Solving the Schrödinger equation inside a bounded domain: application to H2

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1. The hydrogen Atom

1.1 Theoretical aspects

1. The Schrödinger equation for an electron represented by a wave function φ and subject to an effective Coulomb potential generated by an effective charge +Ze placed at O. (We use the Born-Oppenheimer approximation -the mass of the nucleus is much bigger than that of the electron to eliminate the kinetic energy term relative to the nucleus)

$$\frac{-\hbar^2}{2m}\,\Delta_r\varphi - \frac{Z * e^2}{4\,\pi\epsilon * r}\varphi = \in \varphi$$

We choose: $r = a_0 x \; with \; a_0 = \frac{4\,\pi\epsilon\hbar^2}{m\,e^2}$, a_0 being the Bohr radius, we obtain the following equation:

$$\frac{-1}{2}\Delta_x\varphi - \frac{Z}{x}\varphi = \frac{\in}{E_h}\varphi$$

With $E_h = \frac{\hbar^2}{m*a_0}$;

Conclusion:

$$\frac{-1}{2}\Delta_x\varphi - \frac{Z}{x}\varphi = E\,\varphi$$

$$with\ the\ boundary\ condition:\ \varphi(x \to \infty) = 0$$

And $\langle\varphi|\varphi\rangle = 1$

2. The weak form applied to the exact solution:

$$\forall\ \emptyset \quad \int \frac{-1}{2}\emptyset^*\Delta_x\varphi - \emptyset^*\frac{Z}{x}\varphi\,dV = E\int \emptyset^*\varphi\,dV$$

$$\nabla(\emptyset\,\nabla\varphi) = \emptyset\Delta\varphi + \nabla\emptyset\,\nabla\varphi$$

$$\int_\Omega \frac{-1}{2}\nabla(\emptyset\,\nabla\varphi) + \frac{1}{2}\nabla\emptyset\,\nabla\varphi - \emptyset\frac{Z}{x}\varphi\,dV = E\int_\Omega \emptyset\,\varphi\,dV$$

$$\int_\Omega \frac{1}{2}\nabla\emptyset\,\nabla\varphi - \emptyset\frac{Z}{x}\varphi\,dV - \frac{1}{2}\int_{\partial\Omega} n\,(\emptyset\,\nabla\varphi)\,dS = E\int_\Omega \emptyset\,\varphi\,dV$$

We can choose $\emptyset \quad so\ that\ \emptyset = 0\ on\ \partial\Omega, the\ equation\ becomes:$

$$\int_\Omega \frac{1}{2}\nabla\emptyset\,\nabla\varphi - \emptyset\frac{Z}{x}\varphi\,dV = E\int_\Omega \emptyset\,\varphi\,dV$$

$$\frac{1}{2}\langle\nabla\emptyset|\nabla\varphi\rangle + \langle\emptyset|V\varphi\rangle = E\langle\emptyset|\varphi\rangle\ with\ V = \frac{-Z}{x}$$

x being the distance between the electron and the nucleus

3. $\langle n|\nabla\varphi(r=R)\rangle + q\varphi(R,\theta,\gamma) = 0$

$$\left\langle e_r \left| \frac{\partial \varphi}{\partial \mathrm{r}}\, e_r + \frac{1}{r}\frac{\partial \varphi}{\partial \theta}\, e_\theta + \frac{1}{r\sin(\theta)}\frac{\partial \varphi}{\partial \gamma}\, e_\gamma \because (r=R) \right\rangle + q\varphi(R,\theta,\gamma) = 0$$

$$\frac{\partial \varphi}{\partial \mathrm{r}}(r=R) + q\varphi(R,\theta,\gamma) = 0$$

For $r \geq R$ $q = q_\infty$

$$\frac{\partial \varphi}{\partial \mathrm{r}}(r=R) + q_\infty\varphi(R,\theta,\gamma) = 0$$

$$\frac{-1}{2}\left(\frac{\partial^2}{\partial r^2}\varphi + \frac{2}{r}\frac{\partial}{\partial r}\varphi + \frac{1}{r^2}\frac{\partial^2}{\partial \theta^2}\varphi + \frac{1}{r^2 sin^2(\theta)}\frac{\partial^2}{\partial \gamma^2}\varphi + \frac{1}{r^2\tan(\theta)}\frac{\partial}{\partial \theta}\varphi\right) - \frac{Z}{r}\varphi = E\,\varphi$$

