

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 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.

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

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

1.2 Gauss-Legendre Quadrature

Using Gauss-Legendre quadrature 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 $e^{-\alpha r_i} \approx 0$. From FIGURE 1 $\lambda \in [-5, 5]$ is therefor a good approximation for the integration limits.

1.3 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:

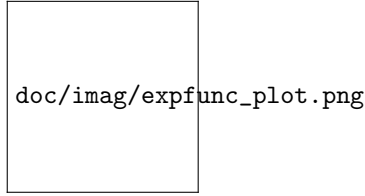


Figure 1: Plot of wavefunction in one dimension

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

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:

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

??

1.4 Monte Carlo

KILDE:<https://cs.dartmouth.edu/~wjarosz/publications/dissertation/appendixA.pdf>

Monte Carlo is numerical methods dependent of a random sampling from a function in order to approximate the integral.

In general the integral, F , of a function, $f(x)$, $x \in [a, b]$

$$F = \int_a^b f(x)dx$$

can be approximated by taking average samples of f with a uniform distribution of points in the interval. Having N uniform random variables $x_i \in [a, b]$ with probability distribution function, PDF $\frac{1}{b-a}$ the Monte-Carlo approximation of F is

$$\langle F^N \rangle = (b-a) \frac{1}{N-1} \sum_{i=0}^N f(x_i)$$

$$x_i$$

is generated: