FYS4411 - Computational Physics II: Quantum Mechanical Systems

Project 2 - Variatonal Monte Carlo Methods

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https://www.github.com/Oo1Insane1oO/FYS4411

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Abstract

I INTRODUCTION

Using the Variational Monte Carlo, this project aims to find and analyze quantities such as the ground state energy and single-particle densities of quantum dots for so-called closed shell systems.

We use the usual approach by estimating expectation value of the ground state energy with the variational principle and minimizing. The algorithm used for the Monte Carlo method is the well known Metropolis algorithm.

The reason for using a Monte Carlo method for minimizing the trial ground state energy is because the expectation value would in general be a multi-dimensional integral depending on the number of particles and number of parameters involved in the total wave function. Such an integral is not adequately solved by traditional methods(i.e Gaussian-quadrature).

The desired result is that the Metropolis algorithm with importance sampling yields a better result both from a computational point of view. That is it finds a good estimate for the ground state energy efficiently without wasting to much time on the configuration space. The wave function only has small values in this large space meaning a homogeneous distribution of calculation points would yield a poor result, a non-homogeneous approach(such as with the Metropolis algorithm) would then, hopefully, gives a better result.

II THEORY

»INSERT DESCRIPTION«

II.A HERMITE POLYNOMIALS

Hermite polynomials $H(x)$ are solutions to the differential equation

$$\frac{\mathrm{d}^2H}{\mathrm{d}x^2} - 2x\frac{\mathrm{d}H}{\mathrm{d}x} + (\lambda - 1)H = 0 \tag{1}$$

The polynomials fulfill the orthogonality relation

$$\int_{-\infty}^{\infty} \mathrm{e}^{-x^2} H_n^2 \mathrm{d}x = 2^n n! \sqrt{\pi} \tag{2}$$

with the recurrence relation

$$H_{n+1} = H_n - 2nH_{n-1} \tag{3}$$

II.B HARMONIC OSCILLATOR

II.B.1 Cartesian Coordinates

The harmonic oscillator system in 2 dimensions and in natural units is given by the following Hamiltonian

$$\hat{H_0} = \frac{1}{2}\sum_{i=1}^{N}\left(-\nabla_i^2 + \omega^2 r_i^2\right) \tag{4}$$

The wave functions in this case is then:

$$\phi_{n_x,n_y}(x,y) = AH_{n_x}(\sqrt{\omega}x)H_{n_y}(\sqrt{\omega}y)\exp\left(-\frac{\omega}{2}(x^2+y^2)\right) \tag{5}$$

where H_n is a hermite polynomial of order n and A is a normalization constant. The quantum numbers n_x and n_y go as $n_x, n_y = 0, 1, 2\ldots$. While ω is the oscillator frequency.
The energies is

$$E = \hbar\omega\left(n_x + n_y + 1\right) \tag{6}$$

II.C METROPOLIS-HASTINGS ALGORITHM

The Metropolis algorithm bases itself on moves (also called transitions) as given in a Markov process(or Markov chain). Define a probability distribution function(PDF) $w_j(t)$ with a transition probability $w(i \to j)$ which for a given time-step yields in the Markov formula

$$w_i(t+\varepsilon) = \sum_j w(j \to i) w_j(t) \tag{7}$$

The transition probability is defined with an acceptance probability distribution $A(j \to i)$ and a proposed probability distribution $T(j \to i)$ as

$$w(j \to i) = A(j \to i) T(j \to i) \tag{8}$$

The acceptance A is the probability for the move to be accepted and the proposal T is different for each problem.
In order for this transition chain to reach a desired convergence and reversibility we have the well known condition for detailed balance »INSERT REF«. This condition gives us that the probability distribution functions satisfy the following condition

$$w_i T_{i\to j} A_{i\to j} = w_j T_{j\to i} A_{j\to i} \Rightarrow \frac{w_i}{w_j} = \frac{T_{j\to i} A_{j\to i}}{T_{i\to j} A_{i\to j}} \tag{9}$$

We now need to choose an acceptance which fulfills equation 9 and a common choice is the Metropolis condition

$$A_{j\to i} = \min\left(1, \frac{w_i T_{i\to j}}{w_j T_{j\to i}}\right) \tag{10}$$

The Metropolis-Hastings algorithm is thus

(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).

