Work in progress

by

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Abstract

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Contents

Symbols List

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

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

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

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

1.2 The Trial Wave Function

1.3 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

$$w_i(t+\varepsilon) = \sum_j w_{i\to j}w_j(t) \tag{2.6}$$

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

$$w_i T_{i \to j} A_{\mathrm{i} \to j} = w_j T_{j \to i} A_{j \to i} \Rightarrow \frac{w_i}{w_j} = \frac{T_{j \to i} A_{j \to i}}{T_{i \to j} A_{i \to j}} \tag{2.7}$$

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 2.6 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

$$A_{i \to j} = \min \left(\frac{P_{i \to j}}{P_{j \to i}} \frac{T_{i \to j}}{T_{j \to i}}, 1 \right) \tag{2.8}$$

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 given in » REF GREENS «. 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).

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