

NUMERICAL INTEGRATION
OF THE HAMILTONIAN MATRIX ELEMENT
FOR THE 1S AND 2S ATOMIC ORBITAL

LENA GASSER

MICHAEL GOBALD

Mat.Nr. 01513492

01530628

Sommersemester 2018

Inhaltsverzeichnis

1 Roothan Equations	3
2 1s Atomic Orbital	4
3 2s Atomic Orbital	6
4 Monte Carlo Method	6
5 Matlab Program	7

Motivation

For our student project we wanted to compare the calculations of the molecular orbital Hamiltonians, energies and overlap matrices of the 1s and 2s Atomic orbitals, as Prof. Hadley provides them in the online course of the lecture. For this web-applications he used the Monte Carlo Method to do the Integrations, this is, as the name implies, an approximation that is based on random numbers. This method is suitable in the context of a web application, because it does not require a lot of computational resources and is therefore more time efficient than exact methods. And so, we wanted to do the calculations in a context, where time is not crucial, and we could emphasize on accuracy. Therefore, we created some MATLAB scripts that do these calculations by using a numerical integration method and compare the results to those generated by the Monte Carlo method.

For the following sections the page [2] is taken as reference.

1 Roothan Equations

In order to solve the molecular orbital Hamiltonian, a method called Linear Combination of Atomic Orbitals (LCAO) is often used. It is assumed that the wave function can be described in terms of hydrogen atomic orbitals, which are centred around the nuclei.

$$\psi_{\text{mo}}(\vec{r}) = \sum_a \sum_{\text{ao}} c_{\text{ao},a} \phi_{\text{ao}}^{Z_a}(\vec{r} - \vec{r}_a) \quad (1)$$

In this equation **ao** labels the atomic orbitals ($1 = 1s, 2 = 2s, 3 = 2p_x, \dots$). The number of calculated molecular orbitals is equal to the number of unknown coefficients **N**. The more atomic orbitals are included the higher the accuracy of the result. But the difficulty of the numerical calculation also increases with the number of atomic orbitals used. Since there is no strict rule on how many **aos** should be included, it is a reasonable choice to take all of the occupied atomic orbitals of the isolated atoms that are part of the molecule. For instance, to calculate the atomic orbitals of water one might use the 1s, 2s and 2p orbitals of oxygen and the 1s orbitals of the two hydrogen atoms. In this case **N** would be 7, and thus 7 terms in the wavefunction of the molecular orbital. Using the relabelling of atomic orbitals as mentioned above the trial wave function can be written as:

$$\psi_{\text{mo}} = \sum_{p=1}^N c_p \phi_p. \quad (2)$$

So the time independent Schrödinger equation is

$$H_{\text{mo}}\psi_{\text{mo}} = E\psi_{\text{mo}}. \quad (3)$$

In order to solve it, one multiplies this equation from the left by each atomic orbital and integrates over all space. This results in a set of \mathbf{N} algebraic equations which are called Roothaan equations.

$$\begin{aligned}\langle \phi_1 | H_{\text{mo}} | \psi_{\text{mo}} \rangle &= E \langle \phi_1 | \psi_{\text{mo}} \rangle \\ \langle \phi_2 | H_{\text{mo}} | \psi_{\text{mo}} \rangle &= E \langle \phi_2 | \psi_{\text{mo}} \rangle \\ &\vdots \\ \langle \phi_N | H_{\text{mo}} | \psi_{\text{mo}} \rangle &= E \langle \phi_N | \psi_{\text{mo}} \rangle\end{aligned}\tag{4}$$

By substituting in the form of ψ_{mo} , the Roothaan equation can be written in matrix form.

$$\begin{bmatrix} H_{11} & H_{12} & \cdots & H_{1N} \\ H_{21} & H_{22} & \cdots & H_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ H_{N1} & H_{N2} & \cdots & H_{NN} \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ \vdots \\ c_N \end{bmatrix} = E \begin{bmatrix} S_{11} & S_{12} & \cdots & S_{1N} \\ S_{21} & S_{22} & \cdots & S_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ S_{N1} & S_{N2} & \cdots & S_{NN} \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ \vdots \\ c_N \end{bmatrix}\tag{5}$$

And out of there we get the matrix elements which we wanted to calculate in this student project.

$$H_{pq} = \langle \phi_p | H_{\text{mo}} | \phi_q \rangle\tag{6}$$

$$S_{pq} = \langle \phi_p | \phi_q \rangle\tag{7}$$

2 1s Atomic Orbital

The wave function of the 1s Atomic Orbital is an Eigenstate of the Hamiltonian and can be described like this

$$\phi_{1s}^Z = \sqrt{\frac{Z^3}{\pi a_0^3}} \exp\left(-\frac{Zr}{a_0}\right).\tag{8}$$

with Z as the charge of the nucleus and a_0 as the Bohr radius. The variable of this function is r , so the cartesian coordinates have to be converted to spherical coordinates to use this wave function.