When r is big, the previous equation can be simplified in the following fashion:

$$\frac{-1}{2}\left(\frac{\partial^2}{\partial r^2}\varphi\right) - \frac{Z}{r}\varphi = E\,\varphi$$

We use the fact that $\frac{-1}{q_\infty}\frac{\partial \varphi}{\partial \mathrm{r}}(r=R) = \varphi(R,\theta,\gamma)\ for\ r \geq R$

And $\frac{-1}{q_\infty}\frac{\partial^2 \varphi}{\partial \mathrm{r}^2}(r=R) = \frac{\partial}{\partial r}\varphi(R,\theta,\gamma)\ for\ r \geq R$ to obtain the following equation:

$$\frac{-1}{2}\left(\frac{\partial^2}{\partial r^2}\varphi\right) + \frac{Z}{rq_\infty}\frac{\partial \varphi}{\partial \mathrm{r}} = E\ \frac{-1}{q_\infty}\frac{\partial \varphi}{\partial \mathrm{r}}\ \ for\ r = R$$

$$-q_\infty\frac{\partial \varphi}{\partial \mathrm{r}} = \frac{2}{q_\infty}\left(E\ + \frac{Z}{r}\right)\frac{\partial \varphi}{\partial \mathrm{r}}\ \ for\ r = R$$

$$q_\infty^2 = -2\left(E\ + \frac{Z}{R}\right)$$

So, if $E \leq \frac{-Z}{R}$:

$$q_\infty = \pm\sqrt{-2\left(E\ + \frac{Z}{R}\right)}\quad \epsilon\, R$$

$(We\ should\ take\ the\ positive\ q\ because\ \varphi(x \to \infty) = 0$ (See the answer for the following question)

And if $E \geq -\frac{Z}{R}$:

$$q_\infty = \pm i\sqrt{2\left(E\ + \frac{Z}{R}\right)}$$

NB: We could have gone further with the approximation for big distances r and choose q to be $q_\infty = +\sqrt{-2E}$, using this approximation doesn't change the result that much (1/30 being very small)

b. Outside of Ω, meaning for $r \geq R$, the wave function obeys to the following equation:

$$\frac{\partial \varphi}{\partial \mathrm{r}}(r=R)+q_{\infty}\varphi(R,\theta,\gamma)=0$$

$$\frac{\partial \varphi}{\partial \mathrm{r}}(r=R)=-q_{\infty}\varphi(R,\theta,\gamma)$$

$$\varphi(r,\theta,\gamma)=A(\theta,\gamma)\exp(-q_{\infty}r)$$

$$\varphi(r,\theta,\gamma)=A(\theta,\gamma)\exp\left(-\sqrt{-2\left(E+\frac{Z}{R}\right)}r\right) \text{ for } E\leq\frac{-Z}{R}\ for\ example$$

c. We know the expression of the energy levels n for hydrogen atoms:

$$E_n=-\left(\frac{Z}{n^2}\right)*13.6\ eV$$

We know that The Hartree Energy

$$E_h=\frac{\hbar^2}{m*a_0}=27.211\ eV$$

So, we would expect the eigen-energies we would get from our computation to be equal to

$$\in=-\left(\frac{Z}{n^2}\right)*\frac{13.6\ eV}{E_h}=-\left(\frac{Z}{n^2}\right)*\frac{13.6\ eV}{27.211eV}\cong-\left(\frac{0.5}{n^2}\right)$$

We would expect for example: $\in_1\cong-0.5$

And as expected, the results from the computations correspond to the theoretical analysis. The next figure represents the wave function φ_{1s} with the corresponding energy $\cong\ -0.5\ Hartree$. The relative error we obtained for the energy is very low = 0.15 %. We used for the FEM the following fine mesh in fig 2:

