Work in progress

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Abstract

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Chapter 1

1.1 Introduction

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Chapter 2

In this chapter we will list general theory regarding functions used in the methods mentioned in chapter 3 and show important properties used in later derivations.

2.1 Lagrange Multiplier Method

See [2, 3]. The optimization method of Lagrange multipliers maximizes(or minimizes) a function $f : \mathbb{R}^N \to \mathbb{R}$ with a constraint $g : \mathbb{R}^N \to \mathbb{R}$ We assume that f and g have continuous first derivatives in all variables(continuous first partial derivatives).
Given the above we can define a so-called Lagrangian $\mathcal{L}$

$$\mathcal{L}[x_1, \ldots, x_N, \lambda_1, \ldots, \lambda_M] = f(x_1, \ldots, x_N) - \lambda g(x_1, \ldots, x_N) \tag{2.1}$$

where the λ is called a Lagrange-multiplier. We now state that if $f(x_1^0, \ldots, x_N^0)$ is a maxima of $f(x_1, \ldots, x_N)$ then there exists a Lagrange-multiplier λ_0 such that $(x_1^0, \ldots, x_N^0, \lambda_0)$ is a stationary point for the Lagrangian. This then yields the $N + 1$ Lagrange-equations

$$\sum_{i=1}^{N} \frac{\partial \mathcal{L}}{\partial x_i} + \frac{\partial \mathcal{L}}{\partial \lambda} = 0 \tag{2.2}$$

to be solved for $x_1, \ldots, x_N$ and λ.

2.2 Gaussian Type Orbitals

Gaussian Type Orbitals or GTO's are functions of the following form » REF GTO here «

$$G_i^\alpha(x, A) \equiv (x - A)^i e^{-\alpha(x-A)^2} \tag{2.3}$$

We call α for the scaling parameter and i for the order of the GTO. The variable A is where the function is centered. These are in many literatures referred to as *primitive gaussians*.

Chapter 3

Many-Body Quantum Theory

This chapter takes forth the theory regarding the basics of identical particles and *many-body quantum mechanics*. The reader is referred to [4] for an introductory text on quantum mechanics(for single particles) and also the so-called *Dirac-notation* used throughout the entire chapter.

3.1   The Hamiltonian and the Born-Oppenheimer Approximation

The task at hand is to solve the many-body system described by *Schrödinger's* equation

$$H \left| \Psi_i \right\rangle = E_i \left| \Psi_i \right\rangle \tag{3.1}$$

for some state $\left| \Psi_i \right\rangle$ with energy E_i. Usually the desired state is the ground-state energy E_0 of the system meaning we are primarily interested in the *ground-state* $\left| \Psi_0 \right\rangle$.
With the goal determined we can define the system to consist of N identical particles[1] with positions $\{ \boldsymbol{r}_i \}_{i=0}^{N-1}$ and A nuclei with positions $\{ \boldsymbol{R}_k \}_{k=0}^{A-1}$. The Hamiltonian H is then

$$H = -\frac{1}{2} \sum_i \nabla_i^2 + \sum_{i<j} f\left(\boldsymbol{r}_j, \boldsymbol{r}_j \right) - \frac{1}{2} \sum_k \frac{\nabla_k^2}{M_k} + \sum_{k<l} g\left(\boldsymbol{R}_k, \boldsymbol{R}_l \right) + V\left(\boldsymbol{R}, \boldsymbol{r} \right) \tag{3.2}$$

The first and second terms represent the kinetic- and inter-particle interaction terms[2] for the N identical particles while the latter three represent kinetic- and interaction terms for the nuclei(with the last one being the nuclei-particle interaction). The constant M_k is the mass of nucleon k and Z_k is the corresponding atomic number.

