Solving Schrödinger equation using Numerov Method

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Abstract—The goal of this paper is to solve the Schrödinger radial equation using Numerov method. An other important goal is to test the strength and stability of Numerov method. First we will introduce Numerov calculation in linear step case. After that, we will explain the theoretical solution for bounded states of Hydrogen atom and Helium atom and compare it with respect to numerical approach. Then, conclude on dark points of the algorithm and possible solution to improve the numerical treatment.

I. STUDY CASE: HYDROGEN ATOM

A simple physical system in the universe is the most common 2 body system: the Hydrogen atom. In this case, only the Coulomb interaction between proton and electron is considered as potential and spin effects will be neglected. Only the stationary equation will be explored. Then, the time dependent part is added as a pure time phase depending on the energy: $\Psi(\overrightarrow{r}, t) = \psi(\overrightarrow{r})e^{i\omega_n t}$.

A. Hamiltonian: from arbitrary referential to Mass Center Referential

Consider an electron and a proton described by the following Hamiltonian:

$$H = H_p + H_e + V_{ep}$$

Partial hamiltonians are pure kinetic energies and the potential is taken as pure Coulomb potential, assuming punctual particles:

$$H_p = \frac{P_p^2}{2m_p}; \quad H_e = \frac{P_e^2}{2m_e}; \quad V = \frac{-e^2}{4\pi\varepsilon_0} \frac{1}{|\overrightarrow{r_p} - \overrightarrow{r_e}|}$$

In order to be independent of the point of view of the observer, the system will be described in Mass Center referential. Then, assume the proton equivalent as Mass Center and the electron mass modified as $\mu = \frac{m_p m_e}{m_p + m_e} \approx m_e$. In this referential, the Hamiltonian is dependent of radial coordinates $\overrightarrow{r} = \{r, \theta, \varphi\}$:

$$H = -\frac{\hbar^2}{2\mu}\triangle - \frac{e^2}{4\pi\varepsilon_0}\frac{1}{r}$$

This problem has spherical symmetry so the global wave function will be split in two parts:

$$\psi(r, \theta, \varphi) = R(r)Y_l^m(\theta, \varphi)$$

with the spherical harmonics

$$Y_l^m(\theta, \varphi) = (-1)^{\frac{1}{2}(m+|m|)}\sqrt{\frac{2l+1}{4\pi}\frac{(l-|m|)!}{(l+|m|)!}}P_{l,|m|}(\cos\theta)e^{im\varphi}$$

and Radius function obeying to the following equation:

$$\left[-\frac{\hbar^2}{2\mu}\frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{\hbar^2}{2\mu}\frac{l(l+1)}{r^2} - \frac{e^2}{4\pi\varepsilon_0}\frac{1}{r} - E_{n,l,m}\right]R_{n,l}(r) = 0$$

Note: Three dimensional laplacian is expressed as:

$\triangle = \frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{\mathbf{L}^2}{\hbar^2 r^2}$ with $\mathbf{L}^2$ the quadratic angular momentum operator. This added term represents the centrifugal effect by analogy with classical mechanics [1]–[3].

This is can be again simplified using $u_l(r) = rR(r)$ and then, the first second order term becomes simple second derivative of $u_l(r)$ with respect to r [4]:

$$\left[-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial r^2} + \frac{\hbar^2}{2\mu}\frac{l(l+1)}{r^2} - \frac{e^2}{4\pi\varepsilon_0}\frac{1}{r} - E_{n,l,m}\right]u_l(r) = 0$$

Note: This transformation implies that $\lim_{r\to 0} u_l(r) = 0$, and this new function has to be normalized to conserve the number of particles.

B. Analytical Solution

In this paper, we are only interested in bounded states. Consequently, only negative energies are considered.

For more simplicity, introduce: $\chi = \frac{\sqrt{2\mu E_{n,l,m}}}{\hbar}$, $\rho = \chi r$ and $\rho_0 = \frac{\mu e^2}{2\hbar^2\pi\varepsilon_0\chi}$

The Schrödinger equation is rewritten in more simple terms as:

$$\left[-\frac{\partial^2}{\partial\rho^2} + \frac{l(l+1)}{\rho^2} - \frac{\rho_0}{\rho} - 1\right]u_l(\rho) = 0$$

Short range and long range behavior is vanishing so these constraints implies