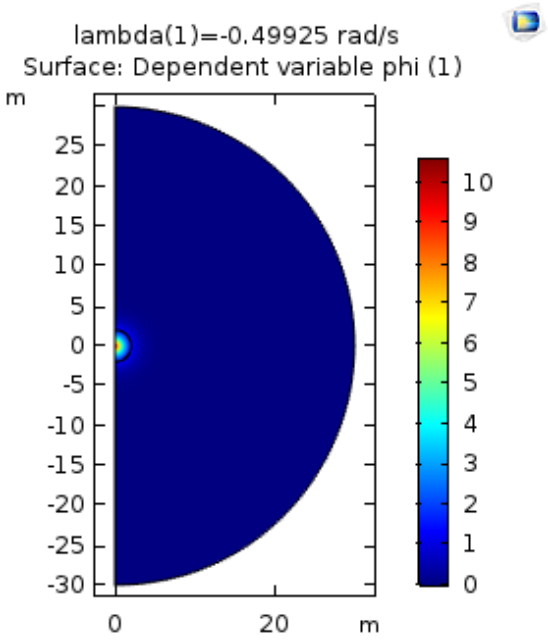


Figure 1

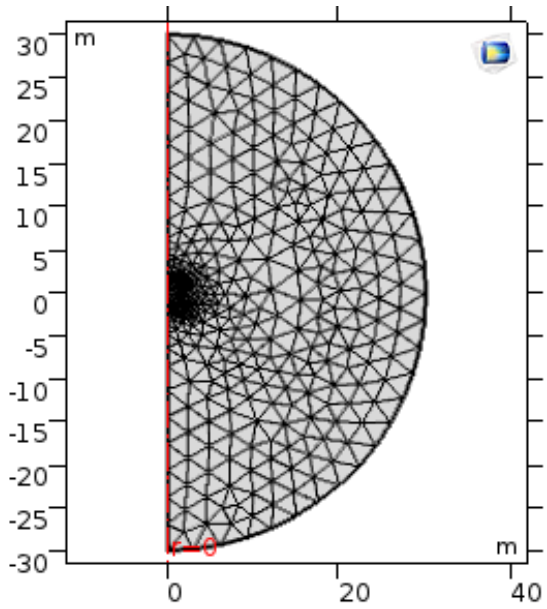


Figure 2

For n=2 we should have $\in_2 \cong -0.125$ and this is what the computation with COMSOL gives us:

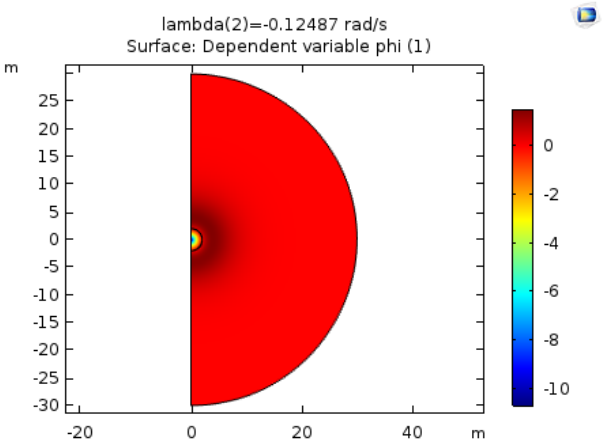


Figure 3

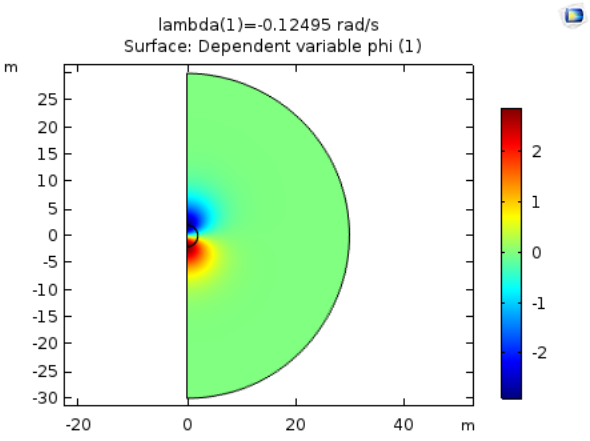


Figure 4

NB: The wave functions given in the last figures are not yet normalized

Let's go back to the ground state level, we want to enforce the constraint $\langle\varphi|\varphi\rangle = 1$ because for now, when we calculate the norm of the wave function we find: 378.5.

