1 Theory

1.1 The Quantum Mechanical Problem

. 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, see below, which will be solved nummericaly 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.

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

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

1.2 Gauss-Legendre Quadrature

To compute this integral we will first be utilizing the Gauss-Legendre quadrature. Step one is to change the integration limits to something a little more suitable for a computer. We will therefore change the limits $-\infty$ and ∞ to $-\lambda$ and λ. The values of λ can be found by inserting it for r_i in the formula $e^{-\alpha r_i}$ and getting it sufficiently close to zero. We will also check that this approximation is satisfactory by plotting the function.

1.3 Improved Gauss-Quadrature

While the Gauss-Legendre quadrature gets the job done, its not a pretty sight. What can be improved is to replace the Legendre polynomials with the Laguerre polynomials. These polynomials are defined for $x \in [0, \infty)$.
We will change our original integral from cartesian coordinates to spherical, thus the following relations:

$$d\vec{r_1} d\vec{r_2} = r_1^2 dr_1 r_2^2 dr_2 dcos(\theta_1) dcos(\theta_2) d\phi_1 d\phi_2$$

$$\frac{1}{r_{12}} = \frac{1}{\sqrt{r_1^2 + r_2^2 - 2r_1r_2cos(\beta)}}$$

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

As previousley described, our integral is:

$$\int_\infty^\infty d\vec{r_1}d\vec{r_2}e^{-2\alpha(r_1+r_2)}\frac{1}{\vec{r_1} - \vec{r_2}}$$

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

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

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:

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

or recursively relations:

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

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