Technische Universität Graz

Institut für Festkörperphysik

Student project

Variational Wavefunction for the Helium Atom

Molecular and Solid State Physics 513.001

submitted on: 30. November 2009

by: Markus Krammer

Contents

1 Problem

The Hamitonian for the helium atom is

$$\hat{H} = -\frac{\hbar^2}{2m}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{2e^2}{4\pi\epsilon_0 r_1} - \frac{2e^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_{12}} \tag{1}$$

where r_{12} is the distance between the two electrons.
There is no analytical solution for the Schrödinger equation for this problem. So in a first step we neglect the electron electron interaction (term 5 in equation 1) to get an idea of how the real wavefunction could look like. Solving the Schrödinger equation for this simplified problem leads to the following wavefunction for the ground state:

$$\psi\left(r_1, r_2\right) = \frac{1}{a_0^3}\exp\left(-2\frac{r_1 + r_2}{a_0}\right) \tag{2}$$

This approximation is, of course, not very good. But it gives us an idea of how a better approximation could look like. So we try a variational wavefunction:

$$\psi\left(r_1, r_2, \alpha\right) = \frac{1}{a_0^3}\exp\left(-\alpha\frac{r_1 + r_2}{a_0}\right) \tag{3}$$

Now, as we have made a decision of how our approximate wavefunction for the ground state should look like, we can optimize it.

2 Optimization of a given wavefunction

To optimize a wavefunction, we have to calculate the energy

$$E\left(\alpha\right) = \frac{\langle\psi|\hat{H}|\psi\rangle}{\langle\psi|\psi\rangle} \tag{4}$$

and find the lowest energy depending on our parameter. If we would have more than one Parameter (e.g. coefficients of a polynomial that we multiply with our wavefunction) we would have to find the global minimum of our energy. But since we have just one parameter, finding the minimum energy is pretty easy.

$$\frac{dE\left(\alpha\right)}{d\alpha} = 0 \tag{5}$$

Equation 5 gives us the optimized parameter α (Energy must be the global minimum for the best α, so we have to check whether this energy is the global minimum or not).

3 Calculating the energy $E\left(\alpha\right)$

3.1 $\langle x|\hat{H}|\psi\rangle$

The Laplace operator in spherical coordinates looks like this:

$$\nabla_i^2 = \frac{1}{r_i^2}\frac{\partial}{\partial r_i}r_i^2\frac{\partial}{\partial r_i} + \frac{1}{r_i^2\sin\theta_i}\frac{\partial}{\partial\theta_i}\left(\sin\theta_i\frac{\partial}{\partial\theta_i}\right) + \frac{1}{r_i^2\sin^2\theta_i}\frac{\partial^2}{\partial\varphi_i^2} \tag{6}$$

Now we let the Laplace operator sink on the wavefunction:

$$\nabla_i^2\psi = \frac{1}{r_i^2}\frac{\partial}{\partial r_i}r_i^2\frac{\partial}{\partial r_i}\frac{1}{a_0^3}\exp\left(-\alpha\frac{r_1 + r_2}{a_0}\right)$$

$$\nabla_i^2\psi = -\frac{\alpha}{a_0^4}\frac{1}{r_i^2}\frac{\partial}{\partial r_i}r_i^2\exp\left(-\alpha\frac{r_1 + r_2}{a_0}\right)$$

$$\nabla_i^2\psi = -\frac{\alpha}{a_0^4}\frac{1}{r_i^2}\left(2r_i\exp\left(-\alpha\frac{r_1 + r_2}{a_0}\right) - \frac{\alpha}{a_0}r_i^2\exp\left(-\alpha\frac{r_1 + r_2}{a_0}\right)\right)$$

$$\nabla_i^2\psi = \frac{\alpha}{a_0^4}\left(\frac{\alpha}{a_0} - \frac{2}{r_i}\right)\exp\left(-\alpha\frac{r_1+r_2}{a_0}\right) \tag{7}$$

Putting this into $\langle x|\hat{H}|\psi\rangle$ returns:

$$\langle x|\hat{H}|\psi\rangle = \left(\sum_{i=1}^{2}\left(-\frac{\hbar^2}{2m}\frac{\alpha}{a_0}\left(\frac{\alpha}{a_0} - \frac{2}{r_i}\right) - \frac{2e^2}{4\pi\epsilon_0 r_i}\right) + \frac{e^2}{4\pi\epsilon_0 r_{12}}\right)\frac{1}{a_0^3}\exp\left(-\alpha\frac{r_1+r_2}{a_0}\right)$$

with

$$\frac{\hbar^2}{ma_0} = \frac{e^2}{4\pi\epsilon_0} \tag{8}$$

this leads to

$$\langle x|\hat{H}|\psi\rangle = \frac{\hbar^2}{ma_0^4}\left(\sum_{i=1}^{2}\left(-\frac{\alpha^2}{2a_0} - \frac{2-\alpha}{r_i}\right) + \frac{1}{r_{12}}\right)\exp\left(-\alpha\frac{r_1+r_2}{a_0}\right) \tag{9}$$

