential function is given by Coulomb's law between charged particles:

$$V(r) = -\frac{e^2}{4\pi\epsilon_0}\frac{1}{r}, \tag{2.51}$$

where ϵ_0 is the vacuum permittivity. The radial equation for the hydrogen atom is then

$$-\frac{\hbar^2}{2m_e}\frac{d^2u}{dr^2} + \left[-\frac{e^2}{4\pi\epsilon_0}\frac{1}{r} + \frac{\hbar^2}{2m_e}\frac{l(l+1)}{r^2}\right]u = Eu. \tag{2.52}$$

We will consentrate on the *bound* states, viz. $E < 0$.

This differential equation is quite tedious and difficult to solve, so in this section I will just state the important results. From solving the equation we will obtain a certain quantum number, n, also called the **principal quantum number**. This number determines the allowed energies for the system given by

$$E = -\left[\frac{m_e}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right]\frac{1}{n^2} = \frac{E_1}{n^2} \tag{2.53}$$

for $n = 1, 2, 3, \ldots$. The ground state of hydrogen is then given as

$$E_1 = -\left[\frac{m_e}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right] = -13.6 \text{ eV}. \tag{2.54}$$

The radial part of the wave function is now labeled by quantum numbers n and l, giving the full wave function the form

$$\psi_{nlm}(r, \theta, \varphi) = R_{nl}(r)Y_l^m(\theta, \varphi). \tag{2.55}$$

By solving the equation, we also find a constraint on l, namely

$$l = 0, 1, 2, \ldots, n-1. \tag{2.56}$$

The mathematical form of radial wave function is expressed as

$$R_{nl} = \sqrt{\left(\frac{2}{na}\right)^3\frac{(n-l-1)!}{2n[(n+l)!]^3}}e^{-r/na}\left(\frac{2r}{na}\right)^l\left[L_{n-l-1}^{2l+1}(2r/na)\right], \tag{2.57}$$

where a is the Bohr radius

$$a \equiv \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} = 0.529 \cdot 10^{-10}\text{m}, \tag{2.58}$$

and

$$L_{q-p}^p(x) \equiv (-1)^p\left(\frac{d}{dx}\right)^p L_q(x) \tag{2.59}$$

is the **associated** Laguerre polynomial. The function $L_q(x)$ is the qth Laguerre polynomial and is defined by

$$L_q(x) \equiv e^x\left(\frac{d}{dx}\right)^q(e^{-x}x^q) \tag{2.60}$$

with $p = 2l + 1$ and $q = n + l$. The radial wave functions needed in this project are

$$R_{10} = 2a^{-3/2}e^{-r/a}, \tag{2.61}$$

$$R_{20} = \frac{1}{\sqrt{2}}a^{-3/2}\left(1 - \frac{1}{2}\frac{r}{a}\right)\frac{r}{a}e^{-r/2a}, \tag{2.62}$$

$$R_{21} = \frac{1}{\sqrt{24}}a^{-3/2}\frac{r}{a}e^{-r/2a}, \tag{2.63}$$

$$R_{30} = \frac{2}{\sqrt{27}}a^{-3/2}\left(1 - \frac{2}{3}\frac{r}{a} + \frac{2}{27}\left(\frac{r}{a}\right)^2\right)e^{-r/3a}, \tag{2.64}$$

$$R_{31} = \frac{8}{27\sqrt{6}}a^{-3/2}\left(1 - \frac{1}{6}\frac{r}{a}\right)\left(\frac{r}{a}\right)e^{-r/3a}. \tag{2.65}$$

In sections 3.3 and 2.3.2 we will see how we can use these functions to construct the wave functions needed in this project.

2.3 Atoms

In quantum mechanics an atom can be viewed as a many-particle system. While the wave function for a single particle system is a function of only the coordinates of that particular particle and time, $\Psi(\mathbf{r}, t)$, a many-particle system will depend on the coordinates of all the particles.

2.3.1 Two-particle systems

The simplest example of a many-particle system is of course a two-particle system. The wave function will now be the function

$$\Psi(\mathbf{r_1}, \mathbf{r_2}, t), \tag{2.66}$$

and the Hamiltonian will take the form

$$\widehat{\mathbf{H}} = -\frac{\hbar^2}{2m_1}\nabla_1^2 - \frac{\hbar^2}{2m_2}\nabla_2^2 + V(\mathbf{r_1}, \mathbf{r_2}, t). \tag{2.67}$$

The indices on the Laplacian operators indicate which electron/coordinates the derivative is taken with respect to. The normalization integral is now

$$\int |\Psi(\mathbf{r_1}, \mathbf{r_2}, t)|^2 \, d^3\mathbf{r_1} d^3\mathbf{r_2} = 1 \tag{2.68}$$

with the integrand $|\Psi(\mathbf{r_1}, \mathbf{r_2}, t)|^2 \, d^3\mathbf{r_1} d^3\mathbf{r_2}$ being the probability of finding particle 1 in the infinitesimal volume $d^3\mathbf{r_1}$, and particle 2 in $d^3\mathbf{r_2}$. For a time-independent potential, this will give the stationary solutions from separation of variables:

$$\Psi(\mathbf{r_1}, \mathbf{r_2}, t) = \psi(\mathbf{r_1}, \mathbf{r_2})e^{-iEt/\hbar}. \tag{2.69}$$

Antisymmetry and wavefunctions

For general particles in a composite system a wave function can be constructed by using the single particle wave functions the particles currently occupy. That is, electron 1 is in state ψ_a and electron 2 is in state ψ_b. A wave function can be constructed as

$$\psi(\mathbf{r_1}, \mathbf{r_2}) = \psi_a(\mathbf{r_1})\psi_b(\mathbf{r_2}). \tag{2.70}$$

The particles that make up an atom are electrons and the protons in the nucleus. As we will see in section 2.3.4, the interesting parts are the electrons. Electrons(and protons) are so-called fermions, that means particles with *half integer* spin, while particles with *integer* spin are called bosons (e.g. photons). An important point with respect to our quantum mechanical approach is how to construct the wave function for a composite system of particles. Quantum physics tells us that the particles are identical, and cannot be distinguished by some classic method like labelling the particles. This is taken care of by constructing a wave function that opens for the possibility of both electrons being in both states. That is,

$$\psi_\pm(\mathbf{r_1}, \mathbf{r_2}) = A[\psi_a(\mathbf{r_1})\psi_b(\mathbf{r_2}) \pm \psi_b(\mathbf{r_1})\psi_a(\mathbf{r_2})], \tag{2.71}$$

with A being a normalization constant. The plus sign is for bosons, while the minus sign. This also shows the **Pauli exclusion principle**, which states: No two identical

fermions can occupy the same state at the same time. E.g. if $\psi_a = \psi_b$ the wave funtion automatically gives zero for fermions.

$$\psi_-(\mathbf{r_1}, \mathbf{r_2}) = A[\psi_a(\mathbf{r_1})\psi_a(\mathbf{r_2}) - \psi_a(\mathbf{r_1})\psi_a(\mathbf{r_2})] = 0. \tag{2.72}$$

It also tells you that two bosons can occupy the same state at the same time. In fact, any number of bosons may occupy the same state at the same time. Eq. (2.71) also underlines an important property of fermionic wave function. That is the antisymmetric property when interchanging two particles. By switching particles 1 and 2 in ψ_-, you will get $-\psi_-$ in return.

