
Numerical integration of the Schrödinger's equation: vibrational energies and wave functions of the H_2 molecule



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I Introduction

The numerical integration of the Schrödinger's equation is very use-full because this equation has rarely an analytical solution, in this practical work we want integrate this equation of H_2 to find this wave function to study these eigenvalues, these eigenvectors and these vibrational energies.

II Theory

II.1 Time-independent Schrödinger's equation

The wave function describing the system is very complex so we use the separation of variables to be able to solve it:

$$\Psi(\vec{R}) = \frac{1}{R} \psi(R) Y_{Jm}(\theta, \varphi),$$

with :

- \vec{R} the vector connecting the two hydrogen atoms and $|\vec{R}| \equiv R$ its norm
- $Y_{Jm}(\theta, \varphi)$ the spherical harmonics
- $J \in \mathbb{N}$ the rotational quantum number
- $m \in \{-J, -J+1, \dots, 0, \dots, J-1, J\}$ the magnetic quantum number

The wave function $\Psi(R)$ is define with :

$$H(R)\psi(R) = \left[-\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + V(R) + \frac{\hbar^2 J(J+1)}{2\mu R^2} \right] \psi(R) = E\psi(R)$$

where ::

- μ is the reduced mass of the two nuclei
- $V(R)$ is the potential relative to the vibrational state of the system
- $\hbar^2 J(J+1) / (2\mu R^2)$ is the centrifugal repulsion produced by the rotation of the molecule

This differential equation is homogeneous second-order DE, in consequence it has two linearly independent solutions.

For $R \rightarrow 0$ $V(R)$ diverges due to the Pauli exclusion principles and the second is 0, so only the second is acceptable.

For $R \rightarrow \infty$ $V(R) \rightarrow 0$ the Schrödinger's equations become :

$$-\frac{\hbar^2}{2\mu} \frac{d^2 \psi}{dR^2} = E\psi,$$

We can study this equation in function of E :

For $E > 0$ Ψ is under this form $A \exp(-ikR) + B \exp(ikR)$, this solution is not in \mathbb{R} so this has no physical sense.

For $E < 0$ Ψ is under this for $A \exp(-kR) + B \exp(kR)$ with the wave number $k = (-2\mu E / \hbar^2)^{1/2}$, this solution is possible only if $B = 0$ but A and B depend on the initial conditions that are already given and the potential too, so we have to quantify E .

II.2 Numerical solution of the Schrödinger's equation

II.2.1 Reduced variables

In numerical study this is common to take reduced variable and have without dimensional variables, our potential is characterized by R_0 (distance between 2 atoms) and V_0 the dissociation energy of the molecule, we can use them to transform our equation :

$$\left[-b \frac{d^2}{dr^2} + v(r) + b \frac{J(J+1)}{r^2} \right] \psi(r) = e\psi(r)$$

- $b = B/V_0$ the reduced rotational constant of $B = \hbar^2 / (2\mu R_0^2)$
- $e = E/V_0$ the reduced value of energy with $-1 < e < 0$

II.2.2 Potential model

In order to solve the Schrödinger's equation we have take a potential for which the solution is analytical, the Morse potential characterized by R_0 (distance between 2 atoms) and V_0 the dissociation energy of the molecule :

$$V(R) = V_0 \left[e^{-2a \frac{R-R_0}{R_0}} - 2e^{-a \frac{R-R_0}{R_0}} \right]$$

- $a \gg 1$

We can express it with reduced variables :

$$v(r) = e^{-2a(r-1)} - 2e^{-a(r-1)}$$

In the lectures we have study the behavior of our Schrödinger's equation with this potential for $J = 0$, after study this result in function of r values (calculus in annex) we have found the number of bound states is limited and that theses levels are called with v the vibrational quantum number :

$$e_v = - \left[1 - a\sqrt{b} \left(v + \frac{1}{2} \right) \right]^2$$

We will use this formula to obtains the theoretical vibrational energies.

To use this formula we need the parameter a and b .

We can get them by the approximation of the rigid rotor model and experimental values :

$$E_{v,J}^0 = E_v + BJ(J+1) v_{0,J \rightarrow v,J+2} = E_{v,J+2}^0 - E_{0,J}^0 = E_v - E_0 + 2B(2J+3)$$

And the experimental values :

$$E_1 - E_0 = 4159,48 \text{ cm}^{-1} \quad E_2 - E_0 = 8083,20 \text{ cm}^{-1} \quad B = 60,80 \text{ cm}^{-1}$$

II.2.3 Shooting method

The shooting method is common method use to find the solution of a problem of integration or derivation with initial condition unknown, in our case this is not a initial condition but we have to try many times to be sure we have find an eigenvalues.

The method is already explained in the practical work and the program will explain this method.

II.2.4 Integration by finite differences

The finite differences method is a method to integrate differential equation with initial conditions. We have to make a line of point space with the same width called the step, our line start with the point r_0 and finish with r_n , we will have N points on our line and for each we can evaluate the function by this method :

$$\psi_i'' = \frac{\psi_{i+1} + \psi_{i-1} - 2\psi_i}{h^2} + O(h^2)$$

We can have the formula for ψ_{i+1} and ψ_{i-1} :

$$\begin{aligned}\psi_{i+1} &= \left\{ 2 + \frac{h^2}{b} \left[b \frac{J(J+1)}{r_i^2} + v_i - e \right] \right\} \psi_i - \psi_{i-1} \\ \psi_{i-1} &= \left\{ 2 + \frac{h^2}{b} \left[b \frac{J(J+1)}{r_i^2} + v_i - e \right] \right\} \psi_i - \psi_{i+1}\end{aligned}$$

The first function can propagate the function to the right that means $r_0 \rightarrow r_m$.