3.2 $\langle\psi|\hat{H}|\psi\rangle$

With equation 9 it is not difficult to write down $\langle\psi|\hat{H}|\psi\rangle$:

$$\langle\psi|\hat{H}|\psi\rangle = \int\cdots\int_{\mathbb{R}^6} dx_1dy_1dz_1dx_2dy_2dz_2\frac{\hbar^2}{ma_0}\left(\sum_{i=1}^{2}\left(-\frac{\alpha^2}{2a_0} - \frac{2-\alpha}{r_i}\right) + \frac{1}{r_{12}}\right)\frac{1}{a_0^6}\exp\left(-2\alpha\frac{r_1+r_2}{a_0}\right) \tag{10}$$

The first four terms in this integral are no problem to solve. Only the last term with the r_{12} is a bit harder to evaluate. So we split it up into two parts:

$$\langle\psi|\hat{H}_1|\psi\rangle = \int\cdots\int_{\mathbb{R}^6} dx_1dy_1dz_1dx_2dy_2dz_2\frac{\hbar^2}{ma_0^7}\left(\sum_{i=1}^{2}\left(-\frac{\alpha^2}{2a_0} - \frac{2-\alpha}{r_i}\right)\right)\exp\left(-2\alpha\frac{r_1+r_2}{a_0}\right) \tag{11}$$

and

$$\langle\psi|\hat{H}_2|\psi\rangle = \int\cdots\int_{\mathbb{R}^6} dx_1dy_1dz_1dx_2dy_2dz_2\frac{\hbar^2}{ma_0^7}\frac{1}{r_{12}}\exp\left(-2\alpha\frac{r_1+r_2}{a_0}\right) \tag{12}$$

3.3 $\langle\psi|\hat{H}_1|\psi\rangle$

The integrals

$$\int\cdots\int_{\mathbb{R}^6} dx_1dy_1dz_1dx_2dy_2dz_2\frac{\hbar^2}{ma_0^7}\left(-\frac{\alpha^2}{2a_0} - \frac{2-\alpha}{r_1}\right)\exp\left(-2\alpha\frac{r_1+r_2}{a_0}\right)$$

and

$$\int\cdots\int_{\mathbb{R}^6} dx_1dy_1dz_1dx_2dy_2dz_2\frac{\hbar^2}{ma_0^7}\left(-\frac{\alpha^2}{2a_0} - \frac{2-\alpha}{r_2}\right)\exp\left(-2\alpha\frac{r_1+r_2}{a_0}\right)$$

are exactly the same, so we can write

$$\langle\psi|\hat{H}_1|\psi\rangle = \int\cdots\int_{\mathbb{R}^6} dx_1dy_1dz_1dx_2dy_2dz_2\frac{\hbar^2}{ma_0^7}\left(-\frac{\alpha^2}{a_0} - 2\frac{2-\alpha}{r_1}\right)\exp\left(-2\alpha\frac{r_1+r_2}{a_0}\right) \tag{13}$$

Now we tansform it into spherical coordinates and with the Jacobi determinant of the transformation we get:

$$dx_1dy_1dz_1dx_2dy_2dz_2 = r_1^2\sin\theta_1 r_2^2\sin\theta_2 dr_1d\varphi_1d\theta_1dr_2d\varphi_2d\theta_2 \tag{14}$$

Our integral does not depend on φ_i and θ_i, so we can integrate these 4 variables seperately:

$$\int_0^{2\pi}d\varphi_1\int_0^{\pi}d\theta_1\int_0^{2\pi}d\varphi_2\int_0^{\pi}d\theta_2\sin\theta_1\sin\theta_2 = (4\pi)^2 \tag{15}$$

$$\langle\psi|\hat{H}_1|\psi\rangle = \frac{\hbar^2\left(4\pi\right)^2}{ma_0^7}\int_0^\infty dr_1\left(-\frac{\alpha^2 r_1^2}{a_0} - 2\left(2-\alpha\right)r_1\right)\exp\left(-2\alpha\frac{r_1}{a_0}\right)\int_0^\infty dr_2 r_2^2\exp\left(-2\alpha\frac{r_2}{a_0}\right)$$

This integrals are all of the following form:

$$\int_0^\infty dx\cdot x^2\exp\left(-\lambda x\right) = \frac{d^2}{d\lambda^2}\int_0^\infty dx\cdot\exp\left(-\lambda x\right) = \frac{d^2}{d\lambda^2}\left(\frac{1}{\lambda}\right) = \frac{2}{\lambda^3} \quad (16)$$

$$\int_0^\infty dx\cdot x\exp\left(-\lambda x\right) = -\frac{d}{d\lambda}\int_0^\infty dx\cdot\exp\left(-\lambda x\right) = -\frac{d}{d\lambda}\left(\frac{1}{\lambda}\right) = \frac{1}{\lambda^2} \quad (17)$$

