Nummerical Integration Using Gaussian Quadrature and Monte Carlo Method

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Abstract

This article set forth to integrate a six-dimensional integral which is used to determine the ground state correlation energy between two electrons in a helium atom. The integral appears in many quantum mechanical applications. We will first solve the integral true a brute force manner and employ both Gauss-Legendre and Gauss-Laguerre quadrature and Monte-Carlo integration.

I. Introduction

II. Theory

The wave function of each electron can be assumed to be modelled like the single-particle wave function of an electron in the hydrogen atom. The single-particle wave function for an electron i in the $1s$ state can the be modelled by:

$$\psi_{1s}(\mathbf{r}_i) = e^{-\alpha r_i}. \tag{1}$$

The parameter α is connected to the charge of the atom and will in our case be set to equal 2 to correspond to the helium atom $Z = 2$. Furthermore r_i is the magnitude of the position vector $\mathbf{r}_i$ and is given by

$$r_i = \sqrt{x_i^2 + y_i^2 + z_i^2}.$$

and

$$\mathbf{r}_i = x_i\mathbf{e}_x + y_i\mathbf{e}_y + z_i\mathbf{e}_z,$$

The ansatz for the wave function for two electrons is then given by the product of two so-called $1s$ wave functions as

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = e^{-\alpha(r_1+r_2)}.$$

Note that it is not possible to find a closed-form or analytical solution to Schrödinger's equation for two interacting electrons in the helium atom.

The integral we need to solve is the quantum mechanical expectation value of the correlation energy between two electrons which repel each other via the classical Coulomb interaction, namely

$$\langle \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \rangle = \int_{-\infty}^{\infty} d\mathbf{r}_1 d\mathbf{r}_2 e^{-2\alpha(r_1+r_2)} \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}. \tag{2}$$

Note that our wave function is not normalized, but we dont nedd to worry about this.

This integral can be solved in closed form and the answer is $5\pi^2/16^2$. This integral can be rewritten in to spherical coordinates by change of variables. We are then only left with 2 infinite integrals. The Laguerre polynomials are defined for $x \in [0, \infty)$ and we change to spherical coordinates

$$d\mathbf{r}_1 d\mathbf{r}_2 = r_1^2 dr_1 r_2^2 dr_2 dcos(\theta_1) dcos(\theta_2) d\phi_1 d\phi_2$$

want to integrate over $d\theta_i$"instead of $d\cos(\theta_i)$ and use that $d\cos(\theta_i) = sin(\theta_i)d\theta_i$ to ge

$$= r_1^2 dr_1 r_2^2 dr_2 sin(\theta_1) sin(\theta_2) d\theta_1 d\theta_2 d\phi_1 d\phi_2$$

with

$$\frac{1}{r_{12}} = \frac{1}{\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 cos(\beta)}}$$

and

$$cos(\beta) = cos(\theta_1)cos(\theta_2) + sin(\theta_1)sin(\theta_2)cos(\phi_1 - \phi_2)).$$

*https://github.com/AndreasFagerheim/Fys4150

This leads to the intgral in speherical coordinates

$$\langle \frac{1}{r_{12}} \rangle = \int d\lambda r_1^2 r_2^2 sin(\theta_1) sin(\theta_2) e^{-2\alpha(r_1+r_2)} \frac{1}{r_{12}} \quad (3)$$

where we used $d\lambda = dr_1 dr_2 d\theta_1 \theta_2 d\phi_1 d\phi_2$. Next making the substitution $4r_1 = u''$ og $4r_2 = v''$ where we use that $\alpha = 2$ we get

$$\frac{1}{(2\alpha)^5} \int d\tilde{\lambda} u^2 v^2 sin(\theta_1) sin(\theta_2) \frac{e^{-(u+v)}}{\sqrt{u^2+v^2-2uv \cdot cos(\beta)}} \quad (4)$$

where $\tilde{d\lambda} = dudvd\theta_1\theta_2 d\phi_1 d\phi_2$

III. Methods

The integral will be solved using four numerical methods. First numerical integration method we set forth to explore is the Gaussian Quadrature which concept is to make use of a weight function $W(x)$ to give more emphasis to one part of the interval we integrate over than another. The basic idea behind this method is to approximate the integral

$$I = \int_a^b f(x)dx = \int_a^b W(x)g(x)dx \approx \sum_{i=1}^{N} w_i g(x_i) \quad (5)$$

Where w_i is the weights and obtained through orthogonal polynomials. These polynomials are orthogonal in some interval $[a, b]$ and the points x_i is constrained to lie in this interval. Different weight functions, $W(x)$ gives rise to different methods and we will look closer at Gaussian-Legendre ($W(x) = 1$) and Gaussian-Laguerre ($W(x) = x^\alpha e^{-x}$). These weight functions get their polynomials from the intervals $[-1, 1]$ and $[0, \infty\rangle$. The integral (2) we are working to solve has the limits $x \in [-\infty, \infty]$ and therefore need to rewrite the integral for to be in the right limits. By changing variable

$$t = \frac{b-a}{2}x + \frac{b+a}{2} \quad (6)$$

we can do this

$$\int_a^b f(x)dx = \frac{b-a}{2} \int_{-1}^{1} f(\frac{b-a}{2}x + \frac{b+a}{2}) \quad (7)$$

i. Gauss-Legendre Quadrature

The weight function $W(x) = 1$ is used in Gauss-Legendre Quadrature and use Legendre polynomials in the interval $[-1, 1]$

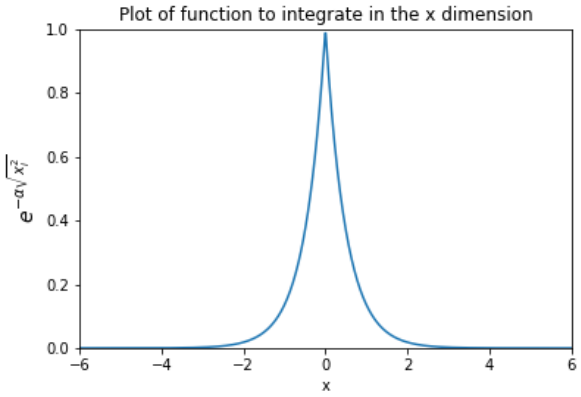

Figure 1: *Plot of the single particle wave function to find appropiate limits*

ii. Gauss-Laguerre Quadrature

$$\tilde{x}_i = tan(\frac{\pi}{4}(1 + x_i) \quad (8)$$

$$\tilde{w}_i = \frac{\pi}{4} \frac{w_i}{\cos^2(\frac{\pi}{4}(1+x_i))} \quad (9)$$

where w_i andx_i are the original weights and mesh points in the interval [-1,1], while $tildew_i$ and $\tilde{x}_i$ are the new weights and mesh points in the interval $[0, \infty\rangle$.

iii. Monte Carlo brute force

iv. Monte Carlo method improved

Text requiring further explanation[1].

IV. Results

i. Gauss-Legendre Quadrature

The implemented Gauss-Legendre Quadrature method yields the results given in **Table 1** when used to solve (2). With $N = 25$ the relative error is at its lowest, but is still 1.9%.

V. Discussion

wichs shows that precisions cost resources and time.

[1]Example footnote

N	Integral	Relative error
5	0.354602	0.83950
10	0.129834	0.32650
15	0.199475	0.03480
20	0.177065	0.08145
25	0.18911	0.01897
30	0.185796	0.03616

Table 1: *Results from using Gauss-Legendre Quadrature for calculating the integral with an exact solution equal to* 0.192766

i. Subsection One

A statement requiring citation [Figueredo and Wolf, 2009]. Lorem ipsum dolor sit amet, consectetuer adipiscing elit. Etiam lobortis facilisis sem. Nullam nec mi et neque pharetra sollicitudin. Praesent imperdiet mi nec ante. Donec ullamcorper, felis non sodales commodo, lectus velit ultrices augue, a dignissim nibh lectus placerat pede. Vivamus nunc nunc, molestie ut, ultricies vel, semper in, velit. Ut porttitor. Praesent in sapien. Lorem ipsum dolor sit amet, consectetuer adipiscing elit. Duis fringilla tristique neque. Sed interdum libero ut metus. Pellentesque placerat. Nam rutrum augue a leo. Morbi sed elit sit amet ante lobortis sollicitudin. Praesent blandit blandit mauris. Praesent lectus tellus, aliquet aliquam, luctus a, egestas a, turpis. Mauris lacinia lorem sit amet ipsum. Nunc quis urna dictum turpis accumsan semper.

ii. Subsection Two

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References

[Figueredo and Wolf, 2009] Figueredo, A. J. and Wolf, P. S. A. (2009). Assortative pairing and life history strategy - a cross-cultural study. *Human Nature*, 20:317–330.