The second can propagate the function to the left that means $r_n \rightarrow r_m$.

These functions we will meet in r_m but for the wrong values of e it can be a discontinuity, so the algorithm of shooting method takes place here with a correction on the energy with δe

II.2.5 Calculation method for δe Cooley's method

In the lectures we have seen ;

$$\langle \psi | H | \psi \rangle / \langle \psi | \psi \rangle = E$$

This equation is true only if E is an eigenvalue, so let's correct the energy if e is not an eigenvalue :

$$\begin{aligned}\delta E &= \langle \psi | H - E | \psi \rangle / \langle \psi | \psi \rangle \\ \delta e &= \frac{\sum_i \psi_i [-b\psi_i'' + (bJ(J+1)/r_i^2 + v_i - e) \psi_i]}{\sum_i \psi_i^2}\end{aligned}$$

We can calculate δe yet, because the method of integration has a term in $O(h^2)$ so the equation is equal to zero except in point r_m . So we have :

$$\delta e = \frac{\psi_m [-b\psi_m'' + (bJ(J+1)/r_m^2 + v_m - e) \psi_m]}{\sum_i \psi_i^2}$$

II.2.6 Case of an arbitrary potential

III Program

The program is given we just have to adapt it to give answers, I have commented it and do a schema to understand it.

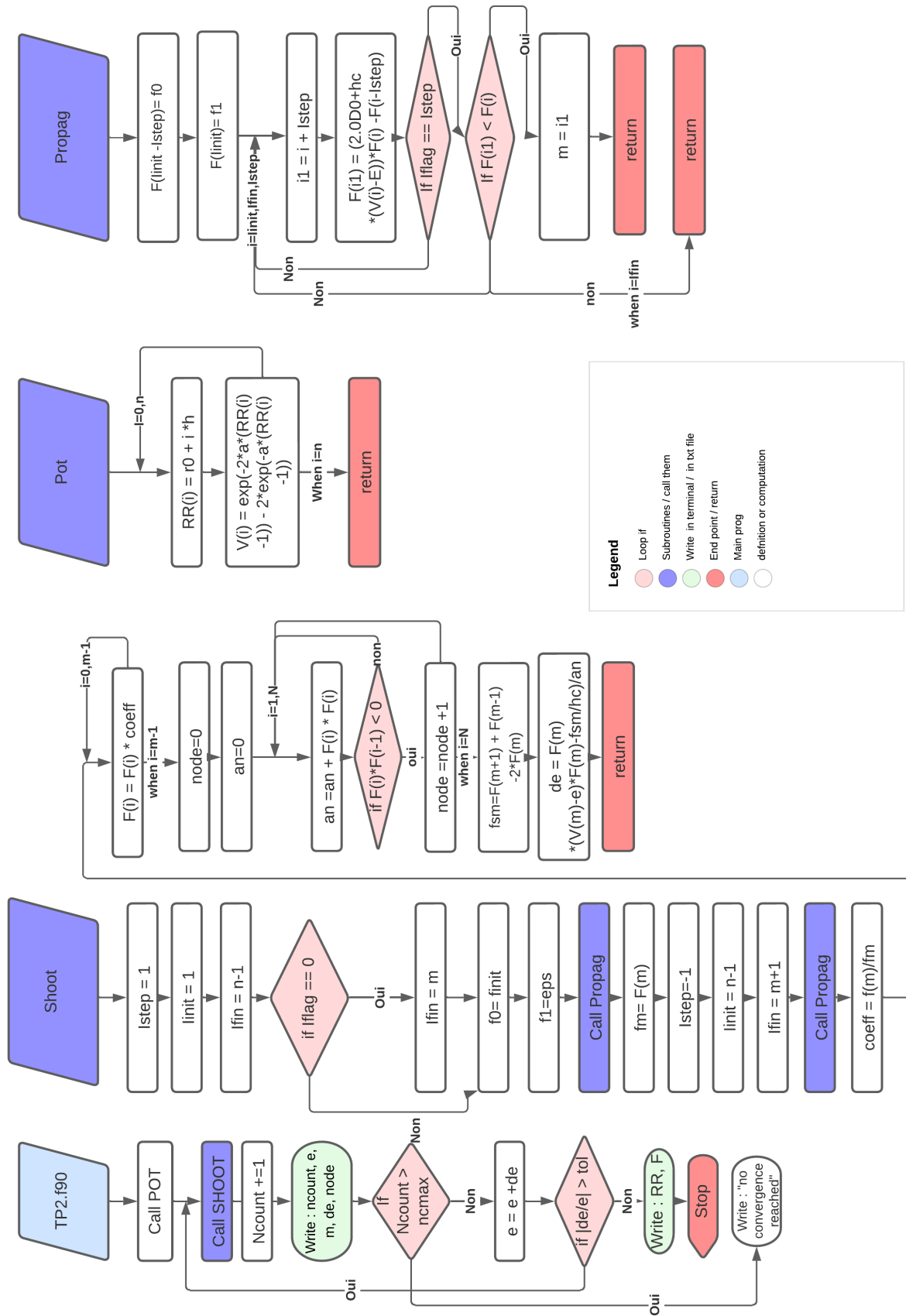


Figure 1: schema of the program

I have added loop to answers to the question but this is the same calculus, to run a part you should comment the other.