So the result is:

$$\langle\psi|\hat{H}_1|\psi\rangle = \frac{\hbar^2\left(4\pi\right)^2}{ma_0^7}\left(-\frac{2\alpha^2}{\left(\frac{2\alpha}{a_0}\right)^3 a_0} - 2\left(2-\alpha\right)\frac{1}{\left(\frac{2\alpha}{a_0}\right)^2}\right)\frac{2}{\left(\frac{2\alpha}{a_0}\right)^3}$$

$$\langle\psi|\hat{H}_1|\psi\rangle = -\frac{\hbar^2}{ma_0^2}\frac{\pi^2\left(4-\alpha\right)}{\alpha^5} \quad (18)$$

3.4 $\langle\psi|\psi\rangle$

For calculating the energy (see equation 4) we need to know $\langle\psi|\psi\rangle$.

$$\langle\psi|\psi\rangle = \int\cdots\int_{\mathbb{R}^6} dx_1 dy_1 dz_1 dx_2 dy_2 dz_2 \psi^*\psi \quad (19)$$

$$\langle\psi|\psi\rangle = \int\cdots\int_{\mathbb{R}^6} dx_1 dy_1 dz_1 dx_2 dy_2 dz_2 \frac{1}{a_0^6}\exp\left(-2\alpha\frac{r_1+r_2}{a_0}\right)$$

There is again no φ_i and θ_i dependence in this term, so with equation 14 and 15 we get

$$\langle\psi|\psi\rangle = \frac{\left(4\pi\right)^2}{a_0^6}\int_0^\infty dr_1 r_1^2\exp\left(-2\alpha\frac{r_1}{a_0}\right)\int_0^\infty dr_2 r_2^2\exp\left(-2\alpha\frac{r_2}{a_0}\right)$$

and with equation 16

$$\langle\psi|\psi\rangle = \frac{\left(4\pi\right)^2}{a_0^6}\left(\frac{2}{\left(\frac{2\alpha}{a_0}\right)^3}\right)^2$$

$$\langle\psi|\psi\rangle = \frac{\pi^2}{\alpha^6} \quad (20)$$

3.5 $\langle\psi|\hat{H}_2|\psi\rangle$

As we see in equation 12 this integral is not that easy. The term $\frac{1}{r_{12}}$ makes it a bit more difficult. So we need to transform the integral clever.

3.5.1 Transforming to spherical coordinates

In a first step we transform the integral into spherical coordinates. But not like we did it in equation 14, because this would not make the integral easier. So we choose a different transformation. We transform x_1, y_1 and z_1 like before:

$$x_1 = r_1\cos\varphi_1\sin\theta_1 \quad (21)$$

$$y_1 = r_1\sin\varphi_1\sin\theta_1 \quad (22)$$

$$z_1 = r_1\cos\theta_1 \quad (23)$$

For the other coordinates we choose a different transformation. We use the r_1 direction as $\tilde{z}$ axis and the $\tilde{x}$ axis is in the $z\tilde{z}$ plane. So the $\tilde{y}$ axis is in the xy plane (see figure 1). In this coordinates we now transform $\tilde{x}_2$, $\tilde{y}_2$