By putting this atomic orbital in the Schrödinger equation, the Energy E_1 can be determined.

$$E_1 = -\frac{\hbar^2}{2m} \frac{\Delta\phi_{1s}(\vec{r})}{\phi_{1s}(\vec{r})} - \frac{Ze^2}{4\pi\epsilon_0|\vec{r}|} \quad (9)$$

The used variables \hbar , which is the reduced Planck constant, the permittivity ϵ_0 , the electric charge e and the electron mass m are constants.

The first step of solving the Roothan equations is to calculate the integral for the S_{12} element.

$$S_{12} = \langle \phi_{1s}(\vec{r} - \vec{r}_1) | \phi_{1s}(\vec{r} - \vec{r}_2) \rangle. \quad (10)$$

The second part is to calculate the Hamiltonian matrix elements. The general form is given in (11).

$$H_{ij} = \langle \phi_{1s}^Z(\vec{r} - \vec{r}_i) | H | \phi_{1s}^Z(\vec{r} - \vec{r}_j) \rangle \quad (11)$$

The Hamiltonian for the 1s Atomic Orbital H can be described by

$$H = -\frac{\hbar^2}{2m} \nabla^2 - \frac{Ze^2}{4\pi\epsilon_0|\vec{r} - \vec{r}_1|} - \frac{Ze^2}{4\pi\epsilon_0|\vec{r} - \vec{r}_2|}. \quad (12)$$

By doing some approximations the diagonal Hamiltonian matrix element can be determined using the following equation:

$$\begin{aligned} H_{11} = E_1 - \frac{Z^4 e^2 \delta^2}{2\pi\epsilon_0 a_0^3} \exp\left(\frac{-2Z|\vec{r}_1 - \vec{r}_2|}{a_0}\right) \\ - \int H(|\vec{r} - \vec{r}_2| - \delta) \phi_{1s}^Z(\vec{r} - \vec{r}_1) \frac{Ze^2}{4\pi\epsilon_0|\vec{r} - \vec{r}_2|} \phi_{1s}^Z(\vec{r} - \vec{r}_1) d^3r \end{aligned} \quad (13)$$

The function $H(|\vec{r} - \vec{r}_2| - \delta)$ is called Heavyside step function and returns the value 0 if $|\vec{r} - \vec{r}_2| < \delta$, otherwise it is going to return 1.

The offdiagonal element H_{12} can be described similarly.

$$\begin{aligned} H_{12} = E_1 S_{12} - \frac{Z^4 e^2 \delta^2}{2\pi a_0^3 \epsilon_0} \exp(-Z|\vec{r}_1 - \vec{r}_2|/a_0) \\ - \int H(|\vec{r} - \vec{r}_1| - \delta) \phi_{1s}^Z(\vec{r} - \vec{r}_1) \frac{Ze^2}{4\pi\epsilon_0|\vec{r} - \vec{r}_1|} \phi_{1s}^Z(\vec{r} - \vec{r}_2) d^3r \end{aligned} \quad (14)$$

These integrals can be solved numerically.

3 2s Atomic Orbital

The 2s Atomic Orbital wave function looks like this

$$\phi_{2s}^Z = \frac{1}{4} \sqrt{\frac{Z^3}{2\pi a_0^3}} \left(2 - \frac{Zr}{a_0} \right) \exp\left(-\frac{Zr}{2a_0}\right). \quad (15)$$

To calculate the Energie E_1 almost the same equation as (9) can be used, just the 1s wave function has to be replaced by the 2s wave function.

$$E_1 = -\frac{\hbar^2}{2m} \frac{\Delta \phi_{2s}(\vec{r})}{\phi_{2s}(\vec{r})} - \frac{Ze^2}{4\pi\epsilon_0|\vec{r}|} \quad (16)$$

The integral for calculating the S_{12} matrix element can be calculated in a similar way than before, by using the right wavefunction.