IV Questions

IV.1 Determination of the vibrational energies

We can determine the vibrational energies with the program given and compare them with the formula obtain in theoretical part "Potential Model", to find these energies i have try many energy and i have take the most accurate :

v	Theoretical energies	Starting energies	Final energies	number of nodes
0	-0,9470	-0,95	-0,9473	0
1	-0,8455	-0,85	-0,8469	1
2	-0,7497	-0,75	-0,7529	2
3	-0,6597	-0,65	-0,6653	3
4	-0,5755	-0,58	-0,5836	4
5	-0,4969	-0,50	-0,5079	5
6	-0,4242	-0,40	-0,4378	6
7	-0,3572	-0,35	-0,3731	7
8	-0,2960	-0,30	-0,3137	8

Figure 2: Value of vibrational energies numerically and theoretically

In this table the for each vibrational level we have their :

- theoretical energies
- starting energies
- final energies
- number of nodes

We can see the final energies are close to the theoretical one , but more v is high more we have an error for the final value. The number of nodes is links with the vibrational level.

So for high energies level our program is less accurate because the potential has a good behavior for small v but not for the high v .

we can draw the wave function associated to this energies :

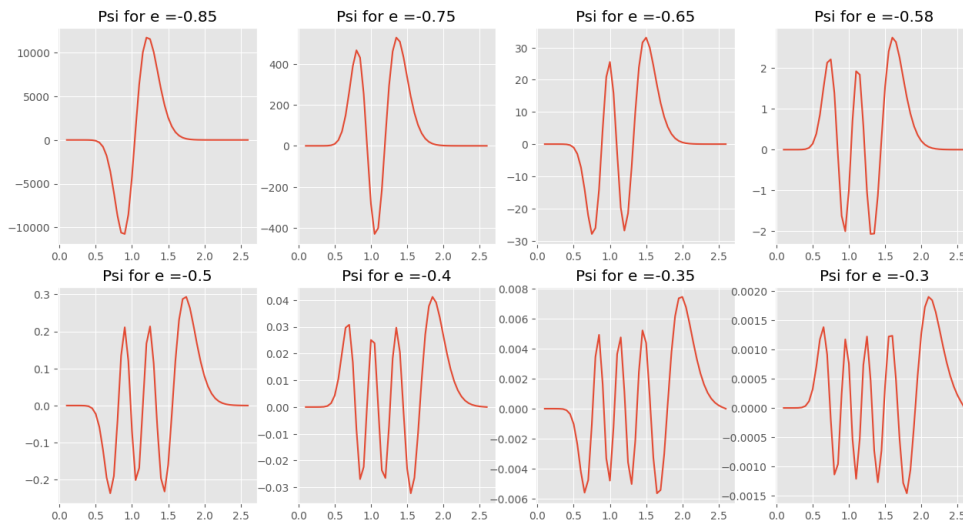


Figure 3: Subplot of the wave function for each numerical energies associated to the vibrational level

I don't specify the axes because with this subplot this becomes unreadable, the x-axis represent r and the y-axis represent Ψ .

On this graph we see clearly the nodes crossing the x-axis in 0, i suppose the value off Ψ is different for each graph because all these wave function are not normalise.

IV.2 Study of variation of the number of iterations

The number of iterations to reach the vibrational energies levels depend on the guess values, in the previous part i just write the most accurate but if try more guess value for the two first v I obtain that :

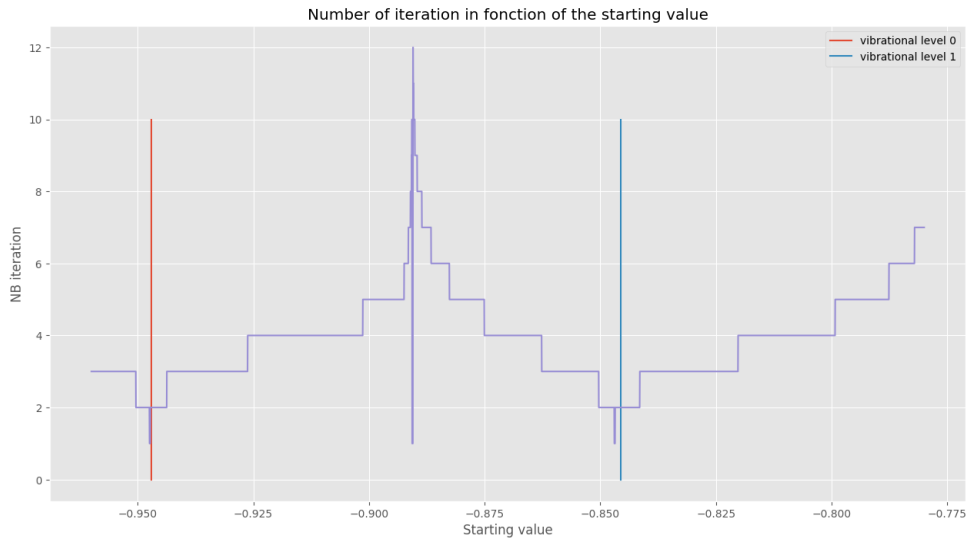


Figure 4: Graph of the variation of iterations in function of the starting value

on this graph we can see the number of iteration decrease more we are close to the theoretical vibrational energies, this make sense because δe is a correction so more we are close of v less is δe . The number of iterations are like step with several starting energies this come from of the parameter τ because for several energies we have quite close correction so we compare them to the same parameter. Finally we can see the important choice of the starting value, if we want v_0 we have to be carefully to don't choose a starting value to far (limit in -0.88).

IV.3 Study of the influence of r_0, r_N, N, ε and τ on the number of iterations

We want study the influence of several parameter on the number of iterations and of the exactness of the vibrational energies. In order to do that I will plot for each parameter two graph, on for the variation of iteration and the other of the variation of the energies found, for the starting energies i have choose $e_1 = 0.85$ to reach the theoretical value of e_1 because in the previous part i have conclude of the accuracy of the first vibrational level:

For r_0 I have change this values from 0.1 at 1.5 and we obtains for v_0 and v_{10} :

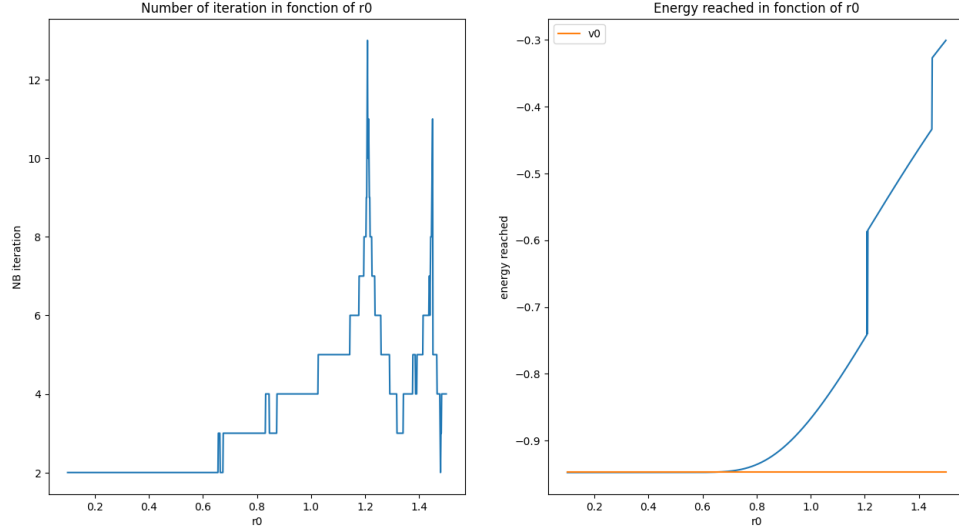


Figure 5: Graph of the variation of iterations in function of r_0 for v_0

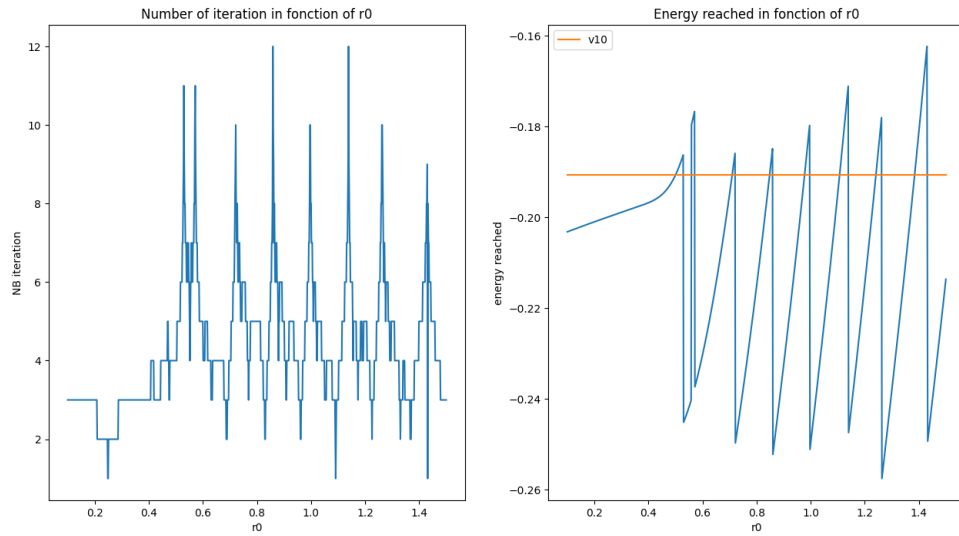


Figure 6: Graph of the variation of iterations in function of r_0 for v_{10}

On these graph we can see the influence of the parameter r_0 , for small value of it the number of iteration is weak and for the big value of it the number of iterations is increasing, we can see the spike like if we missing certain eigenvalue with r_0 too big. The energy has the same behavior at the begging we can see the energy close to the theoretical one and after $r_0 = 0.6$ the final energy diverges.

For $v = 10$ we can see the same behavior for the number of iterations and the final energy but with a more "chaotic" behavior because like i conclude before the high vibrational number are less accurate.

i expect the same behavior for r_n but in opposite.

For r_N I have change this values from 0.1 at 3 and we obtains for v_0 and v_{10} :