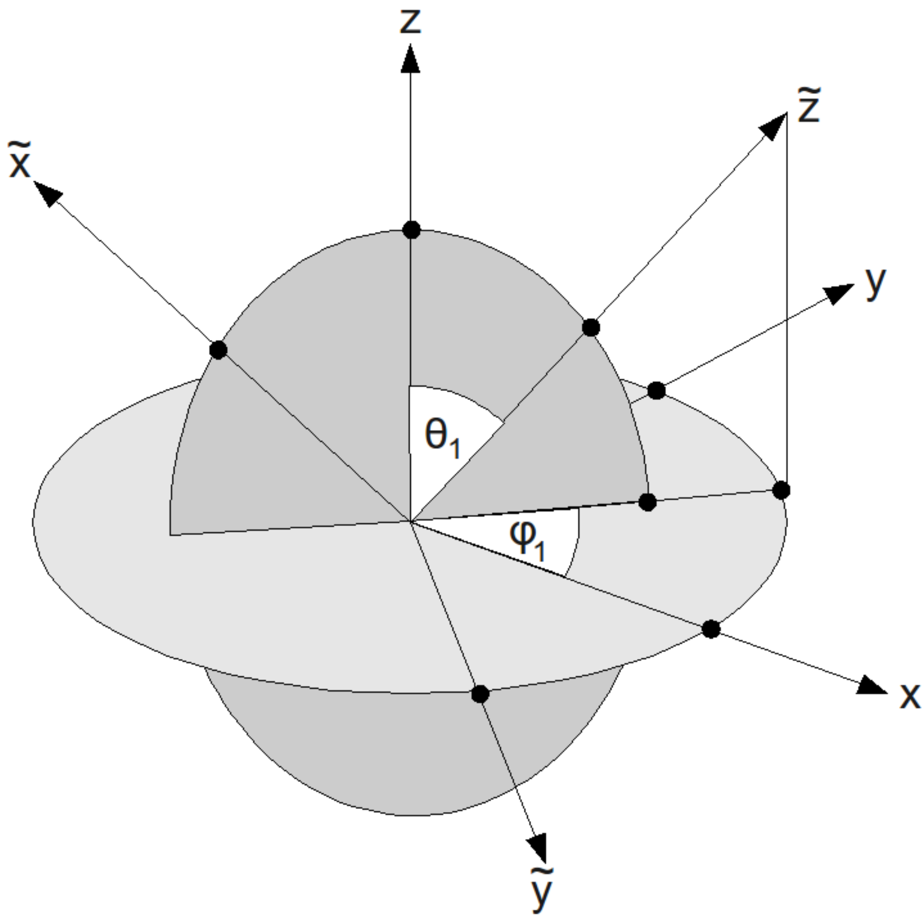

Figure 1: Transformation, the $\tilde{z}$ axis has the same direction as $\vec{r_1}$

and $\tilde{z}_2$ as we are used to.

$$\tilde{x}_2 = r_2 \cos\varphi_{12} \sin\theta_{12} \tag{24}$$
$$\tilde{y}_2 = r_2 \sin\varphi_{12} \sin\theta_{12} \tag{25}$$
$$\tilde{z}_2 = r_2 \cos\theta_{12} \tag{26}$$

So now we need to know the relation between x_2, y_2, z_2 and $\tilde{x}_2$, $\tilde{y}_2$, $\tilde{z}_2$. For this we write down the basis vectors:

$$\hat{e}_{\tilde{z}} = \frac{\vec{r_1}}{r_1}$$

$$\hat{e}_{\tilde{z}} = \begin{pmatrix} \cos\varphi_1 \sin\theta_1 \\ \sin\varphi_1 \sin\theta_1 \\ \cos\theta_1 \end{pmatrix} \tag{27}$$

$$\hat{e}_{\tilde{y}} = \frac{\hat{e}_{\tilde{z}} \times \hat{e}_z}{|\hat{e}_{\tilde{z}} \times \hat{e}_z|}$$

$$\hat{e}_{\tilde{y}} = \frac{1}{|\hat{e}_{\tilde{z}} \times \hat{e}_z|} \begin{pmatrix} \cos\varphi_1 \sin\theta_1 \\ \sin\varphi_1 \sin\theta_1 \\ \cos\theta_1 \end{pmatrix} \times \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$$

$$\hat{e}_{\tilde{y}} = \frac{1}{|\hat{e}_{\tilde{z}} \times \hat{e}_z|} \begin{pmatrix} \sin\varphi_1 \sin\theta_1 \\ -\cos\varphi_1 \sin\theta_1 \\ 0 \end{pmatrix}$$

$$|\hat{e}_{\tilde{z}} \times \hat{e}_z| = \sqrt{\begin{pmatrix} \sin\varphi_1 \sin\theta_1 \\ -\cos\varphi_1 \sin\theta_1 \\ 0 \end{pmatrix} \cdot \begin{pmatrix} \sin\varphi_1 \sin\theta_1 \\ -\cos\varphi_1 \sin\theta_1 \\ 0 \end{pmatrix}}$$

$$|\hat{e}_{\tilde{z}} \times \hat{e}_z| = \sqrt{\sin^2\varphi_1 \sin^2\theta_1 + \cos^2\varphi_1 \sin^2\theta_1}$$

$$|\hat{e}_{\tilde{z}} \times \hat{e}_z| = \sin\theta_1$$

$$\hat{e}_{\tilde{y}} = \begin{pmatrix} \sin\varphi_1 \\ -\cos\varphi_1 \\ 0 \end{pmatrix} \tag{28}$$

$$\hat{e}_{\tilde{x}} = \hat{e}_{\tilde{y}} \times \hat{e}_{\tilde{z}}$$

$$\hat{e}_{\tilde{x}} = \begin{pmatrix} \sin\varphi_1 \\ -\cos\varphi_1 \\ 0 \end{pmatrix} \times \begin{pmatrix} \cos\varphi_1 \sin\theta_1 \\ \sin\varphi_1 \sin\theta_1 \\ \cos\theta_1 \end{pmatrix}$$

$$\hat{e}_{\tilde{x}} = \begin{pmatrix} -\cos\varphi_1 \cos\theta_1 \\ -\sin\varphi_1 \cos\theta_1 \\ \sin\theta_1 \end{pmatrix} \tag{29}$$

