

QUANTUM MONTE CARLO: Documentation

Umberto Pelliccia

INTRODUCTION

The program presented in this project aims to calculate the energy of simple chemical system using the Quantum Monte Carlo method. In general, Monte Carlo methods are used to estimate integrals or to simulate complex system by generating random samples from a probability distribution associated with the problem being studied. In our case, Monte Carlo algorithm is used to approximatively solve the Schrödinger equation, which describe the behavior of quantum systems (hence the name “Quantum Monte Carlo”), instead of computing the average energy through numerical integration on a grid.

Firstly, we know that the probabilistic expected value of an arbitrary function whit respect to a probability density function is determined as follow:

$$\langle f \rangle = \int_{-\infty}^{\infty} f(x)P(x)dx$$

Based on this theory, we can define the energy of the system as the expected value of the local energy with respect to a probability density function:

$$E = \int E_{loc}(r)P(r)dr \equiv \langle E_{loc} \rangle$$

Where the probability density P and the local energy E_{loc} are related to the wavefunction and are defined as follows:

$$P(r) = \frac{|\Psi(r)|^2}{\int |\Psi(r)|^2 dr} \quad E_{loc}(r) = \frac{\hat{H} \Psi(r)}{\Psi(r)}$$

The energy integral can be solved numerically by sampling N configurations of $\{r\}$ distributed according to the probability density function $P(r)$. This allows for estimating E as the average of the local energy computed across all generated configurations:

$$E \approx \frac{1}{N} \sum_{i=1}^N E_{loc}(r_i)$$

In the code presented, two different Monte Carlo methods are employed: the Variational Monte Carlo (VMC) and the Pure Diffusion Monte Carlo (PDMC).

The VMC method evaluates the local energy of a parametrized test wavefunction and try to minimize the energy by adjusting the parameters. In this program, the trial wavefunction used is:

$$\Psi(r) = e^{(-a|r-r_\mu|)}$$

Where a is the wavefunction parameter and needs to be set manually.

The PDMC is a variant of Diffusion Monte Carlo where the potential term is treated as a cumulative product of weights. It operates differently from VMC because, instead of focusing on parameter

minimization, it utilizes the time-dependent Schrödinger equation to approximate the true wavefunction of the system.

$$i \frac{\partial \Psi(r, t)}{\partial t} = (\hat{H} - E_{ref}) \Psi(r, t)$$

By expanding the wavefunction on the eigenfunction $\Phi_n(r)$ and considering $\psi(r, \tau) = \Psi(r, -it)$, the solution to the Schrödinger equation at time t can be obtained as follows:

$$\psi(r, \tau) = \sum_n a_n e^{-\tau(E_n - E_{ref})} \Phi_n(r)$$

Where E_{ref} is a dynamic parameter used to control the number of “walkers,” which represent quantum configurations during the simulation. If this value is well-tuned, the simulations tend to converge toward the ground state.

The PDMC is developed by adding to a simple VMC cycle the process of accumulating statistical weights during the projection time to improve the accuracy of the ground energy E .

USER'S DOCUMENTATION

The program is divided into several parts: the main code and three separate files containing subroutines that perform the calculations. To run the program, it also requires two additional files: an input file and a geometry file.

- Input File

The file *mc_input.inp* contain all the input parameters needed for the calculation.

```
# System parameters:

h3.xyz          # Geometry file
2              # Number of electrons
1.4            # Wavefunction parameter "a"

# Montecarlo simulation parameters:

pdmc           # Monte Carlo: variational (vmc) or pure diffusion (pdmc)
10000          # Number of steps
500            # Number of walkers
0.001          # Time step

-1.5           # Reference energy in a.u. !! ONLY FOR PURE DIFFUSION !!
1000           # Projection time           !! ONLY FOR PURE DIFFUSION !!
```

In the first section, all the system parameters are defined. The first line is used to select the geometry file, followed by the number of electrons (can be a maximum of 2) and the wavefunction parameter a . In the second section, parameters for the Monte Carlo simulations are set. Initially, it is possible to choose between the Variational Monte Carlo method (VMC) or the Pure Diffusion Monte Carlo (PDMC). Then, parameters such as the number of steps, number of walkers and the time step are specified. Additionally, in the case of PDMC, the reference energy (in atomic units) and τ are defined.

- Geometry File

The geometry file, named *[system].xyz*, contains all the information regarding the position of atoms. Along with the number of electrons specified in the input file, can describe the chemical system under analysis.

```
3      # Number of atoms

H      -0.049222   0.000000  -0.085255
H      -0.049222   0.000000   0.785255
H       0.704662   0.000000   0.350000
```

The file shown above describe the H₃ molecule. The first line indicates the number of atoms, followed by the atom type (either hydrogen or helium) and the position in Angstrom.

- Functions and subroutines

The code consists of three files containing functions and subroutines.