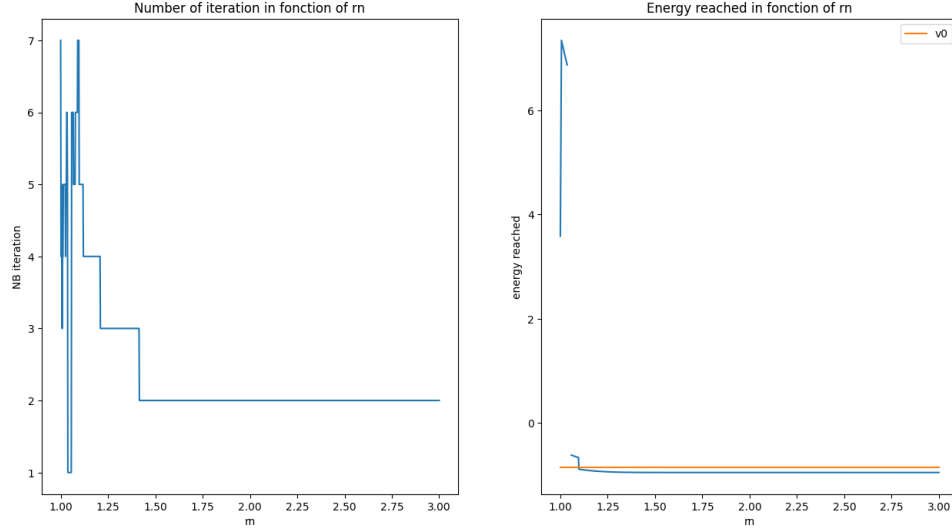


Figure 7: Graph of the variation of iterations in function of rn for v_0

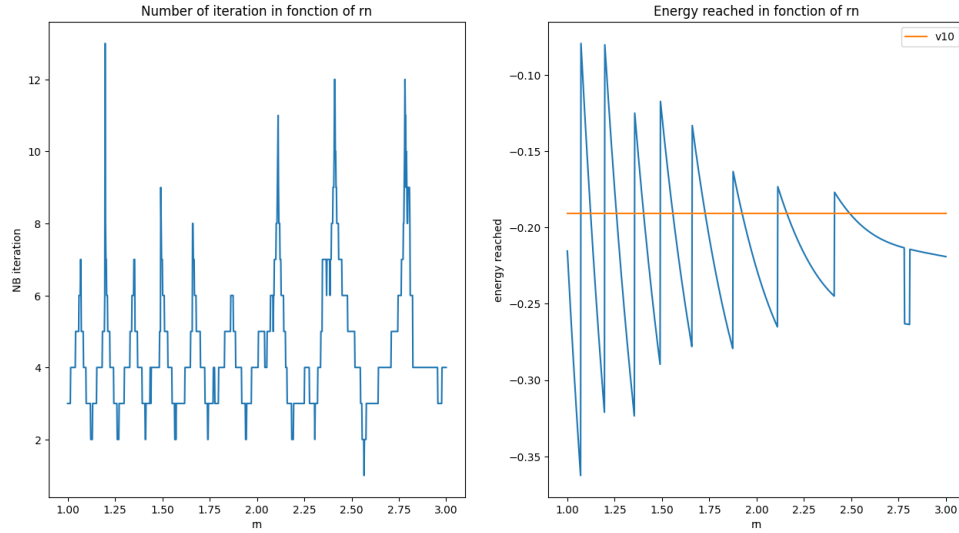


Figure 8: Graph of the variation of iterations in function of rn for v_{10}

On this graph we can see clearly the behavior that i have expected an this is logical because the influence of r_n is the same of r_0 because the both change the distance between the nuclei.

For eps I have change this values from 10^{-7} at 10^{-4} and we obtains for v_0 and v_{10} :