With

$$x \cdot \hat{e}_x + y \cdot \hat{e}_y + z \cdot \hat{e}_z = \tilde{x} \cdot \hat{e}_{\tilde{x}} + \tilde{y} \cdot \hat{e}_{\tilde{y}} + \tilde{z} \cdot \hat{e}_{\tilde{z}} \tag{30}$$

and the equations 27, 28 and 29 we get

$$\begin{pmatrix} x_2 \\ y_2 \\ z_2 \end{pmatrix} = \begin{pmatrix} -\cos\varphi_1 \cos\theta_1 & \sin\varphi_1 & \cos\varphi_1 \sin\theta_1 \\ -\sin\varphi_1 \cos\theta_1 & -\cos\varphi_1 & \sin\varphi_1 \sin\theta_1 \\ \sin\theta_1 & 0 & \cos\theta_1 \end{pmatrix} \begin{pmatrix} \tilde{x}_2 \\ \tilde{y}_2 \\ \tilde{z}_2 \end{pmatrix} \tag{31}$$

Now our transformation is complete. Equations 21 to 26 and 31 are all we wanted to know.

3.5.2 Determinant of the Jacobi matrix

For the integral tranformation we need the Jacobi determinant. The Jacobi matrix has the form

$$J = \begin{pmatrix} \cos\varphi_1 \sin\theta_1 & -r_1 \sin\varphi_1 \sin\theta_1 & r_1 \cos\varphi_1 \cos\theta_1 & \tilde{M}_1 \\ \sin\varphi_1 \sin\theta_1 & r_1 \cos\varphi_1 \sin\theta_1 & r_1 \sin\varphi_1 \cos\theta_1 & \tilde{M}_2 \\ \cos\theta_1 & 0 & -r_1 \sin\theta_1 & \tilde{M}_3 \\ 0 & 0 & 0 & \\ 0 & 0 & 0 & M \\ 0 & 0 & 0 & \end{pmatrix}$$

where $\tilde{M_1}$, $\tilde{M_2}$, $\tilde{M_3}$ and M are the more complicate parts of the Jacobi matrix with the transformation to r_2, φ_{12} and θ_{12}.

$$|J| = \cos\varphi_1 \sin\theta_1 \begin{vmatrix} r_1\cos\varphi_1\sin\theta_1 & r_1\sin\varphi_1\cos\theta_1 & \tilde{M_2} \\ 0 & -r_1\sin\theta_1 & \tilde{M_3} \\ 0 & 0 & \\ 0 & 0 & M \\ 0 & 0 & \end{vmatrix}$$

$$- \sin\varphi_1 \sin\theta_1 \begin{vmatrix} -r_1\sin\varphi_1\sin\theta_1 & r_1\cos\varphi_1\cos\theta_1 & \tilde{M_1} \\ 0 & -r_1\sin\theta_1 & \tilde{M_3} \\ 0 & 0 & \\ 0 & 0 & M \\ 0 & 0 & \end{vmatrix}$$

$$+ \cos\theta_1 \begin{vmatrix} -r_1\sin\varphi_1\sin\theta_1 & r_1\cos\varphi_1\cos\theta_1 & \tilde{M_1} \\ r_1\cos\varphi_1\sin\theta_1 & r_1\sin\varphi_1\cos\theta_1 & \tilde{M_2} \\ 0 & 0 & \\ 0 & 0 & M \\ 0 & 0 & \end{vmatrix}$$

$$|J| = r_1\cos^2\varphi_1\sin^2\theta_1 \begin{vmatrix} -r_1\sin\theta_1 & \tilde{M_3} \\ 0 & \\ 0 & M \\ 0 & \end{vmatrix}$$

$$r_1\sin^2\varphi_1\sin^2\theta_1 \begin{vmatrix} -r_1\sin\theta_1 & \tilde{M_3} \\ 0 & \\ 0 & M \\ 0 & \end{vmatrix}$$

$$-r_1\sin\varphi_1\sin\theta_1\cos\theta_1 \begin{vmatrix} r_1\sin\varphi_1\cos\theta_1 & \tilde{M_2} \\ 0 & \\ 0 & M \\ 0 & \end{vmatrix}$$

$$-r_1\cos\varphi_1\sin\theta_1\cos\theta_1 \begin{vmatrix} r_1\cos\varphi_1\cos\theta_1 & \tilde{M_1} \\ 0 & \\ 0 & M \\ 0 & \end{vmatrix}$$

$$|J| = -r_1^2\sin^3\theta_1\,|M| - r_1^2\sin^2\varphi_1\sin\theta_1\cos^2\theta_1\,|M| - r_1^2\cos^2\varphi_1\sin\theta_1\cos^2\theta_1\,|M|$$

For the integral transformation we need the absolute value of the determinant of the Jacobi matrix.