In atoms however, two partices are allowed to occupy the same spatial wave function state, but only if these have different spin functions(ref. 2.1.2), or *spinors*. An example is helium, an atom consisting of two electrons and and a immovable core with charge Z=2. Since we don't have a method for solving the helium atom exactly we use an ansatz for the wave function, with the two electrons occupying the ψ_{100}-functions found when solving the hydrogen problem. So the two electrons will have the wave function

$$\Psi = 2a^{-3/2}e^{-r/a}\left(\frac{1}{4\pi}\right)^{1/2}\chi_\pm \tag{2.73}$$

with $\chi_+ = \uparrow$ as the spin up spinor, and $\chi_- = \downarrow$ as the spin down spinor.

2.3.2   Wave functions for atoms

The many particle system with most interest in this project is the neutral atom. Examples which will be dealt with in this project are helium, beryllium, neon, magnesium and silicon. As mentioned above, we have no analytical solution to any atomic system other than the hydrogen atom, and we have to make an ansatz for the wave function.

Slater Determinants

The two-electron wave function

$$\psi_-(\mathbf{r_1}, \mathbf{r_2}) = A[\psi_a(\mathbf{r_1})\psi_b(\mathbf{r_2}) - \psi_b(\mathbf{r_1})\psi_a(\mathbf{r_2})] \tag{2.74}$$

can be expressed as a determinant

$$\psi_-(\mathbf{r_1}, \mathbf{r_2}) = A \begin{vmatrix} \psi_a(r_1) & \psi_a(r_2) \\ \psi_b(r_1) & \psi_b(r_2) \end{vmatrix}. \tag{2.75}$$

This is called the **Slater determinant** for the two particle case where the available single particle states are ψ_a and ψ_b. The factor A is in this case $1/\sqrt{2}$. The general expression for a Slater determinant, Φ, with N electrons and N available single particle states is as given in [3]:

$$\Phi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(r_1) & \psi_1(r_2) & \cdots & \psi_1(r_N) \\ \psi_2(r_1) & \psi_2(r_2) & \cdots & \psi_2(r_N) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_N(r_1) & \psi_N(r_2) & \cdots & \psi_N(r_N) \end{vmatrix}. \tag{2.76}$$

This will automatically comply with the antisymmetry principle and is suited as a wave function for a fermionic many-particle system. The general structure is to take the determinant of a $N \times N$-matrix with available particle states in increasing order in the columns. The states are functions of the particle coordinates which are in increasing order in the rows.

2.3.3 Electron configuration

The electron configuration of an atom describes how the electrons are distributed in the given orbitals of the system. The rules for quantum numbers obtained in sections 2.2.1 and 2.2.3 give us the allowed combinations for the configuration. As shown, n can be $n = 1, 2, 3, \ldots$, while l has the allowed values $l = 0, 1, \ldots, n - 1$. Quantum number m can take the values $m = -l, -l + 1, \ldots, l - 1, l$.

A common way to label the orbitals is to use the spectroscopic notation which says that states with $l = 0$ are called s-states, $l = 1$ are called p-states and so on. An orbital with $n = 1$ and $l = 0$ is labelled $1s$, and an orbital with $n = 2$ and $l = 1$ is labelled $2p$. Table 2.2 shows the full list for the azimuthal quantum number, l. The letters s,p,d and

Quantum number l	Spectroscopic notation
0	s
1	p
2	d
3	f
4	g
5	h
6	i
7	j
$\vdots$	$\vdots$

Table 2.1: The table shows the spectroscopic notation for the azimuthal quantum number l.

f are historic names origining from the words *sharp*, *principal*, *diffuse* and *fundamental*. From g and out the letters are just given alphabetically.

The neon atom consists of 10 electrons and it's orbital distribution is given as follows:

- When $n = 1$, l(and therefore m) can only take the value 0. But an electron can either be in a spin up, or a spin down state. This means that two electrons can be in the $1s$-orbital. This is written as $(1s)^2$.

- For $n = 2$ and $l = 0$ there is only $m = 0$, but again two spin states, i.e. $(2s)^2$.

- For $n = 2$ and $l = 1$, we can have $m = -1, 0, 1$, and both spin states. This means 6 electrons in the $2p$-orbital, i.e. $(2p)^6$.

- The electron configuration in neon can then be written short and concise as: $(1s)^2(2s)^2(2p)^6$.

We can now use this notation to describe the distribution of electrons in the different orbitals. Table 2.1 shows a few important examples All this tells us which orbitals to put our electrons in, but doesn't say anything about what the orbitals in fact are. This is taken care of in sections 3.3 and 3.4.

Atom	Full spectroscopic notation
Hydrogen	$(1s)$
Helium	$(1s)^2$
Beryllium	$(1s)^2(2s)^2$
Neon	$(1s)^2(2s)^2(2p)^6$
Magnesium	$(1s)^2(2s)^2(2p)^6(3s)^2$
Silicon	$(1s)^2(2s)^2(2p)^6(3s)^2(3p)^2$

Table 2.2: The table shows the electron configuration for hydrogen, helium, beryllium, neon, magnesium and silicon.

2.3.4 Hamiltonian and scaling

The Hamiltonian, $\widehat{\mathbf{H}}$, for an N-electron atomic system is subject to the Born-Oppenheimer approximation(BOA). The BOA effectively freezes out the nuclear degrees of freedom given the electron mass is small compared to the mass of the nucleus. As a result, the nucleus has no movement, hence no kinetic energy during the calculations. The Hamiltonian consists of only the kinetic energy of electrons in addition to the potential energy between electrons and the core, and between the electrons themselves:

$$\widehat{\mathbf{H}} = \sum_i^N \frac{\widehat{\mathbf{p}}_i^2}{2m_e} - \sum_i^N \frac{Ze^2}{4\pi\epsilon_0 r_i} + \sum_{i<j} \frac{e^2}{4\pi\epsilon_0 r_{ij}}. \tag{2.77}$$

The operator $\widehat{\mathbf{p}}$ is the kinetic energy operator, m_e is the electron mass, Z is the number of protons in the nucleus (equal to the number of electrons in neutral atoms) and ϵ_0 the vacuum permitivity. The variables r_i and r_{ij} represent the distances between an electron and the nucleus and the distance between to different electrons respectively.

By substituting $\widehat{\mathbf{p}}$ with the quantum mechanical operator $\widehat{\mathbf{p}} = -i\hbar\nabla$, i being the imaginary unit and $\hbar$ Planck's original constant divided by 2π, we get

$$\widehat{\mathbf{H}} = -\frac{\hbar^2}{2m_e} \sum_i^N \nabla_i^2 - \sum_i^N \frac{Ze}{4\pi\epsilon_0 r_i} + \sum_{i<j} \frac{e^2}{4\pi\epsilon_0 r_{ij}}. \tag{2.78}$$

It is more desireable to work with a scaled version of the Hamiltonian. By defining

$$r_0 = \frac{4\pi\epsilon_o \hbar^2}{m_e e^2} \tag{2.79}$$

and

$$E_0 = \frac{m_e e^4}{(4\pi\epsilon_0 \hbar)^2}, \tag{2.80}$$

we can again define dimensionless variables such as $H' = H/E_0$, $\nabla' = \nabla/r_0$ and $r' = r/r_0$. The r_0's in ∇' comes from the factors $\mathrm{d}/\mathrm{d}x = \mathrm{d}/\mathrm{d}(x'r_o)$. By analyzing each term in Eq. (2.77) and writing out the original variables in terms of constants r_0 and E_0, and the dimensionless quantities r' and $\widehat{\mathbf{H}}'$ we get

$$\widehat{\mathbf{H}} = \widehat{\mathbf{H}}' E_0 = -\frac{\hbar^2}{2m_e r_0^2} \sum_i^N (\nabla_i')^2 + \frac{e^2}{4\pi\epsilon_0 r_o} \sum_i^N \frac{1}{r_i'} - \frac{Ze^2}{4\pi\epsilon_0 r_0} \sum_{i<j} \frac{1}{r_{ij}'} \tag{2.81}$$

By inserting Eqs. (2.79) and (2.80) into Eq. (2.81) we obtain

$$\widehat{\mathbf{H}}' E_0 = -\frac{E_0}{2} \sum_i^N (\nabla_i')^2 - E_0 \sum_i^N \frac{1}{r_i'} + E_0 \sum_{i<j} \frac{1}{r_{ij}'} \tag{2.82}$$

which divided by E_0 will give the final dimensionless Hamiltonian

$$\widehat{\mathbf{H}} = -\frac{1}{2} \sum_i^N \nabla_i^2 - \sum_i^N \frac{1}{r_i} + \sum_{i<j} \frac{1}{r_{ij}}. \tag{2.83}$$

Now the energy will be measured in the units of Hartree, E_h, which converts as, $1E_h = 2 \cdot 13,6$ eV. These are also called atomic units. We recognize the number $13,6$ as the ground state energy of the hydrogen atom.

2.4   Bra-Ket notation

As we will be dealing a lot with expectiation values, which are integrals, it can be smart to introduce a compact way to describe the wave functions and the integrals. The so-called **ket**, $|\Psi\rangle$, represents our Ψ, while the **bra**, $\langle\Psi|$, represents the Ψ^*. The product

$$\langle\Psi|\,\widehat{\mathbf{H}}\,|\Psi\rangle \tag{2.84}$$

is defined as

$$\langle\Psi|\,\widehat{\mathbf{H}}\,|\Psi\rangle = \int \Psi^*\widehat{\mathbf{Q}}\Psi \mathrm{d}x, \tag{2.85}$$

where x now represents all spatial dimensions and quantum numbers. Now we can write the expectiation values of $\widehat{\mathbf{H}}$ as

$$\langle H\rangle = \langle\Psi|\,\widehat{\mathbf{H}}\,|\Psi\rangle . \tag{2.86}$$

At many times it will still be desireable to use the full notation with integrals.

2.5 Hartree-Fock Theory

Hartree-Fock theory assumes the Born-Oppenheimer approximation and can be used to approximate the ground state energy and ground state wave function of a quantum many body system. In Hartree-Fock we assume the wave function, Φ, to be the N-particle Slater determinant which is an antisymmetric product state of single particle orbits. In order to find the optimal basis one needs to minimize an energy functional by either varying the spatial part, or expand the single particle functions in a known basis, and vary the expansion coefficients. The Hamiltonian

$$H = \sum_{i=1}^{N} \left[-\frac{\hbar^2}{2m} \nabla_i^2 + V(r_i) \right] + \frac{1}{2} \sum_{i<j} \frac{e^2}{r_{ij}} \tag{2.87}$$

will not give a separable Schrödinger equation

$$H\Phi = E\Phi. \tag{2.88}$$

Using Variational Calculus- and Lagrangian multiplier-techniques we can obtain the Hartree-Fock energy functional expressed as

$$E[\Phi] = \sum_{\mu=1}^{N} \int \psi_\mu^*(\mathbf{r_i}) \widehat{\mathbf{h_i}} \psi_\mu(\mathbf{r_i}) d\mathbf{r_i} + \frac{1}{2} \sum_\mu^N \sum_\nu^N \left[\int \psi_\mu^*(\mathbf{r_i}) \psi_\nu^*(\mathbf{r_j}) \frac{1}{r_{ij}} \psi_\mu(\mathbf{r_i}) \psi_\nu(\mathbf{r_j}) d\mathbf{r_i} d\mathbf{r_j} \right.$$
$$\left. - \int \psi_\mu^*(\mathbf{r_i}) \psi_\nu^*(\mathbf{r_j}) \frac{1}{r_{ij}} \psi_\nu(\mathbf{r_j}) \psi_\nu(\mathbf{r_j}) d\mathbf{r_i} d\mathbf{r_j} \right] \tag{2.89}$$

where now $\widehat{\mathbf{h_i}}$ are the one body hamiltonians, that is the sum of the kinetic energy and the one-body interaction with the nucleus. The states ψ_μ and ψ_ν are the Hartree-Fock orbitals which minimizes the energy when we solve the Hartree-Fock equations. The energy functional can be written more compactly as

$$E[\Phi] = \sum_{\mu=1}^{N} \langle \mu | h | \mu \rangle + \frac{1}{2} \sum_{\mu=1}^{N} \sum_{\nu=1}^{N} \left[\langle \mu\nu | \frac{1}{r_{ij}} | \mu\nu \rangle - \langle \mu\nu | \frac{1}{r_{ij}} | \nu\mu \rangle \right]. \tag{2.90}$$

The two terms in the square bracket in Eq. (2.90) are the so-called Hartree- and Fock-terms, also called *Direct*- and *Exchange*-terms. This handles the antisymmetric properties of the wave function.

The Roothaan-Hartree-Fock approach is to minimize this functional with respect to the orbitals themselves. This will in time lead to the Roothan-Hartree-Fock(RHF) equations. The Roothaan-Hartree-Fock orbitals and the solutions are shown in section 3.4 and appendix A. The derivation of the RHF-equations which are solved to get the RHF-orbitals is discussed in [4].

This Hartree-Fock discussion is quite brief due to the fact that I have merely used the results obtained by Clementi and Roetti and not done the HF-calculations myself.

Chapter 3

Quantum Monte Carlo

Monte Carlo methods are designed to simulate a mathematical system, or in our case, a quantum mechanical system. By using random numbers, these methods are considered stochastic, i.e. non-deterministic unlike other simulation techniques, such as *Hartree Fock*, *Coupled Cluster Theory* and *Configuration Interaction*. Monte Carlo methods can be used to simulate quantum mechanical systems, but are also well suited for calculating integrals, especially high-dimension integrals.

These methods have their basis on probability and statistics, and in order to get good expectation values and variances, the quantity in question must be sampled millions of times. Each such sample is called a Monte Carlo cycle, and in many cases closely relates to a time evolution of the system being simulated.

To use the Monte Carlo technique, we will need a probability distribution function(PDF), $P(x)$, to guide our sampling, with x being some set of variables, and of course a quantity to sample, in our case the energy of the system, E. The expectation value of the quantity of interest, e.g. an operator $\widehat{\mathbf{Q}}$, will now be

$$\langle Q \rangle = \int P(x)\widehat{\mathbf{Q}}dx. \tag{3.1}$$

As we will see in section 3.2.1 the operator we are looking for in our case will be the local energy operator

$$\widehat{\mathbf{E}}_L(\mathbf{R}; \alpha) = \frac{1}{\psi_T}\widehat{\mathbf{H}}\psi_T(\mathbf{R}; \alpha). \tag{3.2}$$

where $\mathbf{R}$ will be the set of all spatial variables, ψ_T a trial wave function as we don't have the exact solution Ψ(if we did, we wouldn't have to go through all of this), and α a set of variational parameters which will be discussed in the following section.

This chapter will also discuss the variational principle and the Metropolis algorithm for the Variational Monte Carlo method. The Metropolis-Hastings algorithm will also be discussed including importance sampling which will improve the method further, with more relevant sample points.