After the normalization we obtain the following wave function: (with a norm of approximatively 1.2).

We have also used adaptivity to refine the mesh as a function of the error estimated by the computation at each point of the domain. The final Mesh (to be compared with the figure 2) is shown in Fig. 6

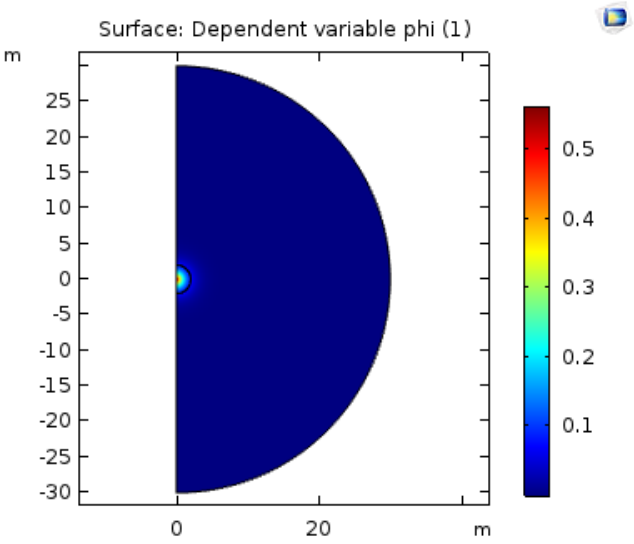


Figure 5

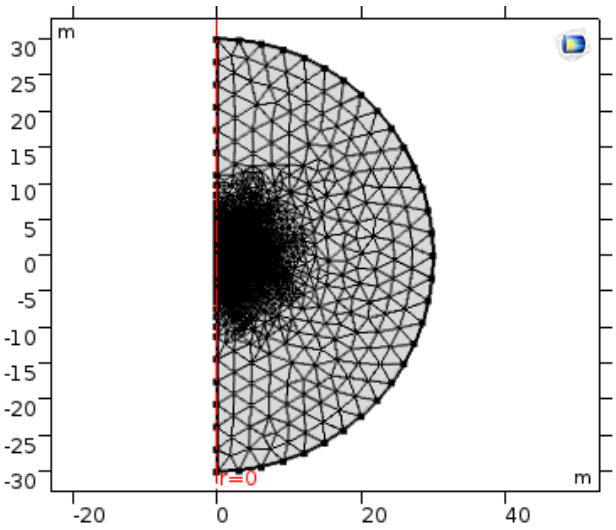


Figure 6

2. The hydrogen molecule using Hartree-Fock approximation

2.1 Theoretical aspects

1. We are in the general case of a Ne electron system:

$$\varphi_i \; is \; one \; of \; the \; Ne \; functions \; solution \; to \; the \; Fock \; System : for \; i \in \{1..N_e\}$$

$$-\frac{1}{2}\Delta_x \varphi_i - \sum_A \frac{Z_A}{\|x - X_A\|}\varphi_i + \sum_j g_{jj}\,\varphi_i - \sum_j \delta_{w_i w_j}\, g_{ij}\varphi_j = \epsilon_i \varphi_i$$

