Computational estimation of H-H ion bond length

Using Newton-Rafson, med-point methods and five point differantiation

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Abstract

In quantum mechanics, the observation of the electrons are descried as a wave function of probability. Then, we can estimate its energy from the most probable state. In this report, the H-H ion bond length had been calculated by using variation method to estimate the hydrogen molecule ion ground state as a function of the separation distance between the two protons. Then by minimize the ground state energy to reach the most probable separation we can determine the bond length.

Introduction

Variation method

The variation method state that the grown state energy of any system must be less than or equal the expectation value of the Hamiltonian operator, which described in equation 1.1.

$$E_g \leq \frac{\langle \psi^*|\hat{H}|\psi \rangle}{\langle \psi^*|\psi \rangle} \quad \textbf{Equation 1.1}$$

Where E_g is the ground state energy, ψ is the probability wave function and $\hat{H}$ is the Hamiltonian operator such that:

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V \quad \textbf{Equation 1.2}$$

Then for a general wave function. We can construct the function from an infinite summation of basis state functions:

$$\psi = \sum_{n=0}^{\infty} c_n \psi_n \quad \textbf{Equation 1.3}$$

Finally, to reach the closest value of the ground state energy, we can minimize the function in equation 1.1 respect to c_n in equation 1.3.

$$\frac{\partial \frac{\langle \psi^*|\hat{H}|\psi \rangle}{\langle \psi^*|\psi \rangle}}{\partial c_n} = 0 \;\forall n \quad \textbf{Equation 1.4}$$

(David J. Griffiths, 2018)

H-H trial function

Before begin the variation method, we need to define a trial wave function to minimize it as equation 1.4. This function can be the closest expected wave function to the ground state. For our problem, we can construct the trial function from the ground state of hydrogen atom.

$$\psi(r) = \frac{1}{\sqrt{\pi a^3}} e^{-\frac{r}{a}} \quad \textbf{Equation 2.1}$$

Where $a = \frac{4\pi\epsilon_0 \hbar^2}{m_e e^2}$

Since our problem has two protons, we can construct a trial function depend on a

combination of two hydrogen ground state each one for each proton.

$$\psi = A\psi(r) + B\psi(r') \quad \textbf{Equation 2.2}$$

From figure 1:

$$|r'| = \sqrt{r^2 + R^2 - 2rR\cos\theta} \quad \textbf{Equation 2.3}$$

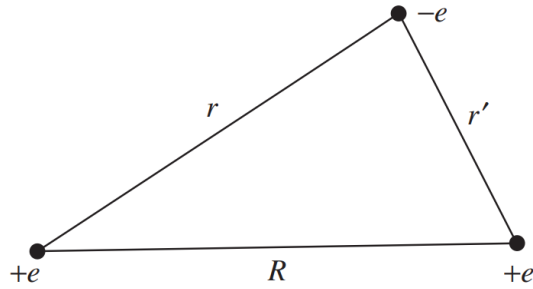θ is the angel between r and R in figure 1.

Figure 1 Hydrogen molecule ion

Finally, we can write equation 2.2 as the following:

$$\psi = A\frac{1}{\sqrt{\pi a^3}}e^{-\frac{r}{a}} + B\frac{1}{\sqrt{\pi a^3}}e^{-\frac{\sqrt{r^2+R^2-2rR\cos\theta}}{a}}$$

Equation 2.4

Applying variation method to the trial function

We can now apply equation 1.4 to the trial function in equation 2.4.

From Appendix A. We can use the result of $A = \pm B$ to normalize the wave function in equation 2.4. The result is shown in Appendix B.