The last sections of the chapter

3.1 The Variational Principle

The main target in quantum mechanics is to solve the Schrödinger equation

$$\widehat{\mathbf{H}}\Psi = E\Psi \tag{3.3}$$

where $\widehat{\mathbf{H}}$ is the Hamiltonian, the operator representing the energy of the system, Ψ the quantum mechanical wave function, and E the total energy of the system. The variational principle tells us that for any given choice of trial wave function, ψ_T, the total energy

$$E = \langle \psi_T | \widehat{\mathbf{H}} | \psi_T \rangle \tag{3.4}$$

will always be larger or equal to the true ground state energy, E_0,

$$E_0 \leq \langle \psi_T | \widehat{\mathbf{H}} | \psi_T \rangle, \tag{3.5}$$

given normalized wave functions. This inequality gives an equality when you find the true ground state wave function, Ψ_0, that is

$$E_0 = \langle \Psi_0 | \widehat{\mathbf{H}} | \Psi_0 \rangle. \tag{3.6}$$

As our main goal is to approximate the ground state energy, this is the basis of our calculations. This gives us an idea to introduce variational parameters to our trial wave function in search for a good approximation. Instead of just having the wave functions $\psi_T = \psi_T(x, y, z)$, we no have

$$\psi_T = \psi_T(x, y, z, \alpha, \beta, \dots) \tag{3.7}$$

We now vary the parameters $\alpha, \beta, \dots$ using Eq. (3.5) to guide us towards the minimum.

3.2   Variational Monte Carlo

The main exercise with the Variational Monte Carlo process for atoms is to move the particles in the system around guided by a probability distribution and sample the energy at these states in order to calculate various expectation values(mainly $\langle E \rangle$ and $\langle E^2 \rangle$). In our case we have a known Hamiltonian, $\widehat{\mathbf{H}}$, and a chosen many-particle trial wave function, ψ_T. The expectation value of the Hamiltonian is

$$\langle H \rangle = \frac{\int d\mathbf{R}\, \psi_T^*(\mathbf{R}; \alpha) \widehat{\mathbf{H}}(\mathbf{R}) \psi_T(\mathbf{R}; \alpha)}{\int d\mathbf{R}\, \psi_T^*(\mathbf{R}; \alpha) \psi_T(\mathbf{R}; \alpha)}, \tag{3.8}$$

where $\mathbf{R} = (\mathbf{R_1}, \mathbf{R_2}, \dots, \mathbf{R_N})$ are all the coordinates for the N particles, and α is the set of all the variational parameters in question. The general procedure will now be

1. Construct a trial wave function, ψ_T as a function of the N particles' coordinates and the chosen variational parameters

2. Calculate $\langle H \rangle$ using Eq. (3.8)

3. Vary the parameters according to some minimization technique

We will first focus on the second item in the list above, with a focus on the Metropolis algorithm.

3.2.1 VMC and the simple Metropolis algorithm

We assume first that our trial wave function, ψ_T, is not normalized so the quantum mechanical probability distribution is then given as

$$P(\mathbf{R}; \alpha) = \frac{|\psi_T(\mathbf{R}; \alpha)|^2}{\int |\psi_T(\mathbf{R}; \alpha)|^2 \, d\mathbf{R}} \tag{3.9}$$

This is the PDF for our system. We now define a new operator, called the local energy operator as

$$\widehat{\mathbf{E}}_L(\mathbf{R}; \alpha) = \frac{1}{\psi_T} \widehat{\mathbf{H}} \psi_T(\mathbf{R}; \alpha) \tag{3.10}$$

and the expectation value of the local energy is given as

$$\langle E_L(\alpha) \rangle = \int P(\mathbf{R}; \alpha) \widehat{\mathbf{E}}_L(\mathbf{R}; \alpha) d\mathbf{R}. \tag{3.11}$$

The dimensionless Hamiltonian in section 2.3.4 is given as

$$\widehat{\mathbf{H}} = -\frac{1}{2} \sum_i^N \nabla_i^2 - \sum_i^N \frac{1}{r_i} + \sum_{i<j} \frac{1}{r_{ij}}. \tag{3.12}$$

Inserting the Hamiltonian from Eq. (3.12) into Eq. (3.10), the local energy operator will then be

$$\widehat{\mathbf{E}}_L = \frac{1}{\psi_T(\mathbf{R}, \alpha)} \left(-\frac{1}{2} \sum_i^N \nabla_i^2 - \sum_i^N \frac{1}{r_i} + \sum_{i<j} \frac{1}{r_{ij}} \right) \psi_T(\mathbf{R}, \alpha). \tag{3.13}$$

By observing that the last two terms don't affect the wave function in any way, we have

$$\widehat{\mathbf{E}}_L = \frac{1}{\psi_T(\mathbf{R}, \alpha)} \left(-\frac{1}{2} \sum_i^N \nabla_i^2 \right) \psi_T(\mathbf{R}, \alpha) - \sum_i^N \frac{1}{r_i} + \sum_{i<j} \frac{1}{r_{ij}}. \tag{3.14}$$

This will be quantity we sample in each Monte Carlo cycle, following our PDF from Eq. (3.9). The more we improve the trial wave function the closer the expectation value of the local energy, $\langle E_L \rangle$, gets to the exact energy E.

As we sample the local energy E_L we also sample E_L^2 in order to get $\langle E_L^2 \rangle$ for the variance

$$\sigma_{E_L}^2 = \langle E_L^2 \rangle - \langle E_L \rangle^2. \tag{3.15}$$

An important note is that in the Metropolis algorithm only involves ratios between probabilities, so the denominator in Eq. (3.9) actually never needs to be calculated. We will see this in the next section.

The Metropolis algorithm

The Metropolis algorithm uses ratios between probabilities to determine whether or not a chosen particles is to be moved to a proposed position or not. When an electron is moved, the set of positions $\mathbf{R}$ change to positions $\mathbf{R}'$. The ratio $w = P(\mathbf{R}')/P(\mathbf{R})$ is now the transition probability from the state with particles being in positions $\mathbf{R}$ to a state where particles are in positions $\mathbf{R}'$. This ratio w will now be

$$w = \frac{\psi_T(\mathbf{R}')}{\psi_T(\mathbf{R})}. \tag{3.16}$$

The Metropolis algorithm tells us that if

$$w > 1,, \tag{3.17}$$

we automatically accept the new positions. If $w < 1$, we compare w with a random number r, with $r \in [0, 1]$. If

$$r \leq w, \tag{3.18}$$

we also accept the new positions. If neither of the two inequalities are true, we stick with the old positions. The most effective way to use this method is to move one particle at a time before running the tests for w.

   We now have enough information to describe the elements needed to calculate the expectation value for the local energy using the Metropolis algorithm. The specifics of the implementation will be discussed in the next chapter, but the following points still show how it's done.

1. Set all electrons in random positions as an initial point, $\mathbf{R}$

2. Start a Monte Carlo cycle and a loop over electrons

3. Calculate the new position,
$$\mathbf{R}' = \mathbf{R} + s * r \tag{3.19}$$
   for the chosen electron using again random numbers, r and a finite stepsize, s

4. Calculate the ratio $w = \psi_T(\mathbf{R}')/\psi_T(\mathbf{R})$

5. Use checks in Eqs. (3.17) and (3.18) to decide whether to accept new positions, $\mathbf{R} = \mathbf{R}'$, or to stay in initial positions $\mathbf{R}$.

6. If accepted, update positions

7. Repeat steps 3 through 6 for each electron

8. After looping over all particles, calculate the local energy and update $\langle E_L \rangle$ and $\langle E_L^2 \rangle$.