II.D VARIATIONAL PRINCIPLE

The variational principle states the following restriction on the ground state energy for a given symmetry

$$E_0 \leq \langle E[\Phi_T] \rangle = \int \phi_T^* \hat{H} \phi_T \mathrm{d}\tau = \langle \phi_T | \hat{H} | \phi_T \rangle \tag{11}$$

that is the ground state energy E_0 is bounded by the expectation value of the trial energy.

II.E IMPORTANCE SAMPLING

In order to use the Metropolis algorithm as explained in section II.C, we need to find the proposal probability distribution labeled $T_{j\to i}$. This is what is known as importance sampling.
This section will derive the importance sampling by using the Fokker-Planck equation for one particle

$$\frac{\partial P}{\partial t} = D \frac{\partial}{\partial x}\left(\frac{\partial}{\partial x} - F\right) P(x,t) \tag{12}$$

where F is a drift term and D is a diffusion constant, and the Langevin equation

$$\frac{\partial x(t)}{\partial t} = DF(x(t)) + \eta \tag{13}$$

where η is a Gaussian distributed random variable.

II.E.1 Quantum Force

Since we are working with a isotropic diffusion characterized by a time-dependant probability density our system must obey the summed total Fokker-Planck equation

$$\frac{\partial P}{\partial t} = \sum_i D \frac{\partial}{\partial x_i}\left(\frac{\partial}{\partial x_i} - F_i\right) P(x,t) \tag{14}$$

where F_i is now the i'th component of the drift velocity term(given by an external potential). Since the probability is assumed to be convergent, that is it converges to a stationary probability density the time dependence at this point is zero for all i. With other words, the left hand side of equation 14. We also know that the drift should be of form $F = g(x)\frac{\partial P}{\partial x}$ giving

$$\frac{\partial^2 P}{\partial {x_i}^2} = P\frac{\partial g}{\partial P}\left(\frac{\partial P}{\partial x_i}\right)^2 + Pg\frac{\partial^2 P}{\partial {x_i}^2} + g\left(\frac{\partial P}{\partial x_i}\right)^2 \tag{15}$$

Now we may use the condition for stationary density meaning the left hand side of equation 15 must equal zero giving that $g = 1/P$(only possibility the derivatives cancel). Inserting in $P = \psi_T$(see »INSERT REF«) we get that the expression for the quantum force is

$$F = \frac{2}{\Psi_T}\nabla\Psi_T \tag{16}$$

II.E.2 Solution

Using Eulers method(Euler-Maruyama method) on the Langevin equation(equation 13) one obtains the new positions

$$y = x + DF(x)\Delta t + \xi\sqrt{\Delta t} \tag{17}$$

with $D = 1/2$ in natural units due to the kinetic energy term and Δt is a time-step parameter. The random variable ξ is within a Gaussian distribution of variance one and standard deviation zero.
Using the force obtained in section II.E.1 given in equation 16 the solution to the Fokker-Planck equations are given by the Greens function

$$G(y,x,\Delta t) = \frac{1}{(4\pi D\Delta t)^{\frac{3N}{2}}}\exp\left(-\frac{\left(x-\xi\sqrt{\Delta t}\right)^2}{4D\Delta t}\right) \tag{18}$$

which gives us the acceptance

$$A_{y\to x} = \min\left(1, \frac{|\psi_T(y)|^2 G(y,x,\Delta t)}{|\psi_T(x)|^2 G(x,y,\Delta t)}\right) \tag{19}$$