At $A = B$:

$$A^2 = \frac{1}{2\left(1+e^{-\frac{R}{a}}\left[1+\left(\frac{R}{a}\right)+\frac{1}{3}\left(\frac{R}{a}\right)^2\right]\right)} \quad \textbf{Equation 3.1}$$

At $A = -B$:

$$A^2 = \frac{1}{2\left(1-e^{-\frac{R}{a}}\left[1+\left(\frac{R}{a}\right)+\frac{1}{3}\left(\frac{R}{a}\right)^2\right]\right)} \quad \textbf{Equation 3.2}$$

Finally, the value of the best approach to E_g can be founded by substitute the value of A for both cases in $\langle\psi|\widehat{H}|\psi\rangle$. And we can now define the Hamiltonian operator by substitute the potential function in equation 1.2:

$$\widehat{H} = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{r}+\frac{1}{r'}\right) \quad \textbf{Equation 3.3}$$

Then from appendix C. The value of the ground state energy is:

For the case $A = B$

$$E(x)$$
$$= -1 + \frac{2}{x}\left\{\frac{\left(1-\frac{2}{3}x^2\right)e^{-x} + (1+x)e^{-2x}}{1+\left(1+x+\frac{1}{3}x^2\right)e^{-x}}\right\}$$

Equation 3.4

For the case $A = -B$

$$E(x)$$
$$= -1 + \frac{2}{x}\left\{\frac{-\left(1-\frac{2}{3}x^2\right)e^{-x} + (1+x)e^{-2x}}{1-\left(1+x+\frac{1}{3}x^2\right)e^{-x}}\right\}$$

Equation 3.5

We can find the bond length of H-H molecule by minimize the function $E(x)$.

(David J. Griffiths, 2018)

Numerical methods

1. Differentiation

Minimizing the potential function requires first finding its derivative, which, although possible symbolically, is much easier using a numerical differentiation method such as the five point formula.

A function $f(x)$ can be approximated near a point x_0 by evaluating f at a few other points around it, say those distanced by multiples of a small number h. Substituting the five points x_0, $x_0 + 1, \cdots, x_0 + 4$ into the Taylor expansion of the function at x_0 then solving the system of five equations for $f'(x_0)$ gives

$f'(x_0)$
$$= \frac{-25f(x) + 48f(x+h) - 36f(x+2h) + 16f(x+3h) - 3f(x+4h)}{12h}$$
$+ E$

where E is the truncation error given by

$\dfrac{f^{(5)}(x)h^4}{5} + \cdots$, which is of order $O(h^4)$.

2. Root finding

After finding the derivative, one must solve for the point at which the derivative equals 0 – the critical point, which, given the function has a single minimum in the interval of interest, is that minimum. To solve the equation $g(x) = 0$, where g is the derivative of the potential function given by the five point formula, we used two methods – the bisection method and the Newton-Raphson method.

In the bisection method, two starting points are required, one at which the function is positive and another where it is negative, so that, by the intermediate value theorem, the function has a root between the two points. The root is approximated by the mid-point of the two points at each iteration. That midpoint becomes one of the starting points for the next iteration, depending on the sign of the function at it. Repeating that process for several iterations, the midpoint will get closer to the root.

The Newton-Raphson method requires a single initial guess x_0, on which the formula

$$x_{n+1} = x_n - \frac{g(x_n)}{g'(x_n)}$$

is applied. The sequence generated by this process, $x_0, x_1, x_2, \cdots$, converges to the root. $g'(x_n)$ was again calculated using the five point formula. (John. H. Mathews, 2004)
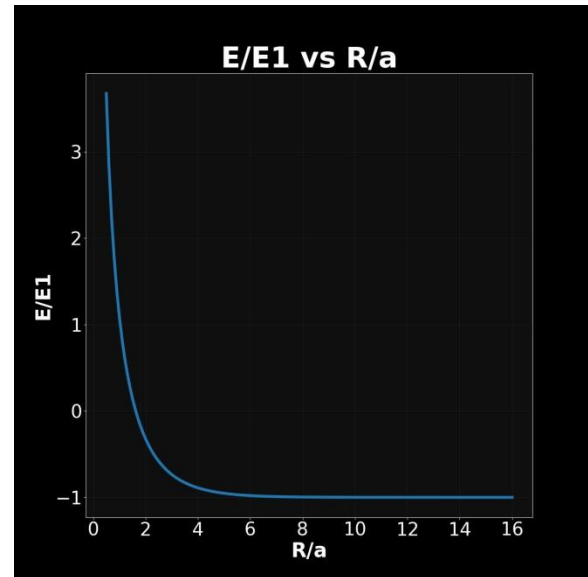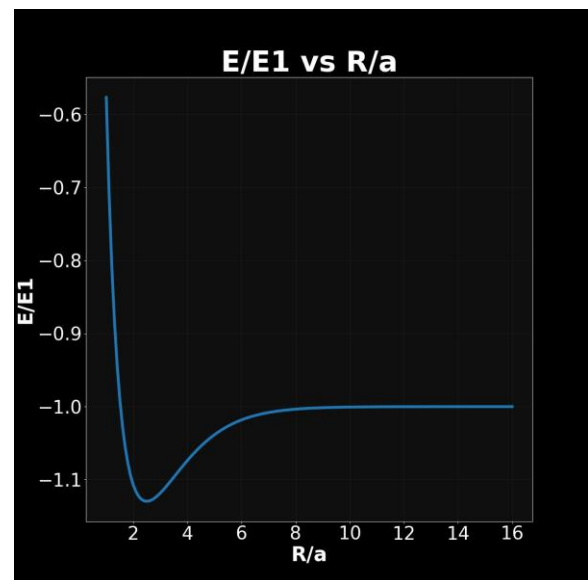
Result

Plot

Figure 2 E/E1 vs R/a at A=-B

Figure 3 E/E1 vs R/a at A=B

Figure 2 and 3 show the relation $\frac{E}{E_1}\ vs\ \frac{R}{a}$, where E is the ground state of energy, E_1 is the ground state of energy of electron in hydrogen atom which is about $E_1 = 13.6\ eV$, R is the distance between H-H bond and a is Bohr's radius which is about $a = 5.291 \times 10^{-11} m$.

Numerical results value

Since figure 2 does not show a bound state, then the true bound state energy relation is that in figure 3 when $A = B$ represent in equation 3.4. So, the value of H-H bond length can be calculated numerically from this equation.

Method	$x = \dfrac{R}{a}$	$F(x) = \dfrac{E}{E_1}$
Mid-point	2.49286	-1.12966
Newton-Raphson	2.49283	-1.12966

Finally, the final result of H-H bond length:

$$R = 2.4928\ Bohr\ radius$$

$$\mathbf{R = 13.19 * 10^{-11} m}$$

And the ground state energy is:

$$\mathbf{E_g = -15.6\ eV}$$

Conclusion

Comparison between Root Finding Methods

The bisection method converges to a root linearly, meaning its error decreases in direct proportion to the number of iterations; the Newton-Raphson method converges quadratically, but only for a root x such that $g'(x) \neq 0$, which is the case in our problem, as $g'(x)$ is the second derivative of the potential function, which, at x, has a minimum, meaning $g'(x) > 0$. As expected, a solution with a specified accuracy can be reached in less iterations using the Newton-Raphson method; for an accuracy of 10^{-4}, 12 iterations of the bisection method were needed, but only 4 of the Newton-Raphson method were enough.

Although the Newton-Raphson method requires less iterations, each iteration requires more computation, as $g'(x_n)$ must be calculated using the five point formula for each iteration; however, in our case the Newton-Raphson method was still more time efficient, taking on average about $8\ \mu s$ to yield a solution accurate to 10^{-4} whereas the bisection method averaged about $50\ \mu s$.

References

David J. Griffiths, D. F. (2018). *Introduction to Quantum Mechanics (3rd Edition).* Pearson Education.

John. H. Mathews, K. D. (2004). *Numerical Methods Using MATLAB Fourth Edition.* Pearson Education.