9. Repeat steps 3 through 8 for the chosen number of Monte Carlo cycles

The transition rules being used here is called a uniform symmetrical transition rule, and it is common to keep the acceptance ratio around 0.5(this is achieved with step length $s \approx 1$). The acceptance ratio is the number of accepted steps divided by total number of particle moves. However, this simple Metropolis algorithm does not seem very efficient, due to the way the new positions are calculated. They depend solely on the previous position and not on any guiding mechanism. In order to make this method more efficient, we introduce the Metropolis-Hastings algorithm with so-called importance sampling. With importance sampling we will get a much higher acceptance ratio

3.2.2 Metropolis-Hastings algorithm and importance sampling

As an improvement to our Metropolis algorithm, we introduce the Metropolis-Hastings algorithm, which involves importance sampling. A new term that has to be implemented is the **quantum force** of the system:

$$F = 2\frac{1}{\psi_T}\nabla\psi_T \tag{3.20}$$

A physical interpretation of the quantum force, and therefore a good reason to implement it, is that the gradient of the wavefunction tells us which direction the electrons are moving. If we rather use the quantum force to steer us in the direction of the electron movement, rather than sampling random points around the nucleus, the points we sample will be more relevant and therefore our acceptance ratio increases to about 0.8-0.9. This will in time decrease our thermalization period, the period for the system to reach a most likely state, and will give us more correct results in less time than for the brute force sampling.

Importance sampling

The starting point is the Langevin equation, a stochastic differential equation describing the dynamics of random walkers:

$$\frac{\partial x(t)}{\partial t} = DF(x(t)) + \eta, \tag{3.21}$$

where η is a random variable following the uniform distribution between 0 and 1, and D is a diffusion constant known from *Random Walk*-theory. Integrating this equation using the consepts of stochastic integration, will yield the equation

$$y = x + DF(x)\Delta t + \xi \tag{3.22}$$

where ξ now is a Gaussian distributed random variable and Δt is a chosen timestep. This equation replaces Eq. (3.19) as the equation that calculates the new position for a particle. We see that is depends on a drift term, the quantum force, $F(x)$.

By using the so-called Fokker-Planck equation (where P is a time-dependent probability density),

$$\frac{\partial P}{\partial t} = D\frac{\partial}{\partial x}\left(\frac{\partial}{\partial x} - F\right)P(x, t) \tag{3.23}$$

an equation describing the time evolution of a probability distribution function, we yield a transition probability in form of a Green's function:

$$G(y, x, \Delta t) = \frac{1}{(4\pi D\Delta t)^{3N/2}}\exp\left(-(y - x - D\Delta t F(x))^2/4D\Delta t\right) \tag{3.24}$$

This new propability must be multiplied with our probability Eq. (3.9) and the ratio of probability from equation 3.16 is then replaced by the modified ratio

$$w = \frac{G(x, y, \Delta t)|\psi_T(\mathbf{R'})^2|}{G(y, x, \Delta t)|\psi_T(\mathbf{R})^2|}, \tag{3.25}$$

or more explicitly

$$w = \frac{|\psi_T(\mathbf{R'})^2|}{|\psi_T(\mathbf{R})^2|}\exp\left(-\frac{(y - x - D\Delta t F(x))^2}{4D\Delta t}\right) \tag{3.26}$$

Now we have an algorithm which speeds up the process as more important or relevant states are sampled, hence the name, importance sampling.

Metropolis-Hastings algorithm

We could now summarize the Metropolis-Hastings algorithm in the same way as for the simple Metropolis algorithm:

1. Set all electrons in random positions as an initial point, x

2. Start a Monte Carlo cycle and a loop over electrons

3. Calculate the new position,

$$y = x + DF(x)\Delta t + \xi \tag{3.27}$$

   for the chosen electron using a Gaussian distributed number, ξ and a chosen timestep, Δt

4. Calculate the quantum force for the new position and then the Green's function

5. Calculate the ratio w from equation Eq. (3.26)

6. Use checks in Eqs. (3.17) and (3.18) to decide whether to accept new positions, y, or to stay in initial positions x

7. If accepted, update positions and quantum force

8. Repeat steps 3 through 7 for each electron

9. After looping over all particles, calculate the local energy and update $\langle E_L \rangle$ and $\langle E_L^2 \rangle$.

10. Repeat steps 3 through 9 for the chosen number of Monte Carlo cycles

The detailed implementation as a computer program will be discussed in the next chapter.

3.3   Orbitals for VMC

In order to construct a trial Slater determinant for the Variational Monte Carlo-method, our first choice is to use the hydrogenic single particle functions obtained when solving the Schrödinger equation for hydrogen.

3.3.1   S-orbitals

An s-orbital is a spatial wave function with quantum number $l = 0$. Introducing the variational parameter α, the s-orbitals needed for calculating up to at least silicon, with $N = 14$ electrons, are $1s$, $2s$ and $3s$. Here we only need the radial part of the wave functions because the constant angular parts factor out in the Metropolis algorithm(see section 3.2.1). The spherical harmonic for $l = 0$ is

$$Y_0^0 = \left(\frac{1}{4\pi}\right)^{1/2}. \tag{3.28}$$

We now don't have to consider changing from spherical to Cartesian coordinates because the expression will remain the same using the simple relation $r = \sqrt{x^2 + y^2 + z^2}$. The hydrogenic radial functions are found in table 4.7 in [1] where non-vanishing factors(cf. Metropolis algorithm) $1/a$ have been replaced by α.

The $1s$ function

For the $1s$ function we only need the exponential function

$$\phi_{1s} = e^{-r\alpha}, \tag{3.29}$$

with the **first derivative** with respect to an arbitrary coordinate, x_i, given as:

$$\frac{\partial \phi_{1s}}{\partial x_i} = -\frac{\alpha x_i}{r} e^{-\alpha r}. \tag{3.30}$$

The Laplacian, $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$, needed for the kinetic energy is given as

$$\nabla^2 \phi_{1s} = \frac{\alpha}{r} \left(\alpha r - 2\right) e^{-\alpha r}. \tag{3.31}$$

The $2s$ function

The $2s$ wave function is given by

$$\phi_{2s} = \left(1 - \frac{\alpha r}{2}\right) e^{-\alpha r/2}, \tag{3.32}$$

with the **first derivative** wrt. x_i is

$$\frac{\partial \phi_{2s}}{\partial x_i} = \frac{\alpha x_i}{2r} \left(2 - \frac{\alpha r}{2}\right) e^{-\alpha r/2}. \tag{3.33}$$

The **second derivative** of the $2s$ function gives the Laplacian of the function:

$$\nabla^2 \phi_{2s} = \frac{\alpha}{4r} \left(5\alpha r - \frac{\alpha^2 r^2}{2} - 8\right) e^{-\alpha r/2}. \tag{3.34}$$

The 3s function

The final s-function is the 3s wave function. It is

$$\phi_{3s} = \left(1 - \frac{2\alpha r}{3} + \frac{2\alpha^2 r^2}{27}\right) e^{-\alpha r/3}. \tag{3.35}$$

The **first derivative** is

$$\frac{\partial \phi_{3s}}{\partial x_i} = \left(-1 + \frac{10\alpha r}{27} - \frac{2\alpha^2 r^2}{81}\right) \alpha x_i e^{-\alpha r/3} \tag{3.36}$$

while the **second derivative** summed up in all three dimensions is

$$\nabla^2 \phi_{3s} = \left(-2 + \frac{13\alpha r}{9} - \frac{2\alpha^2 r^2}{9} + \frac{2\alpha^3 r^3}{243}\right) \frac{\alpha}{r} e^{-\alpha r/3}. \tag{3.37}$$

3.3.2   P-orbitals

The p-orbitals are the single particle functions which have **azimuthal quantum number** $l = 1$. Now the allowed values for the **magnetic quantum number** are $m = -l, -l+1, \ldots, l-1, l$, i.e. $m = -1, 0, 1$. This is only possible for functions with quantum numbers $n = 1, 2, 3, \ldots$. In this project only s- and p-orbitals are needed.

The angular parts for any p-orbital in spherical coordinates are

$$Y_1^0 = \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta, \tag{3.38}$$

$$Y_1^{\pm 1} = \pm \left(\frac{3}{8\pi}\right)^{1/2} \sin\theta e^{\pm i\varphi}. \tag{3.39}$$

In my program however, I am working with real wave functions and Cartesian coordinates. This is taken care of by introducing real solid harmonics, S_{lm}, as described in [2]. The single particle wave functions, ψ_{nlm}, are written in separable form with spherical coordinates as

$$\psi(r, \theta, \varphi)_{nlm} = R_{nl}(r)Y_{lm}(\theta, \varphi). \tag{3.40}$$

These are general solutions of the one-electron system in a central symmetric potential field. Our radial functions are on the form $R_{nl}(r) = r^l \mathcal{R}_{nl}(r)$. The solid harmonics, $\mathcal{Y}$, are related to the spherical harmonics by

$$\mathcal{Y}_{lm}(r, \theta, \varphi) = r^l Y_{lm}(\theta, \varphi). \tag{3.41}$$

We can then write the wave function as

$$\psi(r, \theta, \varphi)_{nlm} = R_{nl}(r)Y_{lm}(\theta, \varphi) = \mathcal{R}_{nl}(r)\mathcal{Y}_{lm}(r, \theta, \varphi). \tag{3.42}$$

Now there is an r-dependence in the angular part. We will only need the real-valued solid harmonics, S_{lm}, related to the solid harmonics by

$$S_{l,0} = \sqrt{\frac{4\pi}{2l+1}} \mathcal{Y}_{l,0} \tag{3.43}$$

$$S_{l,m} = (-1)^m \sqrt{\frac{8\pi}{2l+1}} \text{Re } \mathcal{Y}_{l,m}, \tag{3.44}$$

and

$$S_{l,-m} = (-1)^m \sqrt{\frac{8\pi}{2l+1}} \text{Im } \mathcal{Y}_{l,m}. \tag{3.45}$$

The real solid harmonics needed for us are simply $S_{1,1} = x$, $S_{1,0} = z$ and $S_{1,-1} = y$. As mentioned earlier, the Metropolis algorithm will take care of any multiplicative factors in front of the wave functions, so we only need to consider one single spatial variable from the angular part of the wave function.

The $2p$ wave function

The expression for the $2p$ wave function in spherical coordinates is proportional to

$$R_{21} \propto re^{-\alpha r/2}. \tag{3.46}$$

By reviewing Eq. (3.41) and using the results from the real solid harmonics, we see the factor $r^l = r$ is replaced by a coordinate x_i. That is, $x_i = x, y, z$ depending on the quantum number m. The general case is then

$$\phi_{2p}(m) = x_i(m)e^{-\alpha r/2}. \tag{3.47}$$

with $x_i(1) = x$, $x_i(0) = z$ and $x_i(-1) = y$.

The first derivative depends on whether the coordinate being differentiated with respect to matches the coordinate x_i of the wave function or not. If these are the same, e.g. $m = 1 \rightarrow x_i = x$, the **first derivative** is

$$\frac{\partial \phi_{2p}}{\partial x} = \left(1 - \frac{\alpha x^2}{2r}\right) \frac{e^{-\alpha r/2}}{r}. \tag{3.48}$$

The expression are analogous for y and z as well.

If these coordinates do not match, e.g. $\phi_{2p}(1) = x \exp{-\alpha r/2}$ and the derivative is with respect to y, the expression is

$$\frac{\partial \phi_{2p}(1)}{\partial y} = -\frac{\alpha xy}{r} e^{-\alpha r/2}. \tag{3.49}$$

As for the first derivative, the second derivative also depends on which coordinate we differentiate with respect to. If the coordinates are the same, e.g. $m = 1 \rightarrow x_i = x$, the **second derivative** is

$$\frac{\partial^2 \phi_{2p}}{\partial x^2} = \frac{\alpha}{r} \left(\frac{x^3}{2r}\left(\frac{1}{r} + \frac{\alpha}{2}\right) - \frac{3x}{2}\right) e^{-\alpha r/2} \tag{3.50}$$

while for different coordinates, e.g. $\phi_{2p}(1) = x \exp{-\alpha r/2}$ and the **second derivative** is with respect to y, the expression is

$$\frac{\partial^2 \phi_{2p}(1)}{\partial y^2} = \frac{\alpha x}{2r^3} \left(\frac{\alpha r y^2}{2} - r^2 + y^2\right) e^{-\alpha r/2}. \tag{3.51}$$

The final Laplacian is a sum of Eqs. (3.50) and (3.51) depending on which l-state is being used.

The $3p$ wave function

The $3p$ radial wave function is proportional to

$$R_{31} \propto \left(1 - \frac{r\alpha}{6}\right) \alpha r e^{-\alpha r/3}. \tag{3.52}$$

By using the real solid harmonics for the full single particle wave function, we get our expression for the $3p$ wave function;

$$\phi_{3p}(m) = x_i(m) \left(1 - \frac{\alpha r}{6}\right) \alpha e^{-\alpha r/3}, \tag{3.53}$$

with $x_i(1) = x$, $x_i(0) = z$ and $x_i(-1) = y$. The **first derivative** when differentiating wrt. to the same coordinate x_i, e.g. x, is

$$\frac{\partial \phi_{3p}(1)}{\partial x} = \left(-\left(1 - \frac{\alpha r}{6}\right)\left(\frac{\alpha^2 x^2}{3r} + \alpha\right) - \frac{\alpha^2 x^2}{6r}\right) e^{-\alpha r/3} \tag{3.54}$$

while for different coordinates, e.g. x and y, it is

$$\frac{\partial \phi_{3p}(1)}{\partial y} = \left(-\left(1 - \frac{\alpha r}{6}\right)\frac{\alpha^2 yx}{3r} - \frac{\alpha^2 xy}{6r}\right) e^{-\alpha r/3} \tag{3.55}$$

The **second derivative** wrt. to the coordinate from the solid harmonic, e.g. x, is

$$\frac{\partial^2 \phi_{3p}(1)}{\partial x^2} = \left(\left(1 - \frac{\alpha r}{6}\right)\left(\frac{x^2}{3r^2} + \frac{\alpha x^2}{9r} - 1\right) + \frac{\alpha x^2}{9r} + \frac{x^2}{6r^2} - \frac{1}{2}\right)\frac{\alpha^2 x}{r} e^{-\alpha r/3}, \tag{3.56}$$

while the **second derivative** wrt. to a different coordinate is

$$\frac{\partial^2 \phi_{3p}(1)}{\partial x^2} = \left(\left(1 - \frac{\alpha r}{6}\right)\left(\frac{y^2}{3r^2} + \frac{\alpha y^2}{9r} - \frac{1}{3}\right) + \frac{\alpha y^2}{9r} + \frac{y^2}{6r^2} - \frac{1}{6}\right)\frac{\alpha^2 x}{r} e^{-\alpha r/3}. \tag{3.57}$$

By combining these we can also get the Laplacian of the wave function. One example is $\nabla^2 \phi_{3p}(1)$. The expression is then

$$\nabla^2 \phi_{3p}(1) = \frac{\partial^2 \phi_{3p}(1)}{\partial x^2} + \frac{\partial^2 \phi_{3p}(1)}{\partial y^2} + \frac{\partial^2 \phi_{3p}(1)}{\partial z^2}. \tag{3.58}$$

This consists of one of Eq. (3.56) and two of Eq. (3.57).