We can write the last equation in the following way:

$$\hat{F}\varphi_i = \epsilon_i \varphi_i$$: F being the Fock Operator

With $\hat{F} = -\frac{1}{2}\Delta_x + V_{en} + \sum_j \hat{J_j} - \hat{K_j}$

With $V_{en} = \sum_A \frac{Z_A}{\|x - X_A\|}$

$$\hat{J_j} = \sum_j g_{jj}\,, \qquad J: Coulom \; Operator$$

$$\hat{K_j} = \sum_j \delta_{w_i w_j}\, g_{ij} \quad K: Exchange \; Operator$$

2. We want to write the weak formulation, let's consider a smooth enough function $\emptyset$:

$$\hat{F}\varphi_i = \epsilon_i \varphi_i$$

$$\int_\Omega \emptyset\, \hat{F}\varphi_i \, dV = \int_\Omega \emptyset\, \epsilon_i \varphi_i dV$$

$$\int_\Omega \emptyset\, \hat{F}\varphi_i \, dV = \int_\Omega \emptyset\, \epsilon_i \varphi_i dV$$

$$\int_\Omega \emptyset\, (-\frac{1}{2})\Delta_x\, \varphi_i + \emptyset\; V_{en}\varphi + \emptyset \sum_j \hat{J_j}\varphi - \emptyset\, \widehat{K_j\varphi}\, dV = \int_\Omega \emptyset\, \epsilon_i \varphi_i dV$$

$$\int_\Omega \frac{1}{2}\nabla\emptyset\, \nabla\, \varphi_i + \emptyset\; V_{en}\varphi + \emptyset \sum_j \hat{J_j}\varphi - \emptyset\, \widehat{K_j\varphi}\, dV = \int_\Omega \emptyset\, \epsilon_i \varphi_i dV$$

(With the test function chosen to be equal to 0 everywhere on the boundary when φ has a Dirichlet BC. So, we obtain the obtain the weak formulation for every I in {1...Ne}

$$\frac{1}{2}\langle\nabla\emptyset\,|\nabla\varphi_i\rangle + \langle\emptyset\,|V_{en}\varphi_i\rangle + \langle\emptyset\,|\sum_j \widehat{J_j}\,\varphi_i\rangle + \langle\emptyset\,|K_j\varphi_i\rangle = \epsilon_i\langle\emptyset\,|\varphi_i\rangle$$

$$E = 0.5\sum_i \epsilon_i + h_i$$

$$With\ h_i = \frac{1}{2}\langle\nabla\varphi_i|\nabla\varphi_i\rangle + \langle\varphi_i|V_{en}\varphi_i\rangle$$

3. $\langle n|\nabla\varphi_i(r=R)\rangle + q\varphi_i(R,\theta,\gamma) = 0$

$$\left\langle e_r\middle|\frac{\partial\varphi_i}{\partial \mathrm{r}}\,e_r + \frac{1}{r}\frac{\partial\varphi_i}{\partial\theta}\,e_\theta + \frac{1}{r\sin(\theta)}\frac{\partial\varphi_i}{\partial\gamma}\,e_\gamma \because (r=R)\right\rangle + q\varphi_i(R,\theta,\gamma) = 0$$

$$\frac{\partial\varphi_i}{\partial \mathrm{r}}(r=R) + q\varphi_i(R,\theta,\gamma) = 0$$

For $r \geq R\ q = q_\infty$

$$\frac{\partial\varphi_i}{\partial \mathrm{r}}(r=R) + q_\infty\varphi_i(R,\theta,\gamma) = 0$$

For big distances R:

$\Delta_x\varphi_i\ becomes:$

$$\Delta_x\varphi_i = \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial\theta^2} + \frac{1}{r^2 sin^2(\theta)}\frac{\partial^2}{\partial\gamma^2} + \frac{1}{r^2\tan(\theta)}\frac{\partial}{\partial\theta}\right)\varphi_i = \frac{\partial^2}{\partial r^2}\varphi_i$$

$$V_{en}\varphi_i = \sum_A \frac{Z_A}{\|x - X_A\|}\varphi_i\ can\ be\ neglected$$

We know that $(g_{ij})_{1\leq i,j\leq Ne}\ are\ in\ o(r^{-1})$ so we can neglect these terms as well

So, for very big distances R; we end up with the following equation:

$$\frac{-1}{2}\frac{\partial^2}{\partial r^2}\varphi_i = \epsilon_i\varphi_i$$

We use the fact that $\frac{-1}{q_\infty}\frac{\partial\varphi_i}{\partial \mathrm{r}}(r=R) = \varphi_i(R,\theta,\gamma)\ for\ r \geq R$

