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Abstract

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Chapter 1

1 Introduction

1.1 bleh

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.

1 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

$$E_0 \leq \langle H \rangle = \langle \psi | H | \psi \rangle = \int \psi^* H \psi \mathrm{d}r \tag{2.1}$$

See [1] for proof and more.

2 Gaussian Type Orbitals

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

$$G_i^{\alpha}(x, A) \equiv (x - A)^i \mathrm{e}^{-\alpha(x-A)^2} \tag{2.2}$$

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

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 «

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 «.

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 2 for more details.

1.2 Energy Functional

The general expression (for a general system) for the energy is given in section 1, we restate it

$$E[\Psi_T(\boldsymbol{R};\boldsymbol{\alpha})] = \frac{\langle\Psi_T(\boldsymbol{R};\boldsymbol{\alpha})|\,H\,|\Psi_T(\boldsymbol{R};\boldsymbol{\alpha})\rangle}{\langle\Psi_T(\boldsymbol{R};\boldsymbol{\alpha})|\Psi_T(\boldsymbol{R};\boldsymbol{\alpha})\rangle} \tag{3.1}$$

The denominator is just the normalization factor.
Before we can obtain the Hartree-Fock equations we need an expression for the expectation value of the energy, an *energy functional* (functional in the sense that it is dependant on the wavefunction).
With the mentioned Born-Oppenheimer approximation we set up the Schrödinger equation » REF SL « with the following Hamiltonian » REF HAMILTONIAN «

$$H \equiv H_0 + H_I \tag{3.2}$$

where H_0 is the Hamiltonian of some a system with analytic solutions to the wavefunction(i.e harmonic oscillator) meaning

$$H_0 = V(\boldsymbol{R}) - \frac{1}{2}\sum_i \nabla_i^2 \tag{3.3}$$

where $\boldsymbol{R} = \boldsymbol{r}_1, \ldots, \boldsymbol{r}_N$ (the positions of the particles) and V is the expression for the potential of the system. The second part of equation 3.2 will be referred to as the *Interaction Hamiltonian* and is assumed to be a function of the inter-particle distances $\boldsymbol{r}_i - \boldsymbol{r}_j$ meaning

$$H_I = \sum_{i<j} f(\boldsymbol{r}_i, \boldsymbol{r}_j) \tag{3.4}$$

with f being the function describing the interaction between two particles labeled i and j (for instance the (Coloumb interation due to the charge of particles).
As a summary and later reference the full Hamiltonian of the system is

$$H = V(\boldsymbol{R}) - \frac{1}{2}\sum_i \nabla_i^2 + \sum_{i<j} f(\boldsymbol{r}_i, \boldsymbol{r}_j) \tag{3.5}$$

which, when inserted into equation 3.1, gives

$$E[\Psi_T] = \langle\Psi_T| V |\Psi_T\rangle - \frac{1}{2}\sum_i \langle\Psi_T| \nabla_i^2 |\Psi_T\rangle + \sum_{i<j} \langle\Psi_T| f |\Psi_T\rangle \tag{3.6}$$

where we have omitted the normalization factor and argument variables. We start with the part involving H_0 giving

$$\begin{aligned}\langle\Psi_T| H_0 |\Psi_T\rangle &= \sum_i \langle\Psi_T| h_i |\Psi_T\rangle \\ &= \sum_i \langle\psi_{ii}| h_i |\psi_{ii}\rangle \end{aligned} \tag{3.7}$$

with h_i being the single-particle Hamiltonian (for a particle i).
The final result here is due to the fact that h_i only acts on particle i and that the ψ's are orthogonal.
Before we go any further with H_I let us introduce the so-called permutation operator P which interchanges the labels of particles meaning we can define

$$A \equiv \frac{1}{N!}\sum_p (-1)^p P \tag{3.8}$$

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 out Slater Ψ_T in terms of A as

$$\Psi_T = \sqrt{N!}A\prod_{i,j}\psi_{ij} \tag{3.9}$$

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

$$\langle\Psi_T| H_I |\Psi_T\rangle = N!\prod_{i,j} \langle\psi_{ij}| AH_IA |\psi_{ij}\rangle \tag{3.10}$$

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

$$AH_IA|\psi_{ij}\rangle = \frac{1}{N!^2}\sum_{i<j}\sum_p (-1)^{2p} f_{ij} P |\psi_{ij}\rangle \tag{3.11}$$

$$= \frac{1}{N!^2}\sum_{i<j} f_{ij}(1 - P_{ij})|\psi_{ij}\rangle \tag{3.12}$$

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

$$\langle\Psi_T| H_I |\Psi_T\rangle = \sum_{i<j} \prod_{k,l} [\langle\psi_{kl}| f_{ij} |\psi_{kl}\rangle - \langle\psi_{kl}| f_{ij} |\psi_{lk}\rangle] \tag{3.13}$$

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

$$\langle\Psi_T| H_I |\Psi_T\rangle = \frac{1}{2} \sum_{i,j} [\langle\psi_{ij}\psi_{ji}| f_{ij} |\psi_{ij}\psi_{ji}\rangle - \langle\psi_{ij}\psi_{ji}| f_{ij} |\psi_{ji}\psi_{ij}\rangle] \tag{3.14}$$

Relabeling the indices in terms of just one index p and q to represent just a state (the integration label does not matter) we get the following energy functional

$$E[\Psi_T] = \sum_p \langle\psi_p| h |\psi_p\rangle + \frac{1}{2} \sum_{p,q} [\langle\psi_p\psi_q| H_I |\psi_p\psi_q\rangle - \langle\psi_p\psi_q| H_I |\psi_q\psi_p\rangle] \tag{3.15}$$

We drop the index in h since the integration label does not matter.

1.3 Useful operators $\boldsymbol{J}$ and $\boldsymbol{K}$

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* [1] and all equations stated assume atom units ($\hbar = m_e = e = 4\pi\varepsilon_0$) » REF HERE ATOMIC UNITS «.

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 [1, 5] states that the expectation value of $\hat{H}$

$$E[\psi_T] = \left\langle \hat{H} \right\rangle = \frac{\langle\psi_T| \hat{H} |\psi_T\rangle}{\langle\Psi_T|\Psi_T\rangle} \tag{3.16}$$

is an upper bound to the ground state energy

$$E_0 \leq \left\langle \hat{H} \right\rangle \tag{3.17}$$

Now we can define our PDF as(see section 2.3 for a more detailed reasoning)

$$P(\boldsymbol{R}) \equiv \frac{|\psi_T|^2}{\langle\Psi_T|\Psi_T\rangle} \tag{3.18}$$

and with a new quantity

$$E_L(\boldsymbol{R};\boldsymbol{\alpha}) \equiv \frac{1}{\Psi_T(\boldsymbol{R};\boldsymbol{\alpha})} \hat{H}\Psi_T(\boldsymbol{R};\boldsymbol{\alpha}) \tag{3.19}$$

the so-called local energy, we can rewrite equation 3.16 as

$$E[\Psi_T(\boldsymbol{R};\boldsymbol{\alpha})] = \langle E_L \rangle \tag{3.20}$$

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 2.4.

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

$$\Psi_T(\boldsymbol{R};\boldsymbol{\alpha}) = \sum_i C_i \psi_i(\boldsymbol{R};\boldsymbol{\alpha}) \tag{3.21}$$

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

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 3.19) 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 3.18.
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 [10] for details.

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

$$w_i(t+\varepsilon) = \sum_j w_{i\to j} w_j(t) \tag{3.22}$$

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

$$w_i T_{i\to j} A_{i\to j} = w_j T_{j\to i} A_{j\to i} \Rightarrow \frac{w_i}{w_j} = \frac{T_{j\to i} A_{j\to i}}{T_{i\to j} A_{i\to j}} \tag{3.23}$$

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 3.23 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

$$A_{i\to j} = \min\left(\frac{P_{i\to j}}{P_{j\to i}} \frac{T_{i\to j}}{T_{j\to i}}, 1\right) \tag{3.24}$$

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 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).

2.5 Importance Sampling

Using the selection probability mentioned in section 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 2.3. With

$$\frac{\partial r}{\partial t} = DF(r(t)) + \eta \tag{3.25}$$

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

$$r^{\text{new}} = r^{\text{old}} + DF^{\text{old}}\Delta t + \xi \tag{3.26}$$

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

$$\frac{\partial P}{\partial t} = \sum_i D \frac{\partial}{\partial x_i}\left(\frac{\partial}{\partial x_i} - \boldsymbol{F_i}\right) P \tag{3.27}$$

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 3.27 giving the following equation

$$\frac{\partial^2 P}{\partial {x_i}^2} = P\frac{\partial \boldsymbol{F_i}}{\partial x_i} + \boldsymbol{F_i}\frac{\partial P}{\partial x_i} \tag{3.28}$$

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

$$\boldsymbol{F} = \frac{2}{\psi_T}\nabla\psi_T \tag{3.29}$$

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

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