These are all the explicit expressions needed for the Slater determinant with hydrogen-like wave functions.

3.4 Roothaan-Hartree-Fock-orbitals

Another approach for the single particle basis is to use the so-called Roothaan-Hartree-Fock method. Instead of using the hydrogen orbitals as shown in section 3.3, we now introduce the Roothaan-Hartree-Fock functions. The Slater determinant is of the form

$$\Phi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(r_1) & \phi_1(r_2) & \cdots & \phi_1(r_N) \\ \phi_2(r_1) & \phi_2(r_2) & \cdots & \phi_2(r_N) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_N(r_1) & \phi_N(r_2) & \cdots & \phi_N(r_N) \end{vmatrix}, \tag{3.59}$$

where the functions ϕ are the one-particle states. The Roothaan-Hartree-Fock functions are obtained by solving the Roothaan-Hartree-Fock equations in [4]. The solutions are taken from the work of Clementi and Roetti given in [4], with

$$\phi_{i\lambda\alpha} = \sum_p \psi_{p\lambda\alpha} C_{i\lambda p}, \tag{3.60}$$

where λ corresponds to quantum number l. The index i refers to the ith orbital of symmetry λ, and p to the pth orbital of symmetry λ. The index α corresponds to quantum number m. The **Slater functions** ψ are on the form

$$\psi_{p\lambda\alpha}(r, \theta, \varphi) = R_{\lambda p}(r) Y_{\lambda\alpha}(\theta, \varphi), \tag{3.61}$$

where

$$R_{\lambda p} = [(2n_{\lambda p})!]^{-1/2} (2\xi_{\lambda p})^{n_{\lambda p}+1/2} \, r^{n_{\lambda p}-1} e^{-\xi_{\lambda p} r} \tag{3.62}$$

and Y are the normalized spherical harmonics. By using the idea of real solid harmonics (see section 3.3) and the fact that all basis functions ψ in ϕ will have the same index α, therefore the same spherical harmonic, we can ignore the pre-factor from the spherical harmonics(see section 3.2.1). Now the basis functions ψ will go from the form

$$\psi_i = N_i r^{n-1} exp(-\xi r) Y_{\lambda\alpha} \tag{3.63}$$

in spherical coordinates, to

$$\psi_i = N_i x_i r^{n-2} exp(-\xi r) \tag{3.64}$$

in Cartesian coordinates, where the factor N_i is the normalization constant from Eq. (3.62). The results from helium, beryllium, neon, magnesium and silicon are listed in appendix A. As an example in how to construct the single particle orbitals from the tables in appendix A, I use the example given in [4]:

Consider table 3.1 as a solution of the boron atom. Boron has five electrons distributed as $(1s)^2(2s)^2(2p)$. This means we need 1s-, 2s- and 2p-orbitals. To use the tables, they need a bit of explanation. The first column tells us how many and which s-functions the 1s- and 2s-orbitals for the Slater determinant will consist of. In this case this will be two of each type. The second column gives us the factors, ξ, in the exponents of the exponential functions. These will be the same for both 1s- and 2s, and will also contribute to the prefactors N_i. The third column gives the coefficients for the 1s single particle orbital for the Slater determinant, while the fourth column gives the coefficients for the 2s single particle orbital. The single particle orbitals for 1s and 2s will then

n,λ	Exponent, ξ	1s exp.coeff.	2s exp.coeff.	n,λ	Exponent, ξ	2p exp.coeff.
1S	6.56657	0.19030	0.00754	2P	2.21734	0.21526
1S	4.24927	0.82091	−0.25055	2P	1.00551	0.84052
2S	1.41314	−0.00364	0.87099			
2S	0.87564	0.00251	0.18515			

Table 3.1: The table shows a possible solution for the boron atom.

only differ by the constants in front of Slater functions (the ψ's from Eqs. (3.60)). The fifth column indicates there are only two basis functions needed to describe the p-orbital, namely the $2p$ single particle orbital, while the sixth and seventh give the exponents and $2p$-coefficients respectively.

The single particle orbitals are given in 3.1 as

$$\phi(1s) = 0.19030\psi_1 + 0.82091\psi_2 - 0.00364\psi_3 + 0.00251\psi_4 \tag{3.65}$$

$$\phi(2s) = 0.00754\psi_1 - 0.25055\psi_2 + 0.87099\psi_3 + 0.18515\psi_4 \tag{3.66}$$

$$\phi(2p) = 0.21526\psi_5 + 0.84052\psi_6 \tag{3.67}$$

where now ψ_1 and ψ_2 are Slater functions of type $1s$, ψ_3 and ψ_4 of type $2s$, and ψ_5 and ψ_6 Slater functions of type $2p$. For larger atoms, the P-type single particle orbitals will be linear combinations of different p-type Slater functions. S- and p-type Slater functions do not mix at any point, also seen in Eq. (3.60).

The Slater functions themselves written in Cartesian coordinates are given as

$$\psi_1 = N_1 r^0 \exp(-6.56657r) \tag{3.68}$$

$$\psi_2 = N_2 r^0 \exp(-4.24927r) \tag{3.69}$$

$$\psi_3 = N_3 r^1 \exp(-1.41314r) \tag{3.70}$$

$$\psi_4 = N_4 r^1 \exp(-0.87564r) \tag{3.71}$$

$$\psi_5 = N_5 x_i \exp(-2.21734r) \tag{3.72}$$

$$\psi_6 = N_6 x_i \exp(-1.00551r) \tag{3.73}$$

where x_i corresponds to either x,y or z as described in section 3.3.2, and the factors N_i are the normalization factors from Eq. (3.62).

3.4.1   Derivatives of Slater type orbitals

The analytic expressions needed for the Slater type orbitals are of the form

$$\psi_{1s} \propto \exp(-ar) \tag{3.74}$$

$$\psi_{2s} \propto r \exp(-ar) \tag{3.75}$$

$$\psi_{3s} \propto r^2 \exp(-ar) \tag{3.76}$$

$$\psi_{2p} \propto x_i \exp(-ar) \tag{3.77}$$

$$\psi_{4p} \propto r^2 x_i \exp(-ar) \tag{3.78}$$

where a is some exponent determined by the Roothan-Hartree-Fock calculations and x_i the coordinate from the real solid harmonics. In order to calculate the quantum force(see section 3.2.2) and the kinetic energy we need both the first and second derivatives of the wave functions.

First derivatives

The s-orbitals have first derivatives proportional to

$$\frac{\partial \psi_{1s}}{\partial x_i} \propto -a x_i \exp(-ar) \tag{3.79}$$

$$\frac{\partial \psi_{2s}}{\partial x_i} \propto (1 - ar) \frac{x_i}{r} \exp(-ar) \tag{3.80}$$

$$\frac{\partial \psi_{3s}}{\partial x_i} \propto (2x_i - rax_i) \exp(-ar), \tag{3.81}$$

while the $2p$-orbitals are

$$\frac{\partial \psi_{2p}(x)}{\partial x} \propto \left(1 - \frac{x^2 a}{r}\right) \exp(-ar) \tag{3.82}$$

$$\frac{\partial \psi_{2p}(x)}{\partial y} \propto -\frac{xya}{r} \exp(-ar) \tag{3.83}$$

where the paranthesis, (x), indicates which real solid harmonic the function depends on. Eqs. (3.82) and (3.83) are shown as examples with the solid harmonic being coordinate, x, and the derivatives with respect to x and then y (cf. the discussion in 3.3.2). The $4p$-orbitals are proportional to

$$\frac{\partial \psi_{4p}(x)}{\partial x} \propto \left(2x^2 - r^2 - rx^2 a\right) \exp(-ar) \tag{3.84}$$

$$\frac{\partial \psi_{4p}(x)}{\partial y} \propto (2xy - rxya) \exp(-ar) \tag{3.85}$$