   We assume the nuclei to be much heavier than the identical particles, meaning they move much slower, at which the system can be viewed as electrons moving around the vicinity of stationary nuclei. This means the kinetic term for the nuclei vanish and the nuclei-nuclei interaction becomes a constant[3]. The approximation we end up with is the so-called *Born-Oppenheimer approximation* and the Hamiltonian is now

$$H = H_0 + H_I \tag{3.3}$$

where we have split the Hamiltonian in a *one-body* part and a *two-body* or *interaction* parts defined as

$$H_0 \equiv -\frac{1}{2} \sum_i \nabla_i^2 + V\left(\boldsymbol{R}, \boldsymbol{r} \right) \tag{3.4}$$

and

$$H_I \equiv \sum_{i<j} f\left(\boldsymbol{r}_j, \boldsymbol{r}_j \right) \tag{3.5}$$

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[1] These are in both atomic physics and in the quantum dot case always fermions or bosons.
[2] This is usually the well-known Coulomb interaction.
[3] Adding a constant to an operator does not alter the eigenvector, only the eigenvalues by the constant factor[9].

3.2   Slater Determinant and Permanent

Throughout section 3.1 we only referred to the wavefunction Ψ as a state, a function closely connected to the probabilistic nature of the quantum particles. However, we have not given it a form. One possible solution is the *Hartree product* Ψ_H defined as

$$\Psi_H = \prod_i \psi_i(\boldsymbol{r}_i) \tag{3.6}$$

with $\{\psi\}_{i=0}^N$ being the orbitals which solve the single-particle Schrödinger equation for H_0. The Hartree-product is unfortunately a poor choice since it does not solve the H_I part meaning it is not a physically valid solution. This comes from the fact that the Hartree-product does not take into account the fact that the particles in question are *identical particles*. Since the particles are identical, switching the labels on the particles shouldn't change the expectation value of some observable. If we run this observation through we end up with the conclusion that the state $|\Psi\rangle$ must be either symmetric or antisymmetric with the symmetric part being the *bosonic state* and antisymmetric being the *fermionic state*. The connection between antisymmetric states and fermions is called the *Pauli exclusion principle*.

The problem with the Hartree-product is with the above sentiment, that is not symmetric nor antisymmetric. However we can transform it with an operator

$$\mathcal{B} \equiv \frac{1}{N!} \sum_P \sigma_b P \tag{3.7}$$

where σ_b is a sign operator which is just 1 for the symmetric case and $(-1)^p$ for the antisymmetric case, P is a permutation operator that switches the labels on particles [4] and p is the parity of permutations. The solution Ψ_T to the Schrödinger equation can now be written as

$$\Psi_T(\boldsymbol{r}) = \sqrt{N!}\,\mathcal{B}\Psi_H(\boldsymbol{r}) \tag{3.8}$$

The antisymmetric case of $\mathcal{B}$ results in a *Slater determinant*

$$\Psi_T^{\mathrm{AS}} = \frac{1}{\sqrt{N!}} \sum_P (-1)^p P \prod_i \psi_i \tag{3.9}$$

while the symmetric case gives the so-called *permanent*[5].

$$\Psi_T^{\mathrm{S}} = \frac{1}{\sqrt{N!}} \sum_P P \prod_i \psi_i \tag{3.10}$$

3.3   Variational Principle

One important remark is that the Slater determinant and the permanent do not solve the interaction part, but only serves as a so-called *ansatz* or guess on the true ground-state wavefunction. This is quite useful due to the *variational principle*.

The Variational principle states that for any normalized function Ψ in Hilbert Space » REF HILBERT « with a Hermitian operator H the minimum eigenvalue E_0 for H has an upper-bound given by the expectation value of H in the function Ψ. That is

$$E_0 \leq \langle H \rangle = \langle \Psi | H | \Psi \rangle = \int \Psi^* H \Psi \, \mathrm{d}r \tag{3.11}$$

See [4] for proof and more.

The mentioned ansatz is thereby guaranteed to give energies larger than or equal the true ground state energy meaning a minimization method is sufficient in order to get closer to this minimum.

3.4   Energy Functional

We can find a more convenient expression for this energy by using equations 3.8 and 3.11. This gives us

$$E_0 = N! \langle \Psi_H | H \mathcal{B} | \Psi_H \rangle \tag{3.12}$$

where the hermitian and unitary property of $\mathcal{B}$ as well as the fact that $\mathcal{B}$ and H commute have been used.

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[4] $P\psi_i\psi_j = \psi_j\psi_i$

[5] The permanent is basically just a determinant with all the negative signs replaced by positive ones.

Chapter 4

In this chapter we will address » LIST METHODS « regarding computational quantum mechanics and further deepen into Hartree-Fock methods and Variational Monte Carlo method. Optimization of calculation is also given while structure of program is given in » REF TO PROGRAM STRUCTURE CHAPTER «. General statistical theory used is given in » REF TO STATISTICS CHAPTER «

4.1 Hartree-Fock Theory

Hartree-Fock theory method is a method for approximating the wavefunction of a stationary many-body quantum state and thereby also obtain an estimate for the energy in this state. In this section we will derive the Hartree-Fock equations from scratch, following closely » REF SOMETHING HERE « by » REF AUTHOR « and find the so-called Roothaan-Hall equations known as *Unrestricted Hartree-Fock* method, which is also the method used for obtaining the results given in » REF RESULTS CHAPTER «.

4.1.1 Assumptions

Hartree-Fock method makes the following assumptions of the system

- *The Born-Oppenheimer approximation*, see » REF BO «.

- All relativistic effects are negligible.

- The wavefunction can be described by a single Slater determinant » REF SLATER « or permanent in case of bosons(former is for fermions).

- The *Mean Field Approximation* holds.

With these inherent approximations the last one is the most important to take into account as it can cause large deviations from test solutions (analytic solutions, experimental data etc.) since the electron correlations is in reality, for many cases, not negligible. There exists many methods that try to fix this problem » LIST METHODS «. The *Variational Monte Carlo* (or VMC) is the method for deeper explorations in this Thesis, see section 4.2 for more details.

4.1.2 Hartree-Fock Equations

4.1.3 Restricted Hartree-Fock

Restricted Hartree-Fock, or abbreviated to RHF, we assume a closed-shell system. This means that for a given system the all possible states for a given energy-level is filled. We can achieve this by grouping spin-orbitals with same spatial part, but opposite spin.

4.2 Quantum Monte Carlo

Quantum Monte Carlo, or QMC is a method for solving Schrödinger's equation by a statistical approach using so-called *Markov Chain* simulations (also called random walk). The nature of the wave function at hand is fundamentally a statistical model defined on a large configuration space with small areas of densities. The Monte Carlo method is perfect for solving such a system because of the non-homogeneous

distribution of calculation across the space. An standard approach with equal distribution of calculation would then yield a rather poor result with respect to computation cost.

We will in this chapter address the Metropolis algorithm which is used to create a Markov chain and derive the equations used in the variational method.

The chapter will use *Dirac Notation* [4] and all equations stated assume atomic units ($\hbar = m_e = e = 4\pi\varepsilon_0$) » REF HERE ATOMIC UNITS «.

4.2.1   The Variational Principle and Expectation Value of Energy

Given a Hamiltonian $\hat{H}$ and a trial wave function $\Psi_T(\boldsymbol{R}; \boldsymbol{\alpha})$, the variational principle [4, 8] states that the expectation value of $\hat{H}$

$$E[\psi_T] = \left\langle \hat{H} \right\rangle = \frac{\langle \psi_T | \hat{H} | \psi_T \rangle}{\langle \Psi_T | \Psi_T \rangle} \tag{4.1}$$

is an upper bound to the ground state energy

$$E_0 \leq \left\langle \hat{H} \right\rangle \tag{4.2}$$

Now we can define our PDF as(see section 4.2.3 for a more detailed reasoning)

$$P(\boldsymbol{R}) \equiv \frac{|\psi_T|^2}{\langle \Psi_T | \Psi_T \rangle} \tag{4.3}$$

and with a new quantity

$$E_L(\boldsymbol{R}; \boldsymbol{\alpha}) \equiv \frac{1}{\Psi_T(\boldsymbol{R}; \boldsymbol{\alpha})} \hat{H} \Psi_T(\boldsymbol{R}; \boldsymbol{\alpha}) \tag{4.4}$$

the so-called local energy, we can rewrite equation 4.1 as

$$E[\Psi_T(\boldsymbol{R}; \boldsymbol{\alpha})] = \langle E_L \rangle \tag{4.5}$$

The idea now is to find the lowest possible energy by varying a set of parameters $\boldsymbol{\alpha}$. The expectation value itself is found with the Metropolis algorithm, see section 4.2.4.