$$S_{12} = \langle \phi_{2s}(\vec{r} - \vec{r}_1) | \phi_{2s}(\vec{r} - \vec{r}_2) \rangle \quad (17)$$

The elements of the Hamiltonian matrix by doing some approximations can be described using following equations.

$$H_{11} = E_2 - \frac{Z^4 e^2 \delta^2}{256\pi\epsilon_0 a_0^3} \left(2 - \frac{Z|\vec{r}_2 - \vec{r}_1|}{a_0} \right)^2 \exp\left(-\frac{Z|\vec{r}_2 - \vec{r}_1|}{a_0}\right) - \int H(|\vec{r} - \vec{r}_2| - \delta) \phi_{2s}^Z(\vec{r} - \vec{r}_1) \frac{Ze^2}{4\pi\epsilon_0|\vec{r} - \vec{r}_2|} \phi_{2s}^Z(\vec{r} - \vec{r}_1) d^3r \quad (18)$$

$$H_{12} = E_1 S_{12} - \frac{Z^4 e^2}{\pi\epsilon_0 a_0^2} \left(a_0 - \exp\left(\frac{\delta Z}{a_0}\right) \right) (a_0 + \delta Z) \exp\left(-\frac{Z|\vec{r}_2 - \vec{r}_1|}{a_0}\right) - \int H(|\vec{r} - \vec{r}_1| - \delta) \phi_{2s}^Z(\vec{r} - \vec{r}_1) \frac{Ze^2}{4\pi\epsilon_0|\vec{r} - \vec{r}_1|} \phi_{2s}^Z(\vec{r} - \vec{r}_2) d^3r \quad (19)$$

As written in the section above these integrals can be solved numerically, but there are also some approximation methodes, like the Monte Carlo Method, to solve such integrals.

4 Monte Carlo Method

The Monte Carlo Method can be used to approximate complicated integrals, like those in the equations for the Hamiltonian matrix elements. Assume the integral of a function f should be calculated:

$$F = \int f(\mathbf{x})d\mathbf{x}, \quad (20)$$

with the Volume

$$V = \int d\mathbf{x}. \quad (21)$$

Then the integral can be approximated just by evaluating the function for N sample points, taking the average of these values and multiplying with the Volume V .

$$\tilde{F} = V \frac{1}{N} \sum_{n=1}^N f(\mathbf{x}_n) \quad (22)$$

For a large number N this approximation gets very close to the correct value (see also [1]).

$$\lim_{n \rightarrow \infty} \tilde{F} = F \quad (23)$$

5 Matlab Program

The project consists of two main scripts. One for the 1s and one for the 2s atomic orbital. Each script does essentially three things: first calculating the energies E1 and E2, second calculating the elements of the overlap matrix S11 and S12, and finally calculating the H11 and H12 matrix elements. The formulas for all these calculations were taken from Prof. Hadleys online course. We also needed some functions. Two for calculating the atomic orbitals 1s and 2s, two more to calculate the result of the Laplacian operator acting on those and one to evaluate the Heavysidestep function.

The energies are calculated by the Monte Carlo Method, which gives several different approximate values for the energies, so we took the average over those values to get a proper result.

S11 and S12 are then calculated by numerical integration over a defined region around the position of the nucleus. With those results we were then able to calculate the H11 and H12 matrix elements for the 1s and the 2s atomic orbitals. We calculated them by solving the numerical integral and by using the Monte Carlo integration method. The Monte Carlo calculation can be done arbitrarily often. But we found that doing this calculation for one million points each takes about 1 sec. So this starts getting time consuming pretty fast. We chose to do the Monte Carlo method 100 times. But all these parameters can be altered in the program.

The value that was obtained by solving the integral numerically is plotted (black line) with the different values that were obtained by doing the Monte Carlo method several times (red x). We also calculated the average over the Monte Carlo values and plotted

this value too (blue dashed line), to give an idea about the overall tendency of the Monte Carlo methods results. Thus it is quite easy to show the difference between the results of the Monte Carlo method and the numerical integration.