And $\frac{\partial^2\varphi_i}{\partial \mathrm{r}^2}(r=R) = -q_\infty\frac{\partial}{\partial r}\varphi_i(R,\theta,\gamma)\ for\ r \geq R$ to obtain the following equation:

$$\frac{1}{2}q_\infty\frac{\partial}{\partial r}\varphi_i(R,\theta,\gamma) = \epsilon_i\frac{-1}{q_\infty}\frac{\partial\varphi_i}{\partial \mathrm{r}}(r=R)$$

$$\frac{1}{2}q_\infty = \epsilon_i\frac{-1}{q_\infty}$$

$${q_\infty}^2 = -2 * \epsilon_i$$

$$q_\infty = \sqrt{-2 * \epsilon_i}$$

$\varphi_i(r,\theta,\gamma) = A(\theta,\gamma)\exp\left(-\sqrt{-2\epsilon_i}r\right)$

$$-\Delta g = 4\pi\left|\varphi_i^2\right|$$

For big R $\Delta g = \frac{\partial^2 g}{\partial r^2}$ ->

$$\frac{\partial^2 g}{\partial r^2} = -4\pi\exp\left(-\sqrt{-2\epsilon_i}r\right)^2$$
$$\frac{\partial g}{\partial r} = \frac{4\pi}{3\sqrt{-2\epsilon}}exp\left(-\sqrt{-2\epsilon_i}r\right)^3$$
$$g = -\frac{\pi}{3(-2\epsilon)}exp\left(-\sqrt{-2\epsilon_i}r\right)^4$$

$\langle n|\nabla g(r=R)\rangle + q_g g(R,\theta,\gamma) = 0$

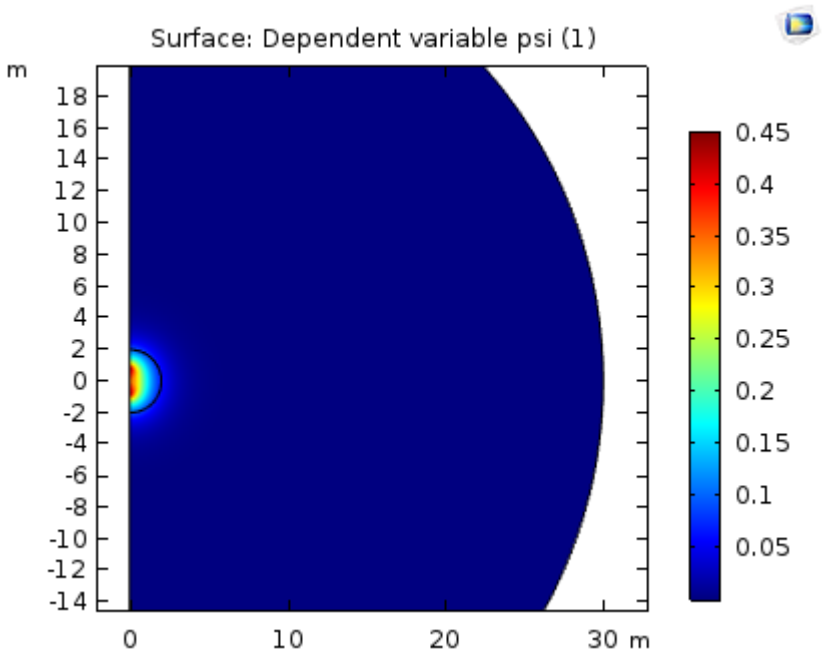
$\frac{\partial g}{\partial \mathrm{r}}(r=R) + q_g g(R,\theta,\gamma) = 0$

$\frac{4\pi}{3\sqrt{-2\epsilon}}exp\left(-\sqrt{-2\epsilon_i}r\right)^3 - q_g\frac{\pi}{3(-2\epsilon)}exp\left(-\sqrt{-2\epsilon_i}r\right)^4 = 0$