Second derivatives

The Laplacian of the s-orbitals are on the form

$$\nabla^2 \psi_{1s} \propto \frac{a}{r} (ar - 2) \exp(-ar) \tag{3.86}$$

$$\nabla^2 \psi_{2s} \propto \left(\frac{2}{r} + a^2 r - 4a\right) \exp(-ar) \tag{3.87}$$

$$\nabla^2 \psi_{3s} \propto \left(6 - 6ar + a^2 r^2\right) \exp(-ar), \tag{3.88}$$

while the Laplacians of the $2p$-orbitals consist of the second derivatives

$$\frac{\partial^2 \psi_{2p}(x)}{\partial x^2} \propto \frac{ax}{r} \left(-3 + \frac{x^2}{r^2} + \frac{x^2 a}{r}\right) \exp(-ar) \tag{3.89}$$

$$\frac{\partial^2 \psi_{2p}(x)}{\partial y^2} \propto \frac{x}{r} \left(\frac{y^2}{r^2} - 1 + \frac{ay^2}{r}\right) \exp(-ar). \tag{3.90}$$

The 4p-orbitals have the second derivatives

$$\frac{\partial^2 \psi_{4p}(x)}{\partial x^2} \propto x \left(6 - \frac{3x^2 a}{r} + 3ar + x^2 a^2 \right) \exp(-ar) \tag{3.91}$$

$$\frac{\partial^2 \psi_{4p}(x)}{\partial y^2} \propto x \left(2 - \frac{3y^2 a}{r} - ar + a^2 y^2 \right) \exp(-ar). \tag{3.92}$$

The expressions for $\partial^2 \psi_{4p}(y)/\partial y^2$, $\partial^2 \psi_{4p}(z)/\partial y^2$ etc. are identical to the ones above and are used to construct e.g.

$$\nabla^2 \psi_{4p}(x) = \frac{\partial^2 \psi_{4p}(x)}{\partial x^2} + \frac{\partial^2 \psi_{4p}(x)}{\partial y^2} + \frac{\partial^2 \psi_{4p}(x)}{\partial z^2}. \tag{3.93}$$

All these expressions are needed for the implementation of the Slater determinant, quantum force and the kinetic energy for our VMC calculation.

Appendix A

Roothaan-Hartree-Fock results

In this part I will present Clementi and Roetti's results from their Roothaan-Hartree-Fock calculations for atoms helium, beryllium, neon, magnesium and silicon. The tables' applications are explained in section 3.4.

A.1   Helium

Helium consists of 2 electrons and a core of charge $2e$ and has the electron distribution $(1s)^2$. Table A.1 shows the Roothaan-Hartree-Fock(RHF) solution for Helium

n,λ	Exponent, ξ	$1s$ exp.coeff.
1S	1.41714	0.76838
1S	2.37682	0.22356
1S	4.39628	0.04082
1S	6.52699	-0.00994
1S	7.94525	0.00230

Table A.1: The table shows the Roothan-Hartree-Fock results for Helium.

A.2   Beryllium

Beryllium has 4 electrons with a nucleus charged $4e$ and has electrons distributed as $(1s)^2(2s)^2$. Table A.2 shows the RHF-solution for beryllium.

n,λ	Exponent, ξ	$1s$ exp.coeff.	$2s$ exp.coeff.
1S	3.47116	0.91796	-0.17092
1S	6.36861	0.08724	-0.01455
2S	0.77820	0.00108	0.21186
2S	0.94067	-0.00199	0.62499
2S	1.48725	0.00176	0.26662
2S	2.71830	0.00628	-0.09919

Table A.2: The table shows the Roothan-Hartree-Fock results for Beryllium.

A.3   Neon

The ten Neon electrons are distributed as $(1s)^2(2s)^2(2p)^6$. The following table shows the RHF-solution.

n,λ	Exponent, ξ	$1s$ exp.coeff.	$2s$ exp.coeff.	n,λ	Exponent, ξ	$2p$ exp.coeff.
1S	9.48486	0.93717	−0.23093	2P	1.45208	0.21799
1S	15.56590	0.04899	−0.00635	2P	2.38168	0.53338
2S	1.96184	0.00058	0.18620	2P	4.48489	0.32933
2S	2.86423	−0.00064	0.66899	2P	9.13464	0.01872
2S	4.82530	0.00551	0.30910			
2S	7.79242	0.01999	−0.13871			

Table A.3: The table shows the Roothan-Hartree-Fock results for Neon.

A.4   Magnesium

The Magnesium atom has 12 electrons in orbitals $(1s)^2(2s)^2(2p)^6(3s)^2$. The RHF-solution is:

n,λ	Exponent, ξ	$1s$ e.c.	$2s$ e.c.	$3s$ e.c.	n,λ	Exponent, ξ	$2p$ e.c.
1S	12.01140	0.96430	−0.24357	0.04691	2P	5.92580	0.52391
3S	13.91620	0.03548	−0.00485	0.00144	4P	7.98979	0.07012
3S	9.48612	0.02033	0.08002	−0.01850	4P	5.32964	0.31965
3S	6.72188	−0.00252	0.39902	−0.07964	4P	3.71678	0.20860
3S	4.24466	0.00162	0.57358	−0.13478	4P	2.59986	0.03888
3S	2.53466	−0.00038	0.05156	−0.01906			
3S	1.46920	0.00015	−0.00703	0.48239			
3S	0.89084	−0.00004	0.00161	0.60221			

Table A.4: The table shows the Roothan-Hartree-Fock results for Magnesium.

A.5   Silicon

The silicon atom consists of a nucleus with charge $14e$ and 14 electrons distributed in orbitals as $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^2$. Table A.5 shows the s-orbitals for the RHF-solution. Table A.6 shows the RHF results for the p-orbitals.

n,λ	Exponent, ξ	$1s$ exp.coeff.	$2s$ exp.coeff.	$3s$ exp.coeff.
1S	14.01420	0.96800	−0.25755	0.06595
3S	16.39320	0.03033	−0.00446	0.00185
3S	10.87950	0.02248	0.11153	−0.03461
3S	7.72709	−0.00617	0.40339	−0.10378
3S	5.16500	0.00326	0.55032	−0.19229
3S	2.97451	−0.00143	0.03381	−0.06561
3S	2.14316	0.00081	−0.00815	0.59732
3S	1.31306	−0.00016	0.00126	0.55390

Table A.5: The table shows the s-orbital Roothan-Hartree-Fock results for Silicon.

n,λ	Exponent, ξ	$2p$ exp.coeff.	$3p$ exp.coeff.
2P	7.14360	0.54290	−0.11535
4P	16.25720	0.00234	−0.00189
4P	10.79720	0.04228	−00473
4P	6.89724	0.32155	−0.07552
4P	4.66598	0.22474	0.01041
4P	2.32046	0.00732	0.46075
4P	1.33470	−0.00105	0.57665
4P	0.79318	0.00041	0.06274

Table A.6: The table shows the p-orbital Roothan-Hartree-Fock results for Silicon.

Bibliography

[1] D. Griffiths, *Introduction to Quantum Mechanics*. 2nd ed., 2005.

[2] T. Helgaker, P. Jørgensen, and J. Olsen, *Molecular Electronic-Structure Theory*. 2000.

[3] S. Raimes, *Many-Electron Theory*. 1972.

[4] E. Clementi and C. Roetti, *Roothaan-Hartree-Fock Atomic Wavefunctions*. 1974.