Appendices

Files

- main.cpp: $c++$ file for finding the data to plot and solve the nonlinear equation.
- Plot.py: a python file for plot the function $\frac{E}{E_1}\ vs\ \frac{R}{a}$.

Appendix A

Let $\psi_A = \psi(r)$ and $\psi_B = \psi(r')$. Then the trial function will be.

$$\psi = A\psi_A + B\psi_B \quad \textbf{Equation A.1}$$

To apply equation 1.4, we need to find the value of $\langle\psi^*|\hat{H}|\psi\rangle$ and $\langle\psi^*|\psi\rangle$.

$$\langle\psi^*|\psi\rangle = A^2\langle\psi_A|\psi_A\rangle + B^2\langle\psi_B|\psi_B\rangle + 2AB\langle\psi_A|\psi_B\rangle = A^2 + B^2 + 2AB\langle\psi_A|\psi_B\rangle$$
Equation A.2

$$\langle\psi^*|\hat{H}|\psi\rangle = A^2\langle\psi_A|\hat{H}|\psi_A\rangle + B^2\langle\psi_B|\hat{H}|\psi_B\rangle + AB\langle\psi_A|\hat{H}|\psi_B\rangle + AB\langle\psi_B|\hat{H}|\psi_A\rangle$$
Equation A.3

Then by the following notations:

$$H_{AA} = \langle\psi_A|\hat{H}|\psi_A\rangle \quad \textbf{Equation A.4}$$

$$H_{BB} = \langle\psi_B|\hat{H}|\psi_B\rangle \quad \textbf{Equation A.5}$$

$$H_{AB} = \langle\psi_A|\hat{H}|\psi_B\rangle \quad \textbf{Equation A.6}$$

$$H_{BA} = \langle\psi_B|\hat{H}|\psi_A\rangle \quad \textbf{Equation A.7}$$

Then, the final value will become:

$$\langle\psi^*|\hat{H}|\psi\rangle = A^2 H_{AA} + B^2 H_{BB} + ABH_{AB} + ABH_{BA}$$
Equation A.8

Substitute in equation 1.1

$$\frac{\langle\psi^*|\hat{H}|\psi\rangle}{\langle\psi^*|\psi\rangle} = \frac{A^2 H_{AA} + B^2 H_{BB} + ABH_{AB} + ABH_{BA}}{A^2 + B^2 + 2AB\langle\psi_A|\psi_B\rangle}$$

Equation A.9

After that, we need to find the values A and B from equation 1.4:

$$\partial\frac{\frac{\langle\psi^*|\hat{H}|\psi\rangle}{\langle\psi^*|\psi\rangle}}{\partial A}$$
$$= \frac{[A^2 + B^2 + 2AB\langle\psi_A|\psi_B\rangle][2AH_{AA} + B(H_{AB} + H_{BA})]}{(A^2 + B^2 + 2AB\langle\psi_A|\psi_B\rangle)^2}$$
$$- \frac{[A^2 H_{AA} + B^2 H_{BB} + ABH_{AB} + ABH_{BA}][2A + 2B\langle\psi_A|\psi_B\rangle]}{(A^2 + B^2 + 2AB\langle\psi_A|\psi_B\rangle)^2}$$
Equation A.10

From equation 1.4: $\frac{\partial\frac{\langle\psi^*|\hat{H}|\psi\rangle}{\langle\psi^*|\psi\rangle}}{\partial A} = 0$ then substitute in equation A.10:

$$[A^2 + B^2 + 2AB\langle\psi_A|\psi_B\rangle][2AH_{AA} + B(H_{AB} + H_{BA})] = [A^2 H_{AA} + B^2 H_{BB} + ABH_{AB} + ABH_{BA}][2A + 2B\langle\psi_A|\psi_B\rangle]$$
Equation A.11

