Project 3, FYS4150

Fredrik E Pettersen
fredriep@student.matnat.uio.no

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Abstract

About the problem

The task of this project is to compute, with increasing degree of cleverness, the six dimensional integral used to determine the ground state correlation energy between two electrons in a helium atom. We will start off with "brute force" Gauss Legendre quadrature, proceed to Gauss Laguerre quadrature, and finish off with Monte Carlo integration. We assume that the wave function of each electron can 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 is given in terms of a dimensionless variable (we ommit normalization of the wave functions)

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

as

$$\psi_{l,s}(\mathbf{r}_i) = e^{-\alpha r_i}$$

where α is a parameter and

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

In this project we will fix $\alpha = 2$ which should correspond to the charge of the Helium atom $Z = 2$. The ansatz for the two-electron wave function is then given by the product of two one-electron wave funtions.

$$\Psi(\mathbf{r}_1, \mathbf{r_2}) = \psi(\mathbf{r}_1)\psi(\mathbf{r_2}) = e^{-2\alpha(r_1+r_2)}$$

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

$$\langle\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}\rangle = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\frac{e^{-\alpha r_i}}{|\mathbf{r}_1 - \mathbf{r}_2|}d\mathbf{r}_1 d\mathbf{r}_2$$

The algorithm

The principle algorithms of this project is Gaussian quadrature and Monte Carlo integration. What we are actually doing when we integrate a function by the use of the rectangle, trapezodial or Simpsons rule is to approximate the integrand with a Taylor polynomial of degree 0,1 and 2 respectively between the integration points. An obvious step forward from here is to approximate the entire function with a Taylor polynomial of degree N-1 for N integration points, but then we realize that Taylor polynomials are a bit crude. A larger step forward can be obtained by approximating the integrand with an orthogonal polynomial, such as Legendre polynomials. We begin with the approximation

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

Where w_i are the integration weights. This is called a Gaussian quadrature formula if it integrates exactly all polynomials $p \in P_{2N-1}$. That is:

$$\int_a^b W(x)p(x)dx = \sum_{i=1}^{N} w_i p(x_i)$$

Let us now approximate $g(x) \simeq P_{2N-1}(x)$ where $P_{2N-1}(x) = \mathcal{L}_N(x)P_{N-1}(x)+Q_{N-1}(x)$. $\mathcal{L}_N(x)$ is an orthogonal polynomial e.g. a Lagendre polynomial. We remember that orthogonal polynomials have the property

$$\int_a^b \mathcal{L}_i(x)\mathcal{L}_j(x)dx = A\delta_{i,j}$$

where $x \in [a,b]$ is determined by the specific polynomial (e.g $x \in [-1,1]$ for Legendre) and A is some orthogonality relation also determined by the specific polynomial ($A = \frac{2}{2i+1}$ for Legende). This means that we have the following

$$\int_a^b f(x)dx \simeq \int_a^b P_{2N-1}(x)dx = \underbrace{\int_a^b \mathcal{L}_N(x)P_{N-1}(x)}_{=0} + \int_a^b Q_{N-1}(x)$$

When we now extrapolate this to our numerics the integrals take the form of sums. To ensure that the term $\int_a^b \mathcal{L}_N(x)P_{N-1}(x) = 0$ we evaluate our sums in the points $\mathcal{L}_N(x_i) = 0$. That is

$$\int_a^b f(x)dx \simeq \sum_{i=1}^{N-1} P_{2N-1}(x_i)w_i = \sum_{i=1}^{N-1} Q_{N-1}(x_i)w_i$$

The most general way to do the Gaussian Quadrature is to use Legendre polynomials. What we end up having to do in order to evaluate our integral is to choose some number of integration points, and then calculate the integration points and weights. That is we need to calculate the zeros of a Legendre polynomial of degree N. We will also need to make a mapping from the original limits of our integral to the limits of Legendre polynomials, $x \in [-1,1]$. This is done by the function "gauleg" found in the resources for the course. What this function is first of all to make a mapping from the limits one gives as input to the Legendre limits of -1 and 1.
xm = 0.5 * (x2 + x1);
xl = 0.5 * (x2 - x1);
After constructing the Legendre polynomial of degree i evaluated at some point x (from the recurrance relation), the function runs Newtons method to find its zeros starting out with an appriximation
pp = n * (z * p1 - p2)/(z * z - 1.0);
z1 = z;
z = z1 - p1/pp;
and stores this in the vector x after scaling it according to the limits xm and xl. The roots of a Legendre polynomial are symmetric, so we actually find two roots for every iteration in "gauleg". The integration weights are also calculated through
w(i-1) = 2.0 * xl/((1.0 - z * z) * pp * pp);
theese are of course also symmetric.