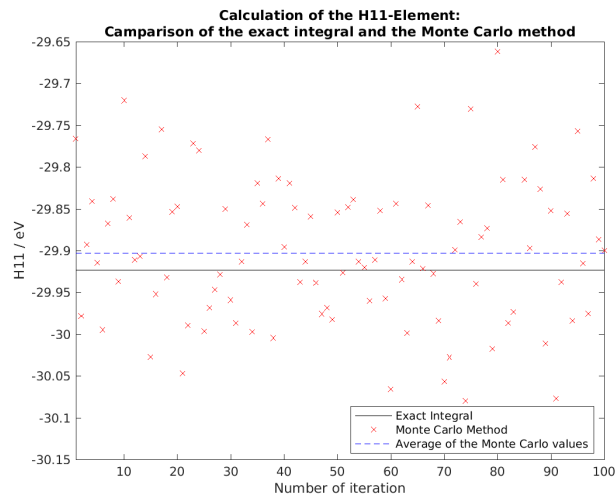


Abbildung 1: Monte Carlo Method and exact solution of the 1s atomic orbital H_{11} element

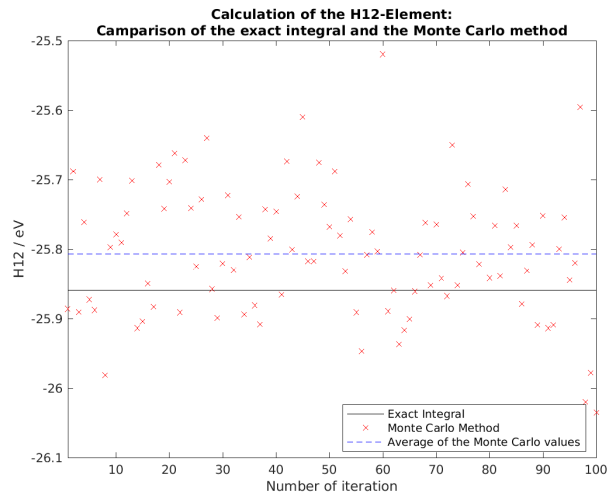


Abbildung 2: Monte Carlo Method and exact solution of the 1s atomic orbital H_{12} element

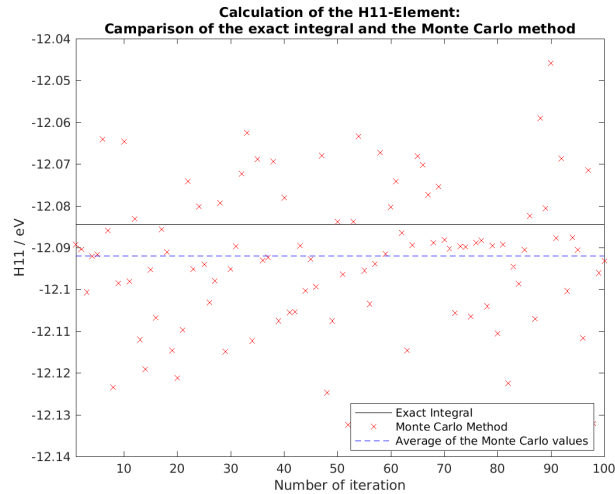


Abbildung 3: Monte Carlo Method and exact solution of the $2s$ atomic orbital H_{11} element

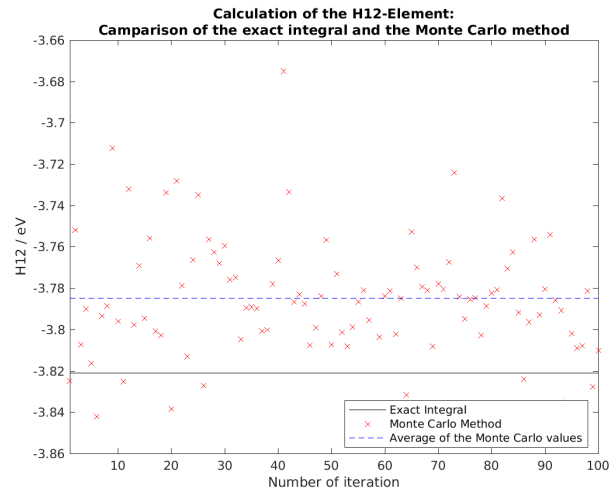


Abbildung 4: Monte Carlo Method and exact solution of the $2s$ atomic orbital H_{12} element

Literatur

- [1] Dave Edwards. Monte carlo integration. <http://www.cs.utah.edu/~edwards/research/mcIntegration.pdf>.
- [2] Peter Hadley. Molecular and solid state physics. <http://lampx.tugraz.at/~hadley/ss1/skriptum/outline.php>.