Then, doing the same respect to B:

$$\partial\frac{\frac{\langle\psi^*|\hat{H}|\psi\rangle}{\langle\psi^*|\psi\rangle}}{\partial B}$$
$$= \frac{[A^2 + B^2 + 2AB\langle\psi_A|\psi_B\rangle][2BH_{BB} + A(H_{AB} + H_{BA})]}{(A^2 + B^2 + 2AB\langle\psi_A|\psi_B\rangle)^2}$$
$$- \frac{[A^2 H_{AA} + B^2 H_{BB} + ABH_{AB} + ABH_{BA}][2B + 2A\langle\psi_A|\psi_B\rangle]}{(A^2 + B^2 + 2AB\langle\psi_A|\psi_B\rangle)^2}$$
Equation A.12

From equation 1.4: $\frac{\partial\frac{\langle\psi^*|\hat{H}|\psi\rangle}{\langle\psi^*|\psi\rangle}}{\partial B} = 0$ then substitute in equation A.12:

$$[A^2 + B^2 + 2AB\langle\psi_A|\psi_B\rangle][2BH_{BB} + A(H_{AB} + H_{BA})] = [A^2 H_{AA} + B^2 H_{BB} + ABH_{AB} + ABH_{BA}][2B + 2A\langle\psi_A|\psi_B\rangle]$$
Equation A.13

By dividing each of equation A.11 and equation A.13 by B and then divide A.13 on A.11:

$$\frac{\left[2H_{BB} + \frac{A}{B}(H_{AB} + H_{BA})\right]}{\left[\frac{2A}{B}H_{AA} + (H_{AB} + H_{BA})\right]} = \frac{\left[1 + \frac{A}{B}\langle\psi_A|\psi_B\rangle\right]}{\left[\frac{A}{B} + \langle\psi_A|\psi_B\rangle\right]}$$
Equation A.14

By define $C = \frac{A}{B}$ equation A.14 become:

$$C^2(2H_{AA}\langle\psi_A|\psi_B\rangle - H_{AB} - H_{BA}) + C(2H_{AA} - 2H_{BB}) + H_{AB} + H_{BA} - 2H_{BB}\langle\psi_A|\psi_B\rangle = 0$$
Equation A.15

Finally, the solution of C can be determined from the general solution of second order polynomial.

After returning to equation A.9, we can write it as the relation:

$$\frac{\langle\psi^*|\hat{H}|\psi\rangle}{\langle\psi^*|\psi\rangle}[A^2 + B^2 + 2AB\langle\psi_A|\psi_B\rangle]$$
$$= A^2 H_{AA} + B^2 H_{BB} + ABH_{AB}$$
$$+ ABH_{BA}$$

Equation A.16

Then, differentiate equation A.16 with respect to A and B and substitute the value of differentiation to 0 as equation1.4. Then the two result of differentiation of A and B are respectively as equations A.17 and A.18:

$$\frac{\langle\psi^*|\hat{H}|\psi\rangle}{\langle\psi^*|\psi\rangle}[2A + 2B\langle\psi_A|\psi_B\rangle]$$
$$= 2AH_{AA} + B(H_{AB} + H_{BA})$$

Equation A.17

$$\frac{\langle\psi^*|\hat{H}|\psi\rangle}{\langle\psi^*|\psi\rangle}[2B + 2A\langle\psi_A|\psi_B\rangle]$$
$$= 2BH_{BB} + A(H_{AB} + H_{BA})$$

Equation A.18

We can differentiate again both of A.17 and A.18 of A and B respectively to conclude the relations:

$$\frac{\langle\psi^*|\hat{H}|\psi\rangle}{\langle\psi^*|\psi\rangle} = H_{AA}$$ **Equation A.19**

$$\frac{\langle\psi^*|\hat{H}|\psi\rangle}{\langle\psi^*|\psi\rangle} = H_{BB}$$ **Equation A.20**

From A.19 and A.20 we can conclude that applying equation 1.4 means that:

$$H_{AA} = H_{BB}$$ **Equation A.21**

However, the step to get equations A.19 and A.20 is not clearly true. But, we can conclude the result in A.21 since the values H_{AA} and H_{BB} represent the ground state energy of the electron respect to one of the protons for each one, which must be the same for both.