Having done the general "brute force" gaussian quadrature and gotten very unsatisfying results we notice that the approach of first cutting the integral off at $\pm\lambda$ and then mapping theese limits to ± 1 for all the variables $x_1, y_1, z_1, x_2, y_2, z_2$ is a rather clumsy one. If we rewrite the integrand into spherical coordinates we can use the Gauss Laguerre quadrature for the radial part instead, seeing as this looks like a typical Gauss Laguerre case:

$$x^\alpha e^{-x}$$

The transformation is

$$\iint \frac{e^{-4(r_1+r_2)}}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1\mathbf{r}_2 = \int \cdots \int \frac{e^{-4(\sqrt{x_1^2+y_1^2+z_1^2}+\sqrt{x_2^2+y_2^2+z_2^2})}}{\sqrt{(x_1-x_2)^2+(y_1-y_2)^2+(z_1-z_2)^2}} dx_1dx_2dy_1dy_2dz_1dz_2$$

$$= \int \cdots \int \frac{r_1^2r_2^2\sin(\theta_1)\sin(\theta_2)e^{-4(r_1+r_2)}dr_1dr_2d\phi_1d\phi_2d\theta_1d\theta_2}{\sqrt{(r_1cos(\phi_1)sin(\theta_1)-r_2cos(\phi_2)sin(\theta_2))^2+(r_1sin(\phi_1)sin(\theta_1)-r_2sin(\phi_2)sin(\theta_2))^2+(r_1cos(\theta_1)-r_2cos(\theta_2))^2}}$$

We now look only at the denominator without the square root

$$\begin{aligned} r_1^2(cos^2(\phi_1)sin^2(\theta_1)+sin^2(\phi_1)sin^2(\theta_1)+cos^2(\theta_1))+ \\ r_2^2(cos^2(\phi_2)sin^2(\theta_2)+sin^2(\phi_2)sin^2(\theta_2)+cos^2(\theta_2))- \\ 2r_1r_2(cos(\phi_1)cos(\phi_2)sin(\theta_1)sin(\theta_2)+sin(\phi_1)sin(\phi_2)sin(\theta_1)sin(\theta_2)+cos(\theta_1)cos(\theta_2) \\ = r_1^2+r_2^2-2r_1r_2(cos(\theta_1)cos(\theta_2)+sin(\theta_1)sin(\theta_2)cos(\phi_1-\phi_2)) \\ = r_1^2+r_2^2-r_1r_2(cos(\theta_1+\theta_2)(1-cos(\phi_1-\phi_2))+cos(\theta_1-\theta_2)(1+cos(\phi_1-\phi_2))) \end{aligned}$$

So in the end we are left with

$$\int_0^\infty \int_0^\infty \int_0^{2\pi} \int_0^{2\pi} \int_0^\pi \int_0^\pi \frac{r_1^2 r_2^2 \sin(\theta_1)\sin(\theta_2) e^{-4(r_1+r_2)} dr_1 dr_2 d\phi_1 d\phi_2 d\theta_1 d\theta_2}{\sqrt{r_1^2 + r_2^2 - r_1 r_2 (cos(\theta_1+\theta_2)(1-cos(\phi_1-\phi_2)) + cos(\theta_1-\theta_2)(1+cos(\phi_1-\phi_2)))}}$$

I need to remark that I use this denominator only because I thought I could simplify the expression more than it allready was in the project text, and had allready implemented the change before I relised I was wrong. I did not however bother changing it back seeing as it was correct, and the chance of introducing typos was rather large.
Now, when we intruduce this expression to the Gauss Laguerre quadrature both the $r_1^2 r_2^2$ terms and the exponential will be baked into the wheight function if we do another small substitution $\rho_1 = 4r_1, \rho_2 = 4r_2$. This substitution will only introduce a factor $\frac{1}{1024}$ from inserting $r_i = \frac{\rho_i}{4}$ for all r_i

$$\frac{\frac{\rho_1^2\rho_2^2}{4^2 4^2} sin(\theta_1) sin(\theta_2) e^{-(\rho_1+\rho_2)} \frac{d\rho_1 d\rho_2}{4^2}}{\sqrt{\frac{\rho_1^2}{4^2} + \frac{\rho_2^2}{4^2} - \frac{2\rho_1\rho_2}{4^2} cos(\beta)}} = \frac{\frac{1}{4^6}}{\frac{1}{4}} \frac{\rho_1^2\rho_2^2 sin(\theta_1) sin(\theta_2) e^{-(\rho_1+\rho_2)} d\rho_1 d\rho_2}{\sqrt{\rho_1^2 + \rho_2^2 - 2\rho_1\rho_2 cos(\beta)}}$$

This clearly results in

$$\frac{4}{4^6} = \frac{1}{1024}$$

Finally we have an expression to send through our six nested for-loops. The Integration points and wheights are now determined by the Gauss Laguerre and Gauss Legendre for the radial and angular parts respectively.