$$||J|| = r_1^2\sin\theta_1\,||M|| \tag{32}$$

So now we just need to calculate the absolute value of the determinant of M:

$$M = \begin{pmatrix} x_2 \\ y_2 \\ z_2 \end{pmatrix} \cdot \begin{pmatrix} \frac{\partial}{\partial r_2} & \frac{\partial}{\partial \varphi_{12}} & \frac{\partial}{\partial \theta_{12}} \end{pmatrix}$$

$$M = \begin{pmatrix} -\cos\varphi_1\cos\theta_1 & \sin\varphi_1 & \cos\varphi_1\sin\theta_1 \\ -\sin\varphi_1\cos\theta_1 & -\cos\varphi_1 & \sin\varphi_1\sin\theta_1 \\ \sin\theta_1 & 0 & \cos\theta_1 \end{pmatrix} \begin{pmatrix} \tilde{x}_2 \\ \tilde{y}_2 \\ \tilde{z}_2 \end{pmatrix} \cdot \begin{pmatrix} \frac{\partial}{\partial r_2} & \frac{\partial}{\partial \varphi_{12}} & \frac{\partial}{\partial \theta_{12}} \end{pmatrix}$$

As the transformation matrix has no dependence on r_2, φ_{12} and θ_{12} we can easily get the determinante:

$$|M| = \left| \begin{pmatrix} -\cos\varphi_1\cos\theta_1 & \sin\varphi_1 & \cos\varphi_1\sin\theta_1 \\ -\sin\varphi_1\cos\theta_1 & -\cos\varphi_1 & \sin\varphi_1\sin\theta_1 \\ \sin\theta_1 & 0 & \cos\theta_1 \end{pmatrix} \begin{pmatrix} \tilde{x}_2 \\ \tilde{y}_2 \\ \tilde{z}_2 \end{pmatrix} \cdot \begin{pmatrix} \frac{\partial}{\partial r_2} & \frac{\partial}{\partial \varphi_{12}} & \frac{\partial}{\partial \theta_{12}} \end{pmatrix} \right|$$

$$|M| = \left| \begin{array}{ccc} -\cos\varphi_1\cos\theta_1 & \sin\varphi_1 & \cos\varphi_1\sin\theta_1 \\ -\sin\varphi_1\cos\theta_1 & -\cos\varphi_1 & \sin\varphi_1\sin\theta_1 \\ \sin\theta_1 & 0 & \cos\theta_1 \end{array} \right| \left| \begin{pmatrix} \tilde{x}_2 \\ \tilde{y}_2 \\ \tilde{z}_2 \end{pmatrix} \cdot \begin{pmatrix} \frac{\partial}{\partial r_2} & \frac{\partial}{\partial \varphi_{12}} & \frac{\partial}{\partial \theta_{12}} \end{pmatrix} \right|$$

The determinante of the second part is the same as we were calculating many times bevor:

$$\left| \begin{pmatrix} \tilde{x}_2 \\ \tilde{y}_2 \\ \tilde{z}_2 \end{pmatrix} \cdot \begin{pmatrix} \frac{\partial}{\partial r_2} & \frac{\partial}{\partial \varphi_{12}} & \frac{\partial}{\partial \theta_{12}} \end{pmatrix} \right| = -r_2^2 \sin\theta_{12}$$

And the first part is also not really difficult:

$$\left| \begin{array}{ccc} -\cos\varphi_1\cos\theta_1 & \sin\varphi_1 & \cos\varphi_1\sin\theta_1 \\ -\sin\varphi_1\cos\theta_1 & -\cos\varphi_1 & \sin\varphi_1\sin\theta_1 \\ \sin\theta_1 & 0 & \cos\theta_1 \end{array} \right| = \cos^2\varphi_1\cos^2\theta_1 + \sin^2\varphi_1\sin^2\theta_1 + \cos^2\varphi_1\sin^2\theta_1 + \sin^2\varphi_1\cos^2\theta_1 = 1$$

So the absolute value of the determinante of the Jacobi matrix is:

$$||J|| = r_1^2 r_2^2 \sin\theta_1 \sin\theta_{12} \tag{33}$$

3.5.3 One more transformation

With the transformation done before the integral is still not easy to solve. So we need one more transformation. We transform θ_{12} to r_{12}:

$$r_{12}^2 = r_1^2 + r_2^2 - 2r_1 r_2 \cos\theta_{12}$$

The Jacobi matrix for this transformation is:

$$|J| = \left| \begin{array}{cccccc} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ \frac{r_{12}}{r_1 - r_2\cos\theta_{12}} & 0 & 0 & \frac{r_{12}}{r_2 - r_1\cos\theta_{12}} & 0 & \frac{r_{12}}{r_1 r_2 \sin\theta_{12}} \end{array} \right|$$

$$||J|| = \frac{r_{12}}{r_1 r_2 \sin\theta_{12}} \tag{34}$$

We need to take a look at the integration limits. In spherical coordinates they were the same as we are used to. But now we have to get the correct limits for r_{12}. The limits for θ_{12} were 0 and π, so r_{12} now needs to go from $|r_1 - r_2|$ to $r_1 + r_2$.