In the *hamiltonian.F90* file, the local energy and the wavefunction are defined. In particular, the wavefunction part is split into two functions. The first calculates the Ψ for a single nucleus, and then in the second, all the previously calculated Ψ values are summed to obtain the correct value for Ψ . Regarding the calculation of local energy, the program first computes the potential energy as follow:

$$U = - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} + \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}}$$

Where N represents the number of electrons, M the number of nuclei, Z_A is the atomic number of atom A , r_{iA} is the distance between electron i and nucleus A , r_{ij} is the distance between electrons i and j , and R_{AB} is the distance between nuclei A and B .

Next, the kinetic contribution is calculated using:

$$T(r) = -\frac{1}{2} \frac{\Delta\Psi(r)}{\Psi(r)}$$

Finally, the potential and kinetic contributions are summed to calculate the local energy.

In the *montecarlo.F90* file, there are three subroutines that perform the core calculations of the program. The first subroutine calculates the drift vector, while the second and the third subroutines perform the Variational Monte Carlo and the Pure Diffusion Monte Carlo simulations, respectively.

The final file, called *utility.F90*, contains three subroutines with various auxiliary functions: one calculate the mean value and error across the simulation, another generates a random Gaussian-distributed number following the Box-Muller method, and the third creates an output file containing the energy values computed by each walker.

- Main Program

The main program is located in the file *code.F90*, where the input and the geometry files are read to set the parameters for the simulation. At this stage, the nuclear coordinates are converted from angstrom to atomic units. Then the main simulation begins by calling the subroutine corresponding to the method chosen in the input file. Once the simulation is completed, the average and error are calculated a printed out in the terminal:

ENERGY =	-0.920362029110	+/-	0.015459
ACCEPTANCE =	0.968774400000	+/-	0.000144

In addition to the result displayed, a file is generated that can be used to plot the energy values across all walkers, allowing a visual representation of the energy distribution throughout the simulation.

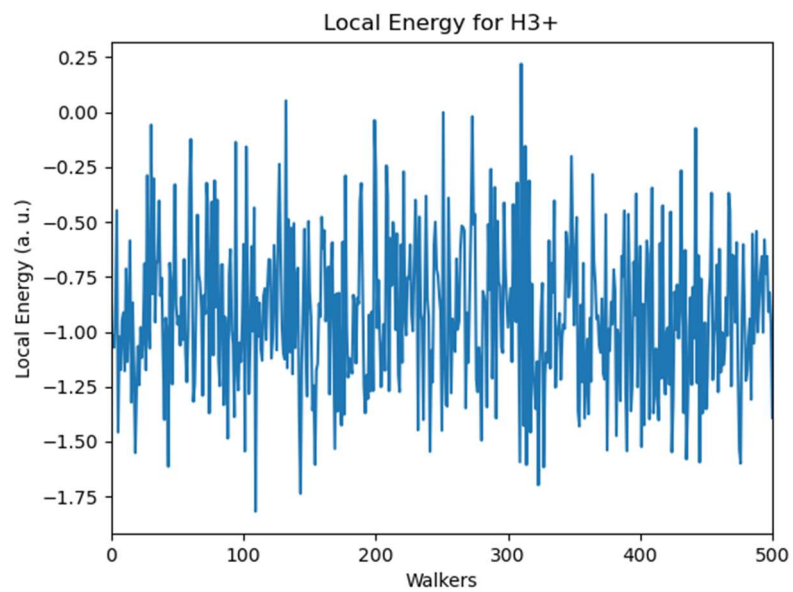


Fig. 1: Plot of local energy over walkers for H_3^+

TESTS AND EXAMPLES

The program is designed to calculate the energy of simple molecules composed by hydrogen and helium. To test the program, 5 different system were considered:

- H (1 nucleus, 1 electron)
- He (1 nucleus, 2 electrons)
- H_2^+ (2 nuclei, 1 electron)
- H_2 (2 nuclei, 2 electrons)
- H_3^+ (3 nuclei, 2 electrons)

The calculation was conducted using the following parameters:

- Wavefunction parameter $a = 1.4$
- Number of steps = 10000
- Number of walkers = 500
- Time step = 0.001

In the case of Pure Diffusion Monte Carlo:

- Reference energy = -1.5
- $\tau = 5000$

The results obtained are presented in the following table:

	VARIATIONAL MONTE CARLO		PURE DIFFUSION MONTE CARLO	
	Energy (a. u.)	Acceptance	Energy (a. u.)	Acceptance
H	-0.171(6)	0.98233(6)	-0.179(6)	0.98240(6)
He	0.94(2)	0.97499(7)	0.88(1)	0.97532(7)
H₂⁺	-0.590(3)	0.99168(6)	-0.590(3)	0.99160(6)
H₂	-0.46(1)	0.9819(1)	-0.47(1)	0.9821(1)
H₃⁺	-0.92(2)	0.9687(1)	-0.94(2)	0.9689(1)

Tab. 1: Results for test calculations

As seen in Table 1, the acceptance rate for each calculation is over 95%, indicating that there are not many out-of-scale values. This suggests that the algorithms used in the program are stable and perform as expected.