We do the Monte Carlo simulations in two different ways. The first is a brute force approach where we draw random points for the variables $r_1, r_2, \theta_1, \theta_2, \phi_1$ and ϕ_2 in their respective intervals. We then evaluate $f(r_1, r_2, \theta_1, \theta_2, \phi_1, \phi_2)$ and calculate the mean of f in the area $r_1, r_2 \in [0, \lambda]$, $\theta_1, \theta_2 \in [0, \pi]$, $\phi_1, \phi 2 \in [0, 2\pi]$ and multiply the mean of f with the "volume" $V = 4\pi^4\lambda^2$ The reason we evaluate f in spherical coordinates is that we only have to make cutoffs for the upper limits of r_1 and r_2, that is we limit ourselves to $r_1, r_2 \in [0, \lambda]$ when $r_1, r_2 \in [0, \infty)$ is correct. Had we evaluated f in cartesian coordinates we would have had to make similar cutoffs for all the variables in both ends.
To get a measure of how good the appriximation is we calculate the variance and standard deviation of the result (we neglect the covaraiance because it is a heavy computation and because it is assumed to be small).

Next we think a little about what the function f looks like, and realize that we can do importance sampling if we draw numbers from the exponential distribution. The integrand is then changed into

$$\frac{r_1^2 r_2^2 \sin(\theta_1)\sin(\theta_2)}{\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos(\beta)}}$$

Analytic solution

It is possible to find a closed form solution to the relevant integral, and put shortly it is $\frac{5\pi^2}{16^2}$.
With some help from David J Griffiths we can find this value ourselves to verify that it is correct. We start out with

$$\int \frac{e^{-4(r_1+r_2)/a}}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2$$

where $a = 1$ in our case. We will now fix $\mathbf{r}_1$ so we can do the $\mathbf{r}_2$ integral first. We also orient the $\mathbf{r}_2$ coordinate system such that the polar axis lies along $\mathbf{r}_1$. This gives us

$$|\mathbf{r}_1 - \mathbf{r}_2| = \sqrt{r_1^2 + r_2^2 - 2r_1 r_2 cos(\theta_2)}$$

which inserted gives

$$I_{r_2} = \int \frac{e^{-4r_2/a}}{\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 cos(\theta_2)}} d\mathbf{r}_2 = \int \frac{r_2^2 sin(\theta_2) e^{-4r_2/a}}{\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 cos(\theta_2)}} dr_2 d\theta_2 d\phi_2$$

The integral over ϕ_2 is trivial and ammounts to 2π. The θ_2 integral is

$$\int_0^\pi \frac{sin(\theta_2)d\theta_2}{\sqrt{r_1^2+r_2^2-2r_1r_2cos(\theta_2)}} = \left.\frac{\sqrt{r_1^2+r_2^2-2r_1r_2cos(\theta_2)}}{r_1r_2}\right|_0^\pi$$
$$= \frac{1}{r_1r_2}\left(\sqrt{r_1^2+r_2^2+2r_1r_2} - \sqrt{r_1^2+r_2^2-r_1r_2}\right)$$
$$= \frac{1}{r_1r_2}[(r_1+r_2)-|r_1-r_2|] = \begin{cases} \frac{2}{r_1}, \text{ if } r_2 < r_1 \\ \frac{2}{r_2}, \text{ if } r_1 < r_2 \end{cases}$$

Which means that

$$I_2 = 4\pi\left(\frac{1}{r_1}\int_0^{r_1} e^{-4r_2/a}r_2^2dr_2 + \int_{r_1}^{\infty} e^{-4r_2/a}r_2dr_2\right) =$$
$$\frac{\pi a^3}{8r_1}\left[1-\left(a+\frac{2r_1}{a}\right)e^{-4r_1/a}\right]$$

And we can now do the integral over r_1

Results

N	Gauss Legendre	Gauss Laguerre	Correct result
10	0.0719797	0.186457	0.192765
15	0.239088	0.189759	0.192765
20	0.156139	0.191081	0.192765
25	0.195817	0.19174	0.192765
30	0.177283	0.192113	0.192765
35	0.189923	0.192343	0.192765
40	0.184417	0.192493	0.192765
45	0.189586	0.192595	0.192765
50	0.18756	0.192667	0.192765

Figure 1: Results of Gaussian quadrature for increasing N

Stability and precision

Final comments

Source code