

1 Theory

1.1 Wavefunction of Helium

. The single-particle wave function of an electron i in the $1s$ state is given in terms of a dimensionless variable (the wave function is not normalized)

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

as

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

Where α is a parameter set to 2, due to the two electrons, and the length r_i is defined by

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

For our system with two electrons, we have the product of the two $1s$ wave functions defined as

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

This leads to the integral (1), which will be solved numerically with the three different methods mentioned earlier. The value of the integral corresponds to the energy between the two electrons repelling each other due to Columb interactions.

$$\left\langle \frac{1}{|\vec{r}_1 - \vec{r}_2|} \right\rangle = \int_{-\infty}^{\infty} d\vec{r}_1 d\vec{r}_2 e^{-2\alpha(r_1 + r_2)} \frac{1}{|\vec{r}_1 - \vec{r}_2|} \quad (1)$$

The analytical result is $5\pi/16^2$.

1.2 Gaussian Quadrature

The main idea of Gaussian quadrature is to integrate over a set of points x_i not equally spaced with weights w_i , which are calculated in the program Gauleg.cpp and Gauss Legendre.cpp). The weights are found through ortogonal polynomials(Laguerre and Legendre polynomials) in a set interval. The points x_i are chosen in a optimal sense and lie in the interval.

The intgral is approximated as

$$\int_a^b W(x) f(x) \approx \sum_{i=1}^n \omega_i f(x_i)$$

For a more detailed derivation and explanation?? of Gaussian qudrature see (Hjort-Jensen, 2015)

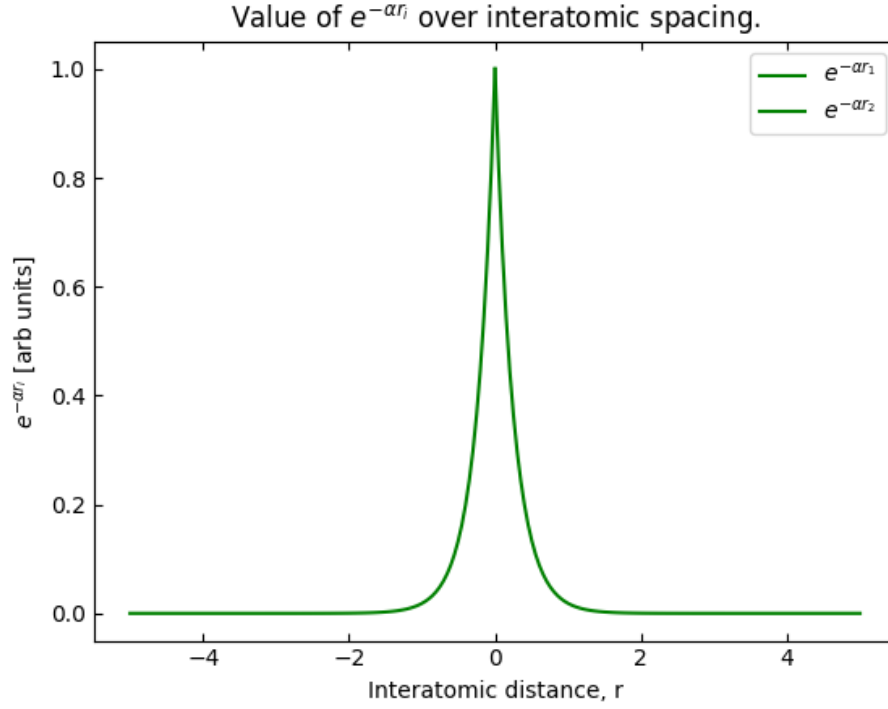


Figure 1: Plot of wavefunction in one dimension

1.2.1 Gauss-Legendre

Using Gauss-Legendre quadrature with Legendre polynomials will make it possible to utilize the integral numerically. The first step is to change the integration limits from $-\infty$ and ∞ to $-\lambda$ and λ . The λ 's are found by inserting it for r_i in the expression $e^{-\alpha r_i}$ because $r_i \approx \lambda$ when $e^{-\alpha r_i} \approx 0$. As we see from figure 1, $\lambda \in [-5, 5]$ is therefore a good approximation for the integration limits.

Furthermore, the weights and mesh points are computed using "gauleg" (see program `exampleprog.cpp`???)

Eventually ending up with a sixdimensional integral, where all six integration limits are the same.

$$\int_a^b \int_a^b \int_a^b \int_a^b \int_a^b \int_a^b e^{-x} f(x) dx \approx \sum_{i=1}^n w_i f(x_i)$$

1.2.2 Improved Gauss-Quadrature- Laguerre

Gauss-Legendre quadrature gets the job done, but it is unstable and unsatisfactory. By changing to spherical coordinates and replacing Legendre- with

Laguerre polynomials an improvement in accuracy is expected. The Laguerre polynomials are defined for $x \in [0, \infty)$, and in spherical coordinates:

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

with

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

and

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

For numerical integration, the deployment of the following relation is necessary:

$$\int_0^\infty e^{-x} f(x) dx \approx \sum_{i=1}^n w_i f(x_i)$$

where x_i is the i -th root of the Laguerre polynomial $L_n(x)$ and the weight w_i is given by

$$w_i = \frac{x_i}{(n+1)^2 [L_{n+1}(x_i)]^2}$$

The Laguerre polynomials are defined by Rodrigues formula:

$$L_n(x) = \frac{e^x}{n!} \frac{d^n}{dx^n} (e^{-x} x^n) = \frac{1}{n!} \left(\frac{d}{dx} - 1 \right)^n x^n$$

or recursively relations:

$$\begin{aligned} L_0(x) &= 1 \\ L_1(x) &= 1 - x \\ L_{n+1}(x) &= \frac{(2n+1-x)L_n(x) - nL_{n-1}(x)}{n+1} \end{aligned}$$

1.2.1

1.3 Monte Carlo

1.3.1 Generalized

Monte Carlo integration is based on the idea of finding the mean of a function in a domain by sampling random function values. This mean multiplied by the volume of the domain will be an approximation of the integral.

Say we have an integral I of $f(\mathbf{x})$ we want to find:

$$I = \int_D f(\mathbf{x}) d\mathbf{x}$$

where \mathbf{x} is in the domain D . This integral can be approximated by using random numbers distributed on D by the probability distribution function (PDF) $p(\mathbf{x})$. Discretizing, the approximated integral now becomes

$$I \approx \langle I \rangle = \frac{1}{N} \sum_{i=0}^N \frac{f(\mathbf{x}_i)}{p(\mathbf{x}_i)}, \quad (2)$$

where N is the number of sampled values.

1.3.2 Naïve approach (uniform PDF)

To solve our six-dimensional integral, we first take the naïve approach and distribute our randomly chosen variables on the uniform distribution

$$\theta(x) = \begin{cases} \frac{1}{b-a}, & \text{for } x \in [a, b] \\ 0 & \text{else} \end{cases},$$

and keep our variables \mathbf{r}_1 and \mathbf{r}_2 in cartesian coordinates. Putting the uniform distribution into (2), we get the naïve approximation of an integral:

$$\langle I \rangle = \frac{V}{N} \sum_{i=0}^N f(\mathbf{x}_i) \quad (3)$$

Here V is the integration volume (for d dimensions in cartesian coordinates $V = (b - a)^d$, with b and a being the integration limits for each dimension).