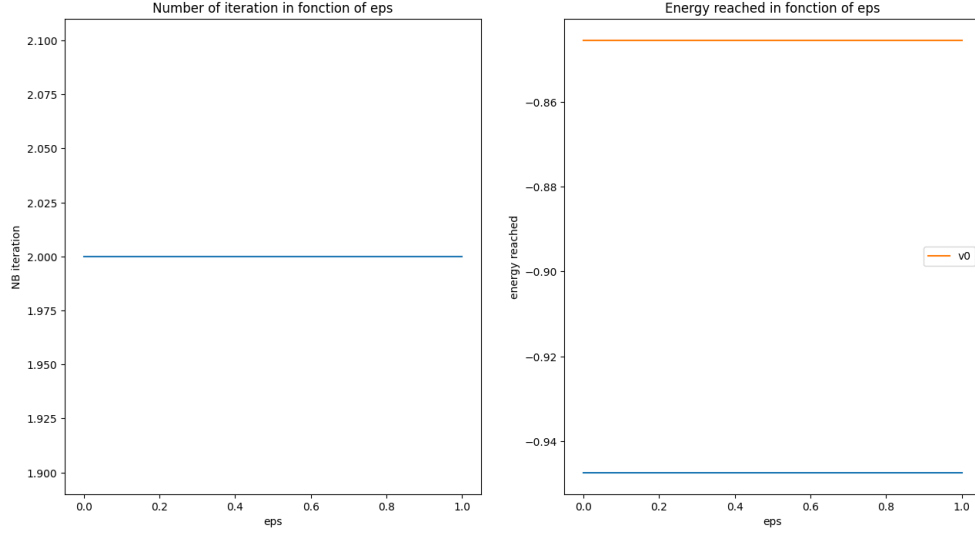


Figure 9: Graph of the variation of iterations in function of ϵ for v_0

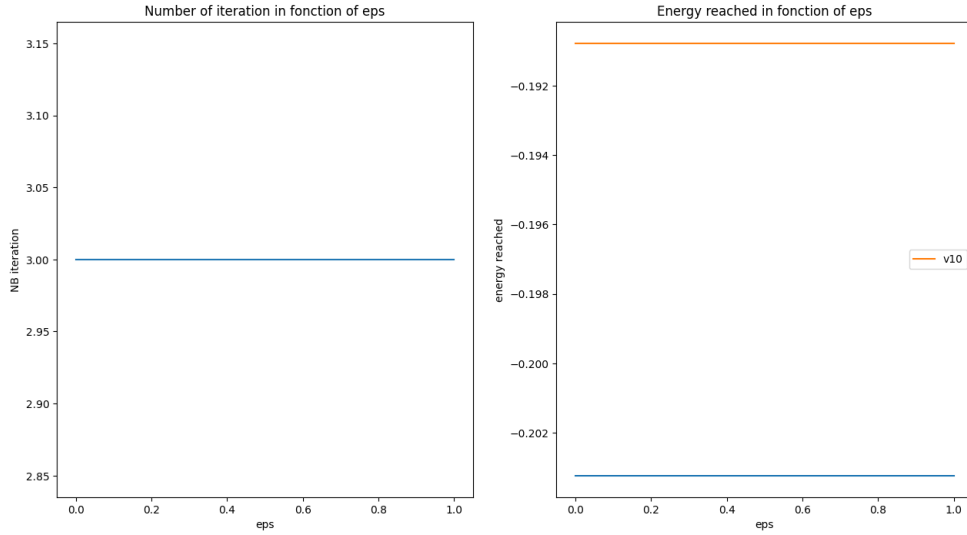


Figure 10: Graph of the variation of iterations in function of ϵ for v_{10}

For these two vibrational the number of iterations or the final energy we can the ϵ has no influence of them. Like that we can think this is strange because ϵ is an important parameter, by it our function is initialize but in the program we normalise the wave-function so the influence is loss with this normalisation.

For tol I have change this values from 10^{-7} at 10^{-4} and we obtains for v_0 and v_{10} :

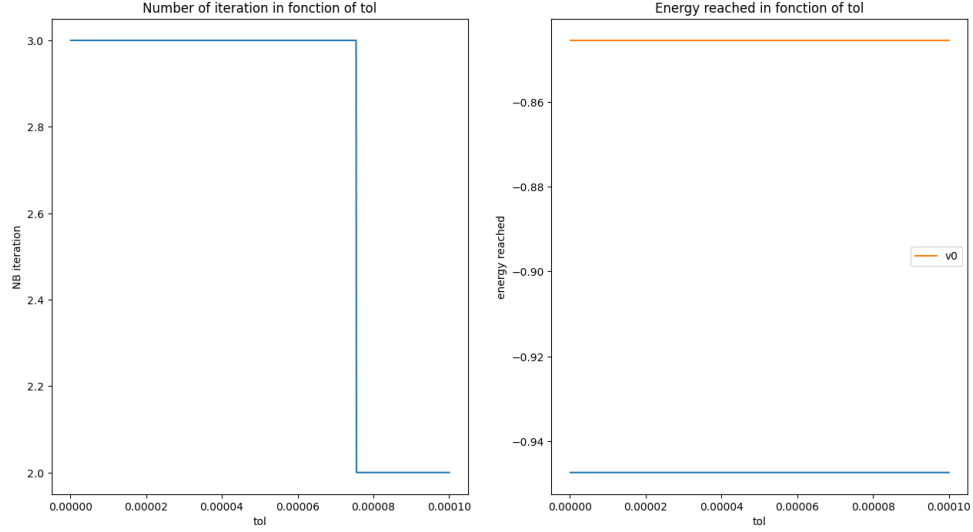


Figure 11: Graph of the variation of iterations in function of tol for v_0

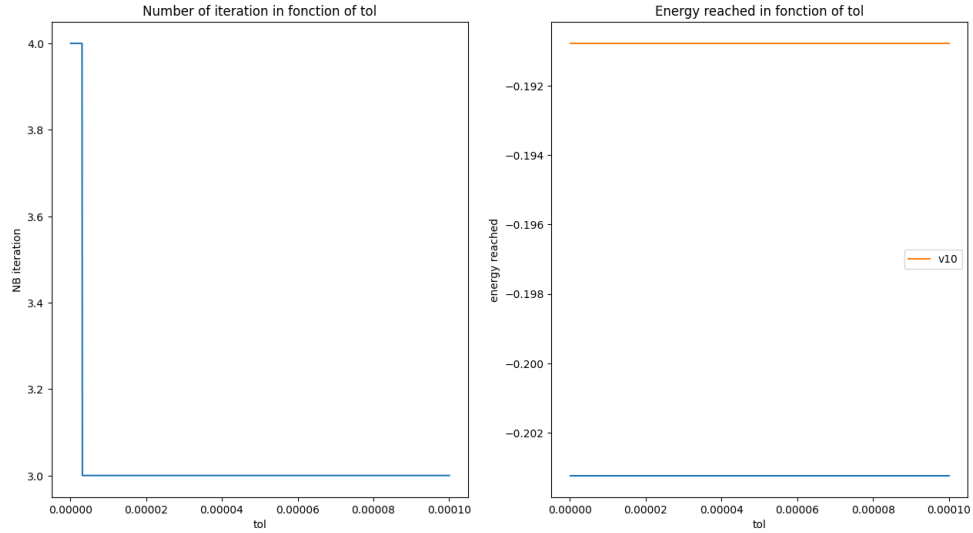


Figure 12: Graph of the variation of iterations in function of tol for v_{10}

On these graph we can see the little influence of τ on the number of iterations and the final energy because this parameter governed our number of iterations so with small values of τ we have more iterations but for final energy value we have the same convergence. We just have to be careful to not choose τ to big.