4.2.2   The Trial Wave Function

The trial wave function is generally an arbitrary choice specific for the problem at hand, however it is in most cases favorable to expand the wave function in the eigenbasis (eigenstates) of the Hamiltonian since they forma complete set. This can be expressed as

$$\Psi_T(\boldsymbol{R}; \boldsymbol{\alpha}) = \sum_i C_i \psi_i(\boldsymbol{R}; \boldsymbol{\alpha}) \tag{4.6}$$

with the ψ_i's are the eigenstates of the Hamiltonian.

4.2.3   Use Diffusion Theory and the PDF

The statistics describing the expectation value states that any distribution may be applied in calculation, however if we take a close look at the local energy(equation 4.4) we see that for all distributions the local energy is not defined at the zeros of $\Psi_T(\boldsymbol{R}; \boldsymbol{\alpha})$. This means that an arbitrary PDF does not guarantee generation of points which makes $\psi_T = 0$. This can be overcome by introducing the square of the wave function to be defined as the distribution function as given in equation 4.3.

Because of the inherent statistical property of the wave function Quantum Mechanics can be modelled as a diffusion process, or more specifically, an *Isotropic Diffusion Process* which is essentially just a random walk model. Such a process is described by the Langevin equation with the corresponding Fokker-Planck equation describing the motion of the walkers(particles). See [5] for details.

4.2.4   Metropolis-Hastings Algorithm

The Metropolis algorithm bases itself on moves (also called transitions) as given in a Markov process. »REF THIS HERE «. This process is given by

$$w_i(t + \varepsilon) = \sum_j w_{i \to j} w_j(t) \tag{4.7}$$

where $w(j \to i)$ is just a transition from state j to state i. In order for the transition chain to reach a desired convergence while reversibility is kept, the well known condition for detailed balance must be fulfilled » REF HERE DETAILED BALANCE «. If detailed balance is true, then the following relations is true

$$w_i T_{i \to j} A_{i \to j} = w_j T_{j \to i} A_{j \to i} \Rightarrow \frac{w_i}{w_j} = \frac{T_{j \to i} A_{j \to i}}{T_{i \to j} A_{i \to j}} \tag{4.8}$$

We have here introduced two scenarios, the transition from configuration i to configuration j and the reverse process j to i. Solving the acceptance A for the two cases where the ratio in 4.8 is either 1(in which case the proposed state j is accepted and transitions is made) and when the ratio is less then 1. The Metropolis algorithm would in this case not automatically reject the latter case, but rather reject it with a proposed uniform probability. Introducing now a probability distribution function(PDF) P the acceptance A can be expressed as

$$A_{i \to j} = \min \left(\frac{P_{i \to j}}{P_{j \to i}} \frac{T_{i \to j}}{T_{j \to i}}, 1 \right) \tag{4.9}$$

The so-called selection probability T is defined specifically for each problem. For our case the PDF in question is the absolute square of the wave function and the selection T is a Green's function derived in section 4.2.5. The algorithm itself would then be

(i) Pick initial state i at random.

(ii) Pick proposed state at random in accordance to $T_{j \to i}$.

(iii) Accept state according to $A_{j \to i}$.

(iv) Jump to step (ii) until a specified number of states have been generated.

(v) Save the state i and jump to step (ii).

4.2.5   Importance Sampling

Using the selection probability mentioned in section 4.2.4 in the Metropolis algorithm is called an *Importance sampling* because is essentially makes the sampling more concentrated around areas where the PDF has large values.