3.5.4 Solving the integral

With all these transformations (equations 33 and 34) the integral finally has a form that is easy to solve:

$$\begin{aligned} \langle\psi|\hat{H}_2|\psi\rangle &= \int_0^\infty dr_1 \int_0^\infty dr_2 \int_{|r_1-r_2|}^{r_1+r_2} dr_{12} \int_0^{2\pi} d\varphi_1 \int_0^{2\pi} d\varphi_{12} \int_0^\pi d\theta_1 r_1^2 r_2^2 \sin\theta_1 \sin\theta_{12} \frac{r_{12}}{r_1 r_2 \sin\theta_{12}} \\ & \frac{\hbar^2}{m a_0} \frac{1}{r_{12}} \frac{1}{a_0^6} \exp\left(-2\alpha \frac{r_1 + r_2}{a_0}\right) \\ &= \frac{\hbar^2}{m a_0^7} 2 (2\pi)^2 \int_0^\infty dr_1 \int_0^\infty dr_2 \int_{|r_1-r_2|}^{r_1+r_2} dr_{12} r_1 r_2 \exp\left(-2\alpha \frac{r_1 + r_2}{a_0}\right) \\ &= \frac{\hbar^2}{m a_0^7} 2 (2\pi)^2 \int_0^\infty dr_1 \left(\int_0^{r_1} dr_2 \int_{r_1-r_2}^{r_1+r_2} dr_{12} + \int_{r_1}^\infty dr_2 \int_{r_2-r_1}^{r_1+r_2} dr_{12} \right) r_1 r_2 \exp\left(-2\alpha \frac{r_1 + r_2}{a_0}\right) \\ &= \frac{\hbar^2}{m a_0^7} 2 (2\pi)^2 \int_0^\infty dr_1 \left(\int_0^{r_1} dr_2 2r_2 + \int_{r_1}^\infty dr_2 2r_1 \right) r_1 r_2 \exp\left(-2\alpha \frac{r_1 + r_2}{a_0}\right) \end{aligned}$$

$$\int_0^{r_1} dr_2 r_2^2 \exp(-\lambda r_2) = \frac{\partial^2}{\partial\lambda^2}\int_0^{r_1} dr_2 \exp(-\lambda r_2) = \frac{\partial^2}{\partial\lambda^2}\left(-\frac{\exp(-\lambda r_1)}{\lambda}+\frac{1}{\lambda}\right) = \frac{\partial}{\partial\lambda}\exp(-\lambda r_1)\left(\frac{r_1}{\lambda}+\frac{1}{\lambda^2}\right)+\frac{2}{\lambda^3}$$

$$= \exp(-\lambda r_1)\left(-r_1\left(\frac{r_1}{\lambda}+\frac{1}{\lambda^2}\right)-\frac{r_1}{\lambda^2}-\frac{2}{\lambda^3}\right)+\frac{2}{\lambda^3} = -\exp(-\lambda r_1)\frac{r_1^2\lambda^2+2r_1\lambda+2}{\lambda^3}+\frac{2}{\lambda^3}$$

$$\int_{r_1}^{\infty} dr_2 r_2 \exp(-\lambda r_2) = -\frac{\partial}{\partial\lambda}\int_{r_1}^{\infty} dr_2 \exp(-\lambda r_2) = -\frac{\partial}{\partial\lambda}\left(\frac{\exp(-\lambda r_1)}{\lambda}\right) = \exp(-\lambda r_1)\left(\frac{r_1}{\lambda}+\frac{1}{\lambda^2}\right)$$

$$\begin{aligned}
\langle\psi|\hat{H}_2|\psi\rangle &= \frac{\hbar^2}{ma_0^7}(4\pi)^2\int_0^\infty dr_1\left(-\exp\left(-\frac{2\alpha}{a_0}r_1\right)\frac{r_1^2\left(\frac{2\alpha}{a_0}\right)^2+2r_1\frac{2\alpha}{a_0}+2}{\left(\frac{2\alpha}{a_0}\right)^3}+\frac{2}{\left(\frac{2\alpha}{a_0}\right)^3}\right)r_1\exp\left(-2\alpha\frac{r_1}{a_0}\right)\\
&\quad+\frac{\hbar^2}{ma_0^7}(4\pi)^2\int_0^\infty dr_1\left(r_1\exp\left(-\frac{2\alpha}{a_0}r_1\right)\left(\frac{r_1}{\frac{2\alpha}{a_0}}+\frac{1}{\left(\frac{2\alpha}{a_0}\right)^2}\right)\right)r_1\exp\left(-2\alpha\frac{r_1}{a_0}\right)\\
&= \frac{\hbar^2}{ma_0^7}(4\pi)^2\int_0^\infty dr_1\left(-\frac{r_1\frac{2\alpha}{a_0}+2}{\left(\frac{2\alpha}{a_0}\right)^3}\exp\left(-\frac{4\alpha}{a_0}r_1\right)+\frac{2}{\left(\frac{2\alpha}{a_0}\right)^3}\exp\left(-2\alpha\frac{r_1}{a_0}\right)\right)r_1\\
&= \frac{\hbar^2}{ma_0^7}\left(\frac{a_0}{2\alpha}\right)^3(4\pi)^2\int_0^\infty dr_1\left(-\left(r_1^2\frac{2\alpha}{a_0}+2r_1\right)\exp\left(-\frac{4\alpha}{a_0}r_1\right)+2r_1\exp\left(-\frac{2\alpha}{a_0}r_1\right)\right)
\end{aligned}$$