Also, there is another useful equality we can get it by knowing that the Hamiltonian operator is Hermit operator:

$$H_{AB} = H_{BA}$$ **Equation A.22**

Finally, substitute equation A.21 and equation A.22 in equation A.15 to evaluate the value of C. The result will be:

$$C = \pm 1$$

Which mean that there is two relations:

$$A = B$$

$$A = -B$$

Appendix B

Let $\psi_A = \psi(r)$ and $\psi_B = \psi(r')$. And using the result $A = B$. Then the trial function will be.

$$\psi = A[\psi_A + \psi_B]$$ **Equation B.1**

Then, we need to normalize ψ to find the value of A as the following:

$$\langle\psi^*|\psi\rangle = 1$$ **Equation B.2**

Substitute equation B.1 in equation B.2:

$$A^2[\langle\psi_A|\psi_A\rangle + \langle\psi_B|\psi_B\rangle + 2\langle\psi_A|\psi_B\rangle] = 1$$
Equation B.3

Since we use the functions ψ_A and ψ_B to be the ground state of hydrogen atom. We can say that each of them is normalized function:

$$\langle\psi_A|\psi_A\rangle = 1$$ **Equation B.4**

$$\langle\psi_B|\psi_B\rangle = 1$$ **Equation B.5**

So, we need to find the value of $\langle\psi_A|\psi_B\rangle$.

$$\langle\psi_A|\psi_B\rangle$$
$$= \int_0^{2\pi} \int_0^\infty \int_0^\pi \psi_A\psi_B \sin\theta \, d\theta \, r^2 dr \, d\phi$$

Equation B.6

Then, substitute ψ_A and ψ_B as equation 2.4 and integrate over ϕ since none of them depend on ϕ.

$$\langle\psi_A|\psi_B\rangle$$
$$= \frac{2}{a^3} \int_0^\infty \int_0^\pi e^{-\frac{r}{a}} e^{-\frac{\sqrt{r^2+R^2-2rR\cos\theta}}{a}} \sin\theta \, d\theta \, r^2 dr$$

Equation B.7

By doing the substitution:

$$u = \sqrt{r^2 + R^2 - 2rR\cos\theta}$$

$$d(u^2) = 2u\,du = 2rR\sin\theta \, d\theta$$

$$\begin{cases} u = |r - R|, & \theta = 0 \\ u = r + R, & \theta = \pi \end{cases}$$

And integrate over θ. The integral in B.7 will become:

$$\langle\psi_A|\psi_B\rangle = \frac{2}{a^3} \int_0^\infty \frac{e^{-\frac{r}{a}}}{rR} \int_{|r-R|}^{r+R} e^{-\frac{u}{a}} u\,du \, r^2 dr$$

Equation B.8

By doing integrating by part of Equation B.8 for the integration of θ:

$$\int_{|r-R|}^{r+R} e^{-\frac{u}{a}} u\,du = -\frac{a}{rR}\left[e^{-\frac{(r+R)}{a}}(r + R + a) - e^{-\frac{|r-R|}{a}}(|r - R| + a)\right]$$ **Equation B.9**

Substitute B.9 into B.8:

$$\langle\psi_A|\psi_B\rangle = \frac{2}{a^2R}\left[-e^{-\frac{R}{a}} \int_0^\infty (r + R + a)e^{-\frac{2r}{a}} r\,dr + e^{-\frac{R}{a}} \int_0^R (R - r + a) r\,dr + e^{\frac{R}{a}} \int_R^\infty (r - R + a)e^{-\frac{2r}{a}} r\,dr\right]$$

Equation B.10

Then after integrate the middle part straightforward and do the integration by part for the first and third parts:

$$\langle\psi_A|\psi_B\rangle = e^{-\frac{R}{a}}\left[1 + \left(\frac{R}{a}\right) + \frac{1}{3}\left(\frac{R}{a}\right)^2\right]$$

