# Work in progress

by

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# Abstract

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# Acknowledgements

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Work in progress make for $w_{i \to j} \equiv w\left(i|j\right)$

# Source Code

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# Chapter 1

## 1 Introduction

### 1.1 bleh

# Chapter 2

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 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 «.

### 1.1 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 $\hat{H}$

$$E[\psi_T] = \left\langle \hat{H} \right\rangle = \frac{\langle \psi_T | \hat{H} | \psi_T \rangle}{\langle \psi_T | \psi_T \rangle} \tag{2.1}$$

is an upper bound to the ground state energy

$$E_0 \leq \left\langle \hat{H} \right\rangle \tag{2.2}$$

Now we can define our PDF as(see section 1.3 for a more detailed reasoning)

$$P(\boldsymbol{R}) \equiv \frac{|\psi_T|^2}{\langle \psi_T | \psi_T \rangle} \tag{2.3}$$

and with a new quantity

$$E_L(\boldsymbol{R};\boldsymbol{\alpha}) \equiv \frac{1}{\psi_T(\boldsymbol{R};\boldsymbol{\alpha})} \hat{H}\psi_T(\boldsymbol{R};\boldsymbol{\alpha}) \tag{2.4}$$

the so-called local energy, we can rewrite equation 2.1 as

$$E[\psi_T(\boldsymbol{R};\boldsymbol{\alpha})] = \langle E_L \rangle \tag{2.5}$$

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 1.4.

### 1.2 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

$$\psi_T(\boldsymbol{R};\boldsymbol{\alpha}) = \sum_i C_i \psi_i(\boldsymbol{R};\boldsymbol{\alpha}) \tag{2.6}$$

with the $\psi_i$'s are the eigenstates of the Hamiltonian.

## 1.3 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 2.4) 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 2.3.
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 [10] for details.

## 1.4 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

$$w_i(t+\varepsilon) = \sum_j w_{i\to j} w_j(t) \tag{2.7}$$

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

$$w_i T_{i\to j} A_{i\to j} = w_j T_{j\to i} A_{j\to i} \Rightarrow \frac{w_i}{w_j} = \frac{T_{j\to i} A_{j\to i}}{T_{i\to j} A_{i\to j}} \tag{2.8}$$

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 2.8 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

$$A_{i\to j} = \min\left(\frac{P_{i\to j}}{P_{j\to i}}\frac{T_{i\to j}}{T_{j\to i}}, 1\right) \tag{2.9}$$

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 1.5. 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).

## 1.5 Importance Sampling

Using the selection probability mentioned in section 1.4 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 1.3. With

$$\frac{\partial r}{\partial t} = DF(r(t)) + \eta \tag{2.10}$$

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

$$r^{\text{new}} = r^{\text{old}} + DF^{\text{old}}\Delta t + \xi \tag{2.11}$$

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 $\xi$ 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

$$\frac{\partial P}{\partial t} = \sum_i D \frac{\partial}{\partial x_i} \left( \frac{\partial}{\partial x_i} - \boldsymbol{F_i} \right) P \tag{2.12}$$

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 2.12 giving the following equation

$$\frac{\partial^2 P}{\partial {x_i}^2} = P \frac{\partial \boldsymbol{F_i}}{\partial x_i} + \boldsymbol{F_i} \frac{\partial P}{\partial x_i} \tag{2.13}$$

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

$$\boldsymbol{F} = \frac{2}{\psi_T} \nabla \psi_T \tag{2.14}$$

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

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