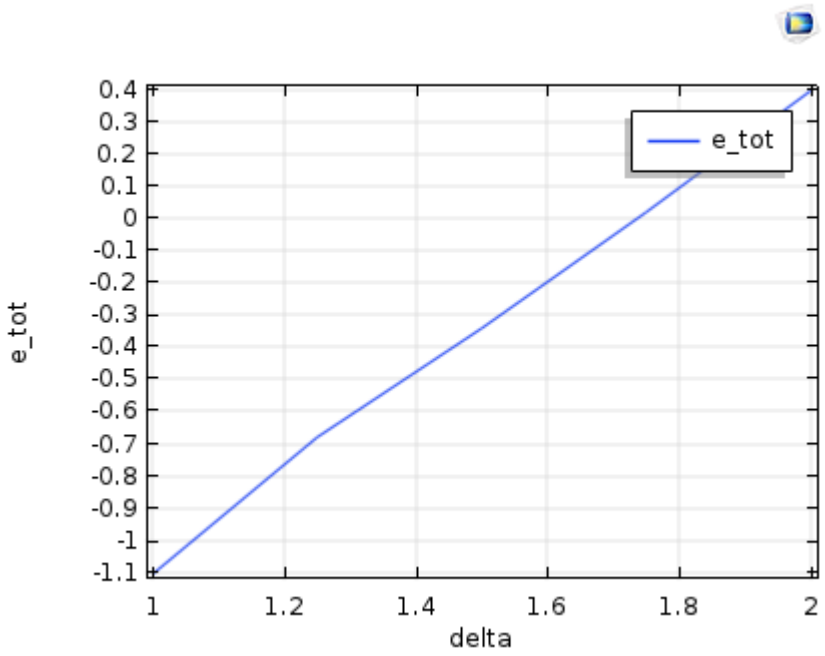
$\frac{4}{3} - q_g\frac{1}{3\sqrt{-2\epsilon}}exp\left(-\sqrt{-2\epsilon_i}r\right)^1 = 0$

$q_g = \frac{4*\sqrt{-2\epsilon}}{exp\left(-\sqrt{-2\epsilon_i}R\right)^1}$

We launch the COMSOL program using the previous boundary conditions: We obtain the following result:



We made a parametric sweep over the value of delta and conducted the studies, the resulted can be seen in the following plot:



We choose delta=1, we have at this value a minimum of the total energy (-1.1 Hartree)

We want to calculate the force applied on one of the two atoms, force which gets null when reaching the equilibrium, we take the nucleus i at $\frac{\delta}{2}\begin{pmatrix}0\\0\\1\end{pmatrix}$

$$F_i = -\nabla V_{nn} - 2\langle\psi|\nabla V_{ne}\psi\rangle$$

$$V_{nn} = \frac{Z * Z\ e^2}{4\,\pi\epsilon_0 a_0 \|R_i - R_j\|}$$

$$\nabla_{Ri} V_{nn} = \frac{-Z * Z\ e^2}{4\,\pi\epsilon_0 a_0 \|R_i - R_j\|^2}$$

We are using atomic units so in our program:

$$\nabla_{Ri} V_{nn} = \frac{-1}{\|R_i - R_j\|^2}$$

$$\frac{\partial Vnn}{\partial z_i} = \frac{2(z_i - z_j)}{2\left(\sqrt{(r_i - r_j)^2 + (z_i - z_j)^2}\right)^3}$$

$$\frac{\partial Vnn}{\partial z_i}\left(z_i = \frac{\delta}{2}\right) = \frac{\delta}{\sqrt{\delta^2}^3} = \frac{\delta}{\delta^3} = \frac{1}{\delta^2}$$

$$V_{en} = \frac{-1}{\|x - X_i\|}$$

$$\frac{\partial Ven}{\partial ri} = \frac{r}{2\sqrt{r^2 + \left(\frac{\delta}{2} - z\right)^2}^3}$$

$$\frac{\partial Ven}{\partial zi} = \frac{z - \frac{\delta}{2}}{2\sqrt{r^2 + \left(\frac{\delta}{2} - z\right)^2}^3}$$

When we calculate F we obtain (see the third COMSOL file for details): $\mathrm{Fr} = -1.355$ and $\mathrm{Fz} = -0.375$

With the same method we can derive the bond stiffness k