Equation B.11

Finally, substitute B.4, B.5 and B.11 in B.3:

$$A^2 = \frac{1}{2\left(1 + e^{-\frac{R}{a}}\left[1 + \left(\frac{R}{a}\right) + \frac{1}{3}\left(\frac{R}{a}\right)^2\right]\right)}$$

Equation B.12

If we use the same method to find the normalization constant A when $A = -B$:

$$A^2 = \frac{1}{2\left(1 - e^{-\frac{R}{a}}\left[1 + \left(\frac{R}{a}\right) + \frac{1}{3}\left(\frac{R}{a}\right)^2\right]\right)}$$

Equation B.13

Appendix C

We need to evaluate the value of $\langle\psi|\hat{H}|\psi\rangle$. Firstly, let's start from the case $A = B$.

Let $\psi_A = \psi(r)$ and $\psi_B = \psi(r')$. Then the trial function will be:

$$\psi = A[\psi_A + \psi_B] \quad \textbf{Equation C.1}$$

Then let's start from evaluating $\hat{H}\psi$:

$$\widehat{H}\psi = A\left[-\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{r}+\frac{1}{r'}\right)\right][\psi_A + \psi_B]$$
Equation C.2

Since the functions ψ_A and ψ_B are the ground state of hydrogen atom. Then from Schrodinger equation and the Hamiltonian of hydrogen atom we know that:

$$\left(-\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{r}\right)\right)\psi_A = E_1\psi_A$$
Equation C.3

$$\left(-\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{r'}\right)\right)\psi_B = E_1\psi_B$$
Equation C.4

Where E_1 is the ground state energy of hydrogen atom.

Substitute C.3 and C.4 in equation C.2:

$$\widehat{H}\psi = E_1\psi - A\frac{e^2}{4\pi\epsilon_0}\left[\frac{1}{r'}\psi_A + \frac{1}{r}\psi_B\right]$$
Equation C.5

It follows that

$$\langle\psi|\widehat{H}|\psi\rangle = E_1 - 2A^2\frac{e^2}{4\pi\epsilon_0}\left[\left\langle\psi_A\left|\frac{1}{r'}\right|\psi_A\right\rangle\right.$$
$$\left.+ \left\langle\psi_A\left|\frac{1}{r}\right|\psi_B\right\rangle\right]$$
Equation C.6

Finally, we need to evaluate the value of $\left\langle\psi_A\left|\frac{1}{r'}\right|\psi_A\right\rangle$ and $\left\langle\psi_A\left|\frac{1}{r}\right|\psi_B\right\rangle$. By defining the direct integral:

$$D = a\left\langle\psi_A\left|\frac{1}{r'}\right|\psi_A\right\rangle \quad \textbf{Equation C.7}$$

And the exchange integral:

$$X = a\left\langle\psi_A\left|\frac{1}{r}\right|\psi_B\right\rangle \quad \textbf{Equation C.8}$$

Firstly, let's start with the direct integral.

$$D = a\left\langle\psi_A\left|\frac{1}{r'}\right|\psi_A\right\rangle$$

$$= \frac{1}{a^2\pi}\int_0^{2\pi}\int_0^\pi\int_0^\infty \frac{e^{-2\frac{r}{a}}}{\sqrt{r^2 + R^2 - 2rR\cos\theta}}r^2\,dr\sin\theta\,d\theta\,d\phi$$

Then, by make the substitution

$$k = r^2 + R^2 - 2rR\cos\theta \rightarrow dk = 2rR\sin\theta\,d\theta$$

$$\begin{cases}\theta = \pi, & k = (r+R)^2 \\ \theta = 0, & k = (r-R)^2\end{cases}$$

$$dk = 2rR\sin\theta\,d\theta =\rightarrow \sin\theta\,d\theta = \frac{1}{2rR}dk$$