IV.4 Study of the variation of δe in function of e

Now we want to see the influence of e on δe :

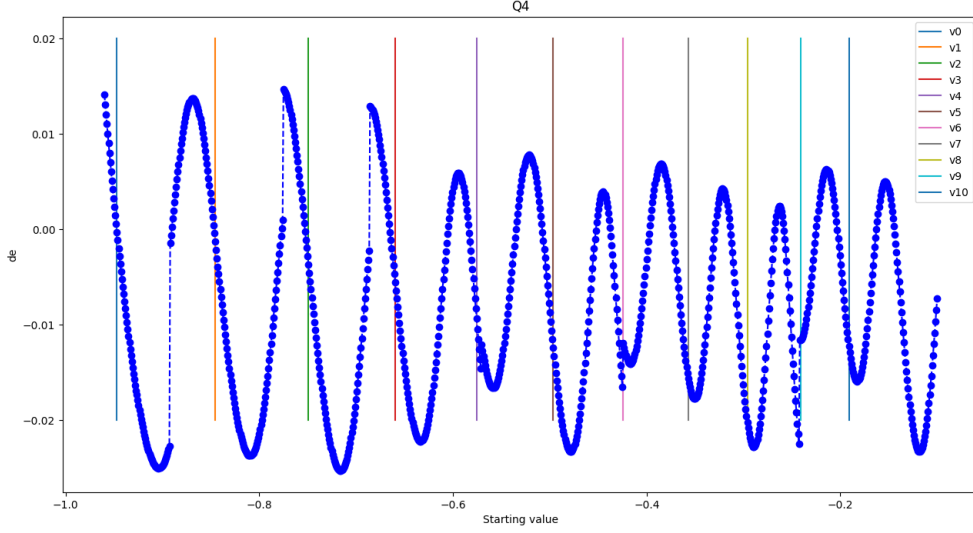


Figure 13: Graph of the variation of δe in function of starting energy

On this graph we can see the graph that we should obtain but we have some cut in the behavior, this is related of the correction on energy and the starting value. If we choose a starting value to far of the theoretical value that we want the program will correct our starting value to converge to the previous of the next. We can see another thing, when the derivative of δe is negative and equal to 0 the starting value is the theoretical one.

V Conclusion

On this practical work we have integrated the Schrödinger's equation with the finite difference method, find the eigenvalue by the shooting method and correct the energy by the Cooley's method. I have seen the flatly computation with FORTRAN because many loops are needed to get all the data. We have seen the influence of several parameter and understand how to get good result.

VI annex

For $J = 0$ we have :

$$\begin{aligned}
 J &= 0 \\
 -b\psi''(r) + [v(r) - e]\psi(r) &= 0 \\
 -b\psi''(r) + [e^{-2a(r-1)} - 2e^{-a(r-1)} - e]\psi(r) &= 0 \\
 x = e^{-a(r-1)} \rightarrow \frac{dx}{dr} = -ae^{-a(r-1)} = -ax \rightarrow dr &= -\frac{dx}{ax} \\
 \psi'(r) \equiv \frac{d\psi(r)}{dr} = \frac{d\psi}{dx}(-ax) = -ax \frac{d\psi}{dx} \\
 \psi''(r) \equiv (\psi'(r))'_r = -a \left(x \frac{d\psi}{dx} \right)'_r &= -a \left(\frac{dx}{dr} \frac{d\psi}{dx} + x \frac{d^2\psi}{dx dr} \right) = \\
 &= -a \left(-ax\psi' + x \frac{d^2\psi}{dx^2}(-ax) \right) = a^2x\psi' + a^2x^2\psi'' \\
 &= -ba^2x(\psi' + x\psi'') + [x^2 - 2x - e]\psi = 0
 \end{aligned}$$

Now we can study his behavior for different values of r :

behavior for $r \rightarrow 0$ (i.e. $x = e^a \gg 1$)

A. Behavior for $r \rightarrow 0$ (i.e. $x = e^a \gg 1$)

$$\exists \Psi(x) \sim e^{-\alpha x}$$

$$-ba^2x(-\alpha e^{-\alpha x} + x\alpha^2 e^{-\alpha x}) + [x^2 - 2x - e]e^{-\alpha x} = 0$$

$$ba^2\alpha x - ba^2\alpha^2x^2 + x^2 - 2x - e = 0$$

$$x^2(1 - a^2b\alpha^2) + x(a^2b\alpha - 2) - e = 0$$

$x \gg 1 \rightarrow$ the coefficient for x^2 must be $= 0$

$$a^2b\alpha^2 = 1$$

$$\alpha^2 = \frac{1}{a^2b}$$

$$\alpha = \frac{1}{a\sqrt{b}}$$

$$\psi(x) \sim e^{-\frac{x}{a\sqrt{b}}}$$

behavior for $r \rightarrow \infty$ (i.e. $x \rightarrow 0$)

$$\Psi(x) \sim x^\beta$$

$$-ba^2 \times (\beta x^{\beta-1} + x\beta(\beta-1)x^{\beta-2}) + [x^2 - 2x - e]x^\beta = 0$$

$$-ba^2(\beta x^\beta + \beta(\beta-1)x^\beta) + [x^2 - 2x - e]x^\beta = 0$$

$$-ba^2\beta^2 + x\downarrow x_0^2 - 2x - e = 0$$

$$-ba^2\beta^2 = e$$

$$\beta^2 = -\frac{e}{ba^2}$$

$$\beta = \sqrt{\frac{-e}{a^2b}} \leftarrow \exists \text{ for } e < 0$$

$$\psi(x) \sim x\sqrt{\frac{-e}{a^2b}}$$

behavior for intermediate r values:

