FYS4411 - Computational Physics II: Quantum Mechanical Systems

Project 2

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

April 3, 2017

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

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.B.2 Polar Coordinates

In order to change to polar coordinates (r, θ) we introduce the usual transformations for Cartesian

$$\begin{aligned} x &= r\cos\theta \\ y &= r\sin\theta \\ r &= \sqrt{x^2+y^2} \end{aligned} \tag{7}$$

Introducing a separable solution in the radial and angular coordinates as an ansatz ($\psi(r,\theta) = R(r)Y(\theta)$) gives

$$\begin{aligned} R_{nm}(r) &= \sqrt{\frac{2n!}{(n+|m|)!}}\left(\frac{m_q\omega}{\hbar}\right)^{\frac{1}{2}(|m|+1)} r^{|m|}\mathrm{e}^{-\frac{m_q\omega}{2\hbar}r^2} L_n^{|m|}\left(\frac{m_q\omega}{\hbar}r^2\right) \quad n = 0,1,2\ldots \\ Y_m(\theta) &= \frac{1}{\sqrt{2\pi}}\mathrm{e}^{im\theta} \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad m = 0,\pm1,\pm2,\ldots \end{aligned} \tag{8}$$

where m_q is the particle mass, $L_n^{|m|}$ is the associated Laguerre polynomials.
The eigenfunction is thus

$$\psi_{nm}(r,\theta) = \sqrt{\frac{n!}{\pi(n+|m|)!}}\left(\frac{m_q\omega}{\hbar}\right)^{\frac{1}{2}(|m|+1)} r^{|m|}\mathrm{e}^{-\frac{m_q\omega}{2\hbar}r^2} L_n^{|m|}\left(\frac{m_q\omega}{\hbar}r^2\right)\mathrm{e}^{im\theta} \tag{9}$$

with eigenenergies

$$E = \hbar\omega(2n+|m|+1) \tag{10}$$

II.C 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.D 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

$$\psi_T(\vec{r}_1,\ldots,\vec{r}_N) \equiv \det(\phi_1(\vec{r}_1,\alpha),\ldots,\phi(\vec{r}_N,\alpha))\prod_{i<j}^{N}\exp\left(\frac{ar_{ij}}{1+\beta r_{ij}}\right) \tag{12}$$

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

$$a = \begin{cases} 1, & \text{anti-parallel spin} \\ \dfrac{1}{3}, & \text{parallel spin} \end{cases} \tag{13}$$

We also define the total Hamiltonian of the system for the quantum dot case as

$$\hat{H} = \hat{H}_O + \hat{H}_I \tag{14}$$

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

$$\hat{H}_I = \sum_{i<j}\frac{1}{r_{ij}} \tag{15}$$

Lastly, we work in natural units setting $\hbar = c = 1$, and all the above equations(equations 12, 13, 14 and 15) also assume natural units.

II.D.1 EXPECTATION VALUE AND LOCAL ENERGY

Given the Hamiltonian equation 14 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

$$E[\hat{H}(R,\Lambda)] \leq \left\langle\hat{H}\right\rangle = \frac{\langle\Psi_T|\hat{H}|\Psi_T\rangle}{\langle\Psi_T|\Psi_T\rangle} \tag{16}$$

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)

$$\Psi_T(r) = \sum_i c_i\Psi_i(r) \tag{17}$$

and the upper bound given in equation 16 is

$$E_0 \leq \frac{\sum_{ij} c_i c_j^* \left\langle \Psi_j \right| \hat{H} \left| \Psi_i \right\rangle}{\sum_{ij} c_i c_j^* \left\langle \Psi_j | \Psi_i \right\rangle} = \frac{\sum_n a_n^2 E_n}{\sum_n a_n^2} \tag{18}$$

where the eigenequation for the Hamiltonian $\hat{H}\Psi_n = E_n\Psi_n$ was used. The expression given in equation 16 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 »INSERT REF« the expectation value, equation 18, needs to be rewritten in terms of a probability distribution function(PDF). We can define this as

$$P(R) \equiv \frac{|\Psi_T(R)|^2}{\int |\Psi_T(R)|^2 \mathrm{d}R} \tag{19}$$

Now we observe that if we define a quantity

$$E_L(R,\Lambda) \equiv \frac{1}{\Psi_T(R,\Lambda)} \hat{H}\Psi_T(R,\Lambda) \tag{20}$$

which is the so-called local energy. The expectation value given in equation 18 can be rewritten as

$$E[H] = \int P(R) E_L(R\Lambda) \mathrm{d}R \approx \frac{1}{N} \sum_{i=1}^{N} P(r_i,\Lambda) E_L(R_i,\Lambda) \tag{21}$$

which is of the form given in »INSERT REF HERE«.

II.D.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

$$E_L = \frac{1}{\psi_T} \hat{H}\psi_T \tag{22}$$

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

II.D.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 12

$$\psi_T(\vec{r}_1,\vec{r}_2) = A \exp\left(-\frac{\alpha\omega}{2}\left(r_1^2 + r_2^2\right)\right) \exp\left(\frac{a r_{12}}{1+\beta r_{12}}\right) \tag{23}$$

Using the definition of the trial wave function, equation 20 and the total Hamiltonian(equation 14) the local energy with equation 20 is

$$E_L = \frac{1}{\psi_T}\left(\hat{H}_O\psi_T + \hat{H}_I\psi_T\right) \tag{24}$$

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

$$\hat{H}_O\psi_T = \frac{1}{2}\left(-\nabla_1^2 - \nabla_2^2 + \omega^2\left(r_1^2 + r_2^2\right)\right)\psi_T \tag{25}$$

Starting with the Laplacian for electron 1

$$\nabla_1^2\psi_T = \frac{\mathrm{d}^2\psi_T}{\mathrm{d}x_1^2} + \frac{\mathrm{d}^2\psi_T}{\mathrm{d}y_1^2} \tag{26}$$

The first differential is

$$\frac{\mathrm{d}^2\psi_T}{\mathrm{d}x_1^2} = A\exp\left(-\frac{\alpha\omega}{2}r_2^2\right)\exp\left(-\frac{\alpha\omega}{2}y_1^2\right)\frac{\mathrm{d}^2}{\mathrm{d}x_1^2}\left[\exp\left(-\frac{\alpha\omega}{2}x_1^2\right)\exp\left(\frac{a r_{12}}{1+\beta r_{12}}\right)\right] \tag{27}$$

using the product rule for differentiation we get

$$\frac{\mathrm{d}^2}{\mathrm{d}x_1^2}\left[\exp\left(-\frac{\alpha\omega}{2}x_1^2\right)\exp\left(\frac{a r_{12}}{1+\beta r_{12}}\right)\right] = \frac{\mathrm{d}}{\mathrm{d}x}\left[\exp\left(\frac{a r_{12}}{1+\beta r_{12}}\right)\frac{\mathrm{d}}{\mathrm{d}x}\exp\left(-\frac{\alpha\omega}{2}x_1^2\right) + \exp\left(-\frac{\alpha\omega}{2}x_1^2\right)\frac{\mathrm{d}}{\mathrm{d}x}\exp\left(\frac{a r_{12}}{1+\beta r_{12}}\right)\right] \tag{28}$$

$$-2.0\alpha\omega - \frac{2.0\beta^3 a x_{12}^2}{(\beta r_{12}+1)^4} - \frac{2.0\beta^3 a y_{12}^2}{(\beta r_{12}+1)^4} - \frac{2.0\beta^2 a x_{12}^2}{r_{12}(\beta r_{12}+1)^4} - \frac{2.0\beta^2 a y_{12}^2}{r_{12}(\beta r_{12}+1)^4} + \frac{2.0\beta a}{(\beta r_{12}+1)^2} + \frac{1.0\beta a x_{12}^2}{r_{12}^2(\beta r_{12}+1)^2} + \frac{1.0\beta a y_{12}^2}{r_{12}^2(\beta r_{12}+1)^2}$$
$$+0.5\omega^2 r_1^2 + 0.5\omega^2 r_2^2 + \frac{1.0a x_{12}^2}{\beta r_{12}^4 + r_{12}^3} + \frac{1.0a y_{12}^2}{\beta r_{12}^4 + r_{12}^3} - \frac{2.0a}{\beta r_{12}^2 + r_{12}} + \frac{1}{r_{12}}$$
$$-\frac{0.5}{r_{12}^2(\beta r_{12}+1)^4}(\alpha\omega r_{12}x_1(\beta r_{12}+1)^2 + a x_{12})^2 - \frac{0.5}{r_{12}^2(\beta r_{12}+1)^4}(\alpha\omega r_{12}x_2(\beta r_{12}+1)^2 - a x_{12})^2$$
$$-\frac{0.5}{r_{12}^2(\beta r_{12}+1)^4}(\alpha\omega r_{12}y_1(\beta r_{12}+1)^2 + a y_{12})^2 - \frac{0.5}{r_{12}^2(\beta r_{12}+1)^4}(\alpha\omega r_{12}y_2(\beta r_{12}+1)^2 - a y_{12})^2$$

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