With equations 16 and 17 this leads to:

$$\begin{aligned}
\langle\psi|\hat{H}_2|\psi\rangle &= \frac{\hbar^2}{ma_0^7}\left(\frac{a_0}{2\alpha}\right)^3(4\pi)^2\left(-\left(\frac{2}{\left(\frac{4\alpha}{a_0}\right)^3}\frac{2\alpha}{a_0}+2\frac{1}{\left(\frac{4\alpha}{a_0}\right)^2}\right)+2\frac{1}{\left(\frac{2\alpha}{a_0}\right)^2}\right)\\
&= \frac{\hbar^2}{ma_0^7}\left(\frac{a_0}{2\alpha}\right)^5(4\pi)^2\left(-\frac{2}{8}-\frac{2}{4}+2\right)
\end{aligned}$$

So finally we solved the integral:

$$\langle\psi|\hat{H}_2|\psi\rangle = \frac{\hbar^2}{ma_0^2}\frac{\pi^2}{\alpha^5}\frac{5}{8} \tag{35}$$

4 Optimizing the Energy

Now we calculated all terms to get the energy (see equation 4):

$$\begin{aligned}
E(\alpha) &= \frac{\langle\psi|\hat{H}|\psi\rangle}{\langle\psi|\psi\rangle}\\
&= \frac{\langle\psi|\hat{H}_1|\psi\rangle+\langle\psi|\hat{H}_2|\psi\rangle}{\langle\psi|\psi\rangle}
\end{aligned}$$

With equation 18, 20 and 35 we get the result:

$$E(\alpha) = \frac{-\frac{\hbar^2}{ma_0^2}\frac{\pi^2(4-\alpha)}{\alpha^5}+\frac{\hbar^2}{ma_0^2}\frac{\pi^2}{\alpha^5}\frac{5}{8}}{\frac{\pi^2}{\alpha^6}}$$

$$E(\alpha) = -\frac{\hbar^2}{ma_0^2}\left(\frac{27}{8}\alpha-\alpha^2\right) \tag{36}$$

As already explained in equation 5 the first derivative of the energy must be zero

$$\begin{aligned}
\frac{dE(\alpha)}{d\alpha} = \quad 0 &= \frac{d}{d\alpha}\left(-\frac{\hbar^2}{ma_0^2}\left(\frac{27}{8}\alpha - \alpha^2\right)\right) \\
0 &= -\frac{\hbar^2}{ma_0^2}\left(\frac{27}{8} - 2\alpha\right) \\
0 &= \frac{27}{8} - 2\alpha
\end{aligned}$$

So the optimized value for α is:

$$\alpha = \frac{27}{16} \tag{37}$$

As we can easily see from the energy $E(\alpha)$ this is the global minimum. The corresponding energy is (with equation 36):

$$\begin{aligned}
E_{opt} &= E\left(\frac{27}{16}\right) \\
&= -\frac{\hbar^2}{ma_0^2}\left(\frac{27}{8}\frac{27}{16} - \left(\frac{27}{16}\right)^2\right) \\
&= -\frac{\hbar^2}{ma_0^2}\left(\frac{729}{128} - \frac{729}{256}\right)
\end{aligned}$$

$$E_{opt} = -\frac{\hbar^2}{ma_0^2}\frac{729}{256} \tag{38}$$

$$\tag{39}$$

The hartree E_h is the atomic unit of energy (see also equation 8):

$$E_h = \frac{\hbar^2}{ma_0^2} = \frac{e^2}{4\pi\epsilon_0 a_0} \tag{40}$$

So in hartree the energy would be

$$E_{opt} = -\frac{729}{256} hartree \tag{41}$$

$$= -2.8477 hartree \tag{42}$$

Putting the values

$$\hbar = 1.054571628 \cdot 10^{-34} Js \tag{43}$$

$$m = 9.10938215 \cdot 10^{-31} kg \tag{44}$$

$$a_0 = 5.291772186 \cdot 10^{-11} m \tag{45}$$

$$e = -1.602176487 \cdot 10^{-19} C \tag{46}$$

into equation 39 results in:

$$E_{opt} = -1.24151 \cdot 10^{-17} J \tag{47}$$

$$= -77.4887 eV \tag{48}$$