$$\begin{aligned}
\Psi(x) &= e^{-\alpha x} x^\beta \varphi(x) \\
\Psi'(x) &= (e^{-\alpha x} x^\beta \varphi(x))'_x = (e^{-\alpha x} x^\beta)'_1 \varphi(x) + e^{-\alpha x} x^\beta \varphi'(x) = \\
&= [-\alpha e^{-\alpha x} x^\beta + e^{-\alpha x} \beta x^{\beta-1}] \varphi(x) + e^{-\alpha x} x^\beta \varphi'(x) \\
\psi''(x) &= [-\alpha e^{-\alpha x} x^\beta + e^{-\alpha x} \beta x^{\beta-1}]'_x \varphi(x) + [-\alpha e^{-\alpha x} x^\beta + e^{-\alpha x} \beta x^{\beta-1}] \varphi'(x) + \\
&+ [e^{-\alpha x} x^\beta]'_x \varphi'(x) + e^{-\alpha x} x^\beta \varphi''(x) = \\
&= [\alpha^2 e^{-\alpha x} x^\beta - \alpha e^{-\alpha x} \beta x^{\beta-1} - \alpha e^{-\alpha x} \beta x^{\beta-1} + e^{-\alpha x} \beta(\beta-1)x^{\beta-2}] \varphi(x) + \\
&+ [-\alpha e^{-\alpha x} x^\beta + e^{-\alpha x} \beta x^{\beta-1}] \varphi'(x) + \\
&+ [-\alpha e^{-\alpha x} x^\beta + e^{-\alpha x} \beta x^{\beta-1}] \varphi'(x) + e^{-\alpha x} x^\beta \varphi''(x) = \\
&= [\alpha^2 e^{-\alpha x} x^\beta - 2\alpha \beta e^{-\alpha x} x^{\beta-1} + \beta(\beta-1)e^{-\alpha x} x^{\beta-2}] \varphi(x) + \\
&+ 2[-\alpha e^{-\alpha x} x^\beta + \beta e^{-\alpha x} x^{\beta-1}] \varphi'(x) + \\
&+ e^{-\alpha x} x^\beta \varphi''(x) \\
&- ba^2 x \left\{ \frac{[-\alpha e^{-\alpha x} x^\beta + \beta e^{-\alpha x} x^{\beta-1}] \varphi(x) + e^{-\alpha x} x^\beta \varphi'(x)}{\psi'} + \right. \\
&+ x [(\alpha^2 e^{-\alpha x} x^\beta - 2\alpha \beta e^{-\alpha x} x^{\beta-1} + \beta(\beta-1)e^{-\alpha x} x^{\beta-2}) \varphi(x) + 2(-\alpha e^{-\alpha x} x^\beta + \beta e^{-\alpha x} x^{\beta-1}) \varphi'(x) + e^{-\alpha x} x^\beta \varphi''(x)] + \\
&+ [x^2 - 2x - e] e^{-\alpha x} x^\beta \varphi(x) = 0 \quad | : e^{-\alpha x} x^\beta \\
&- ba^2 x \left\{ \left[\left[-\alpha + \frac{\beta}{x} \right] \varphi(x) + \varphi'(x) + x \left[\left(\alpha^2 - 2\alpha \frac{\beta}{x} + \frac{\beta(\beta-1)}{x^2} \right) \varphi(x) + 2 \left(-\alpha + \frac{\beta}{x} \right) \varphi'(x) + \varphi''(x) \right] \right\} + (x^2 - 2x - e) \varphi(x) = \\
&- ba^2 \{ [-\alpha x + \beta] \varphi(x) + x \varphi'(x) + [(\alpha^2 x^2 - 2\alpha \beta x + \beta(\beta-1)) \varphi(x) + 2(-\alpha x^2 + \beta x) \varphi'(x) + x^2 \varphi''(x)] \} + (x^2 - 2x - e) \varphi(x) \\
&[-ba^2 \{ -\alpha x + \beta + \alpha^2 x^2 - 2\alpha \beta x + \beta(\beta-1) \} + x^2 - 2x - e] \varphi(x) + \\
&+ [-ba^2 \{ x + 2(-\alpha x^2 + \beta x) \}] \varphi'(x) + \\
&+ [-ba^2 x^2] \varphi''(x) = 0
\end{aligned}$$

$$\beta a \sqrt{b} = \sqrt{-e}$$

$$\alpha = \frac{1}{a\sqrt{b}} \text{ and } \beta = \frac{\sqrt{-e}}{a\sqrt{b}} \longrightarrow -ba^2 = -\alpha^{-2} \rightarrow \frac{\beta}{\alpha} = \sqrt{-e}$$

$$-e = \frac{\beta^2}{\alpha^2}$$

Normally, $n = 0, 1, 2, \dots$

so that instead considering $\frac{a_n}{a_{n-1}}$

we must consider

$$\frac{a_{n+1}}{a_n} = \frac{\alpha[2(n+1+\beta-\alpha)-1]}{(n+1)(n+1+2\beta)}$$

To get the right homogeneous side of our equation equal to zero, we must have

$$2(n+1+\beta-\alpha)-1=0$$

$$2+2(n+\beta-\alpha)-1=0$$

$$2(n+\beta-\alpha)=-1$$

$$n+\beta-\alpha=-\frac{1}{2}$$

$$n=\alpha-\beta-\frac{1}{2}$$

$$n=\frac{1}{a\sqrt{b}}-\frac{\sqrt{-e}}{a\sqrt{b}}-\frac{1}{2} \leftarrow \text{maximal value: } n \leq \frac{1}{a\sqrt{b}}-\frac{1}{2}$$

$$2a\sqrt{b}n=2(1-\sqrt{-e})-a\sqrt{b} \quad \text{for } e \approx 0$$

$$2(1-\sqrt{-e})=a\sqrt{b}(2n+1)$$

$$1-\sqrt{-e}=a\sqrt{b}\left(n+\frac{1}{2}\right)$$

$$1-a\sqrt{b}\left(n+\frac{1}{2}\right)=\sqrt{-e}$$

$$e=-\left[1-a\sqrt{b}\left(n+\frac{1}{2}\right)\right]^2$$