II.F VMC

This section will explain and derive the equations involved in the Variational Monte Carlo method. The whole section will assume that we have the following trial wave function, ψ_T

$$\psi_T(\vec{r}_1,\ldots,\vec{r}_N) \equiv \det(\phi_1(\vec{r}_1,\alpha),\ldots,\phi(\vec{r}_N,\alpha))\prod_{i<j}^{N}\exp\left(\frac{a r_{ij}}{1+\beta r_{ij}}\right) \tag{20}$$

with the $\vec{r}$'s being the position of the electrons and the ϕ's being the wave function to some known system(i.e harmonic oscillator). The position r_{ij} is a relative distance $\left|\vec{r}_i - \vec{r}_j\right|$ while α and β are variational parameters and a is a specific constant dependant of the total spin symmetry of electron i and j as

$$a = \begin{cases} 1, & \text{anti-parallel spin} \\ \dfrac{1}{3}, & \text{parallel spin} \end{cases} \tag{21}$$

This is also known as a $Pade - Jatrow$ factor.
We also define the total Hamiltonian of the system for the quantum dot case as

$$\hat{H} = \hat{H}_O + \hat{H}_I \tag{22}$$

with $\hat{H}_O$ being the harmonic oscillator defined in equation 4 and $\hat{H}_I$ being the Hamiltonian for the electron interactions(Coulomb interaction) defined as

$$\hat{H}_I = \sum_{i<j}\frac{1}{r_{ij}} \tag{23}$$

Lastly, we work in natural units setting $\hbar = c = 1$, and all the above equations(equations 20, 21, 22 and 23) also assume natural units.

II.F.1 Expectation Value and Local Energy

Given the Hamiltonian equation 22 and a trial wave function $\Psi_T(R,\Lambda)$ and using the variational principle, as given in equation 11 the upper bound for the ground state energy E_0 if $H(r)$ is

$$E[\hat{H}(R,\Lambda)] \leq \left\langle \hat{H} \right\rangle = \frac{\langle \Psi_T | \hat{H} | \Psi_T \rangle}{\langle \Psi_T | \Psi_T \rangle} \tag{24}$$

where $R = (r_1, \ldots, r_N)$ is the positions to N particles and $\Lambda = (\lambda, \ldots, \lambda_M)$ are the M variational parameters.
Now we can expand the trial wave function $\Psi_T(R,\Lambda)$ in the orthonormal eigenstates of the Hamiltonian $\hat{H}$(which form a complete set)

$$\Psi_T(r) = \sum_i c_i \Psi_i(r) \tag{25}$$

and the upper bound given in equation 24 is

$$E_0 \leq \frac{\sum_{ij} c_i c_j^* \left\langle \Psi_j \middle| \hat{H} | \Psi_i \right\rangle}{\sum_{ij} c_i c_j^* \left\langle \Psi_j \middle| \Psi_i \right\rangle} = \frac{\sum_n a_n^2 E_n}{\sum_n a_n^2} \tag{26}$$

where the eigenequation for the Hamiltonian $\hat{H}\Psi_n = E_n \Psi_n$ was used. The expression given in equation 24 is the expectation value we evaluate in each variational step that is we choose α according to some minimization algorithm and re-evaluate the expectation value.
In order to introduce the transition probability as given in the Metropolis algorithm(see section II.C) the expectation value, equation 26, needs to be rewritten in terms of a PDF. We can define this as

$$P(R) \equiv \frac{|\Psi_T(R)|^2}{\int |\Psi_T(R)|^2 \mathrm{d}R} \tag{27}$$

Now we observe that if we define a quantity

$$E_L(R,\Lambda) \equiv \frac{1}{\Psi_T(R,\Lambda)} \hat{H} \Psi_T(R,\Lambda) \tag{28}$$

which is the so-called local energy. The expectation value given in equation 26 can be rewritten as

$$E[H] = \int P(R) E_L(R,\Lambda) \mathrm{d}R \approx \frac{1}{N} \sum_{i=1}^{N} P(r_i,\Lambda) E_L(r_i,\Lambda) \tag{29}$$

which is of the form given in equation 7 and N is the number of states(or Monte Carlo cycles).

II.F.2 Analytical Expression for Local Energy

We use the Metropolis algorithm to find an estimate for the expectation value to the energy. In this expression we have a so-called local energy defined as

$$E_L = \frac{1}{\psi_T} \hat{H} \psi_T \tag{30}$$

This expression shows up in the integrand as the multiplied function to the PDF which is used in the Metropolis algorithm.

II.F.3 Two Electron Case

We start by finding the local energy in the case with two electrons. The trial wave function is in this case(related to equation 5) using equation 20

$$\psi_T(\vec{r}_1, \vec{r}_2) = A \exp\left(-\frac{\alpha\omega}{2} \left(r_1^2 + r_2^2 \right) \right) \exp\left(\frac{a r_{12}}{1 + \beta r_{12}} \right) \tag{31}$$

Using the definition of the trial wave function, equation 28 and the total Hamiltonian(equation 22) the local energy with equation 28 is

$$E_L = \frac{1}{\psi_T} \left(\hat{H}_O \psi_T + \hat{H}_I \psi_T \right) \tag{32}$$

we solve the first part $\hat{H}_O \psi_T$

$$\hat{H}_O \psi_T = \frac{1}{2} \left(-\nabla_1^2 - \nabla_2^2 + \omega^2 \left(r_1^2 + r_2^2 \right) \right) \psi_T \tag{33}$$

Starting with the Laplacian for electron 1

$$\nabla_1^2\psi_T = \frac{\mathrm{d}^2\psi_T}{\mathrm{d}x_1^2} + \frac{\mathrm{d}^2\psi_T}{\mathrm{d}y_1^2} \tag{34}$$

The first differential is

$$\frac{\mathrm{d}^2\psi_T}{\mathrm{d}x_1^2} = A\exp\Big(-\frac{\alpha\omega}{2}r_2^2\Big)\exp\Big(-\frac{\alpha\omega}{2}y_1^2\Big)\frac{\mathrm{d}^2}{\mathrm{d}x_1^2}\left[\exp\Big(-\frac{\alpha\omega}{2}x_1^2\Big)\exp\Big(\frac{ar_{12}}{1+\beta r_{12}}\Big)\right] \tag{35}$$

using the product rule for differentiation we get

$$\frac{\mathrm{d}^2}{\mathrm{d}x_1^2}\left[\exp\Big(-\frac{\alpha\omega}{2}x_1^2\Big)\exp\Big(\frac{ar_{12}}{1+\beta r_{12}}\Big)\right] = \frac{\mathrm{d}}{\mathrm{d}x}\left[\exp\Big(\frac{ar_{12}}{1+\beta r_{12}}\Big)\frac{\mathrm{d}}{\mathrm{d}x}\exp\Big(-\frac{\alpha\omega}{2}x_1^2\Big) + \exp\Big(-\frac{\alpha\omega}{2}x_1^2\Big)\frac{\mathrm{d}}{\mathrm{d}x}\exp\Big(\frac{ar_{12}}{1+\beta r_{12}}\Big)\right] \tag{36}$$

III SETUP

IV RESULTS

V DISCUSSION

VI CONCLUSION

VII References

[1] David J. Griffiths Chapters 2, 4 and 7, *Introduction to Quantum Mechanics Second Edition*, Pearson, 2005, ISBN 0-13-111892-7.

[2] Morten Hjort-Jensen, *Computational Physics: Hartree-Fock methods and introduction to Many-Body Theory.* https://www.github.com/CompPhysics/ComputationalPhysics2/blob/gh-pages/doc/pub/basicMB/pdf, 2017

[3] Morten Hjort-Jensen, *Computational Physics: Variational Monte Carlo methods.* https://www.github.com/CompPhysics/ComputationalPhysics2/blob/gh-pages/doc/pub/vmc/pdf, 2017

[4] M. Taut, *Two Electrons in an External Oscillator Potential; Particular analytic solutions of a Coulomb Correlation Problem*, Physical Review A 48, 3561, 1993.

[5] Negele and Orland, *Quantum Many-Particle Systems*, Addison-Wesley.

[6] Fetter and Walecka, *Quantum Theory of Many-Particle Systems*, Mcgraw-Hill, 1971.

[7] Dickhoss and Van Neck, *Many-Body Theory Exposed*, World Scientific, 2006