In order to derive the form of this equation we use the statements presented in section 4.2.3. With

$$\frac{\partial r}{\partial t} = DF(r(t)) + \eta \tag{4.10}$$

the *Langevin equation* »REF HERE LANGEVIN« and apply Euler's method (Euler-Maryama »REF«) and obtain the new positions

$$r^{\text{new}} = r^{\text{old}} + DF^{\text{old}} \Delta t + \xi \tag{4.11}$$

with the r's being the new and old positions in the Markov chain respectively and $F^{\text{old}} = F(r^{\text{old}})$. The quantity D is a diffusion therm equal to $1/2$ due to the kinetic energy(remind of natural units) and ξ is a Gaussian distributed random number with 0 mean and $\sqrt{\Delta t}$ variance.

As mentioned a particle is described by the Fokker-Planck equation

$$\frac{\partial P}{\partial t} = \sum_i D \frac{\partial}{\partial x_i} \left(\frac{\partial}{\partial x_i} - \boldsymbol{F_i} \right) P \tag{4.12}$$

With P being the PDF(in current case the selection probability) and F being the drift therm. In order to achieve convergence, that is a stationary probability density, we need the left hand side to be zero in equation 4.12 giving the following equation

$$\frac{\partial^2 P}{\partial x_i^2} = P \frac{\partial \boldsymbol{F_i}}{\partial x_i} + \boldsymbol{F_i} \frac{\partial P}{\partial x_i} \tag{4.13}$$

with the drift-therm being on the form $\boldsymbol{F} = g(x)\partial P/\partial x$ we finally have that

$$\boldsymbol{F} = \frac{2}{\psi_T}\nabla\psi_T \tag{4.14}$$

This is the so-called *Quantum Force* which pushes the walkers towards regions where the wave function is large.

Appendix A

Introducing the so-called permutation operator P which interchanges the labels of particles meaning we can define

$$A \equiv \frac{1}{N!} \sum_p (-1)^p P \tag{A.1}$$

the so-called *antisymmetrization* operator. This operator has the following traits

- The Hamiltonian H and A commute since the Hamiltonian is invariant under permutation.

- A applied on itself (that is A^2) is equal to itself since permuting a permuted state reproduces the state.

We can now express our Slater Ψ_T in terms of A as

$$\Psi_T = \sqrt{N!} A \prod_{i,j} \psi_{ij} \tag{A.2}$$

where $\psi_{ij} = \psi_j(\boldsymbol{r}_i)$ is element i,j of the Slater matrix (the matrix associated with the Slater determinant Ψ_T).

The interaction part of H is then

$$\langle \Psi_T | H_I | \Psi_T \rangle = N! \prod_{i,j} \langle \psi_{ij} | A H_I A | \psi_{ij} \rangle \tag{A.3}$$

The interaction H_I and A commute since A commutes with H giving

$$A H_I A | \psi_{ij} \rangle = \frac{1}{N!^2} \sum_{i<j} \sum_p (-1)^{2p} f_{ij} P | \psi_{ij} \rangle \tag{A.4}$$

$$= \frac{1}{N!^2} \sum_{i<j} f_{ij} (1 - P_{ij}) | \psi_{ij} \rangle \tag{A.5}$$

The factor $1 - P_{ij}$ comes from the fact that contributions with $i \neq j$ vanishes due to orthogonality when P is applied. The final expression for the interaction term is thus

$$\langle \Psi_T | H_I | \Psi_T \rangle = \sum_{i<j} \prod_{k,l} [\langle \psi_{kl} | f_{ij} | \psi_{kl} \rangle - \langle \psi_{kl} | f_{ij} | \psi_{lk} \rangle] \tag{A.6}$$

Writing out the product and realizing the double summation over pairs of states we end up with

$$\langle \Psi_T | H_I | \Psi_T \rangle = \frac{1}{2} \sum_{i,j} [\langle \psi_{ij} \psi_{ji} | f_{ij} | \psi_{ij} \psi_{ji} \rangle - \langle \psi_{ij} \psi_{ji} | f_{ij} | \psi_{ji} \psi_{ij} \rangle] \tag{A.7}$$

More comprehensive details and derivations are given in [6, 12].

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