It follows that

$$D = \frac{1}{Ra^2}\int_0^\infty e^{-2\frac{r}{a}}r\int_{(r-R)^2}^{(r+R)^2}\frac{1}{\sqrt{k}}dk\,dr$$

$$= \frac{2}{Ra^2}\int_0^\infty e^{-2\frac{r}{a}}r(r+R$$
$$- |r-R|)dr$$

Then, split the integration into to parts

$$D = \frac{2}{Ra^2}\left[2\int_0^R e^{-2\frac{r}{a}}r^2\,dr + 2R\int_R^\infty re^{-2\frac{r}{a}}dr\right]$$

Finally, by do the integration by parts

$$D = \frac{a}{R} - \left(1 + \frac{a}{R}\right)e^{-\frac{2R}{a}} \quad \textbf{Equation C.9}$$

We need now to evaluate the value of the exchange integral.

$$X = a\left\langle\psi_A\left|\frac{1}{r}\right|\psi_B\right\rangle$$

$$= \frac{1}{a^2\pi}\int_0^{2\pi}\int_0^\pi\int_0^\infty e^{-\frac{r}{a}}e^{-\frac{\sqrt{r^2+R^2-2rR\cos\theta}}{a}}r\,dr\sin\theta\,d\theta\,d\phi$$

By reorder the integrals

$$X$$
$$= \frac{2}{a^2}\int_0^\infty re^{-\frac{r}{a}}\int_0^\pi e^{-\frac{\sqrt{r^2+R^2-2rR\cos\theta}}{a}}\sin\theta\,d\theta\,dr$$

Then, by make the substitution

$$k = r^2 + R^2 - 2rR\cos\theta \to dk = 2rR\sin\theta\, d\theta$$

Equation C.13

$$\begin{cases} \theta = \pi, & k = (r+R)^2 \\ \theta = 0, & k = (r-R)^2 \end{cases}$$

For the case $A = -B$

$$E(x)$$

$$dk = 2rR\sin\theta\, d\theta \Longrightarrow \sin\theta\, d\theta = \frac{1}{2rR}dk$$

$$= -1 + \frac{2}{x}\left\{ \frac{-\left(1 - \frac{2}{3}x^2\right)e^{-x} + (1+x)e^{-2x}}{1 - \left(1 + x + \frac{1}{3}x^2\right)e^{-x}} \right\}$$

$$X = \frac{1}{Ra^2}\int_0^\infty e^{-\frac{r}{a}} \int_{(r-R)^2}^{(r+R)^2} e^{-\frac{\sqrt{k}}{a}} dk\, dr$$

Equation C.14

Finally by doing another substitution $u = \sqrt{k}$ and then do the integration by parts

$$X = \left(1 + \frac{R}{a}\right)e^{-\frac{R}{a}} \quad \textbf{Equation C.10}$$

Finally, substitute C.9 and C.10 in C.6 and substitute the value of the ground state energy of hydrogen atom $E_1 = -\frac{e^2}{4\pi\epsilon_0}\frac{1}{2a}$

$$\langle\psi|\widehat{H}|\psi\rangle = [1 + 4A^2(D+X)]E_1$$
Equation C.11

If we use the case $A = -B$, then the final result will be

$$\langle\psi|\widehat{H}|\psi\rangle = [1 + 4A^2(D-X)]E_1$$
Equation C.12

However, this is just the electron ground state energy. But the system has another energy which is due to proton-proton repulsive:

$$V_{pp} = \frac{e^2}{4\pi\epsilon_0}\frac{1}{R} = -\frac{2a}{R}E_1 \quad \textbf{Equation C.13}$$

The total energy at a unit $-E_1$ and as a function of $x = \frac{R}{a}$ will be:

For the case $A = B$

$$E(x)$$

$$= -1 + \frac{2}{x}\left\{ \frac{\left(1 - \frac{2}{3}x^2\right)e^{-x} + (1+x)e^{-2x}}{1 + \left(1 + x + \frac{1}{3}x^2\right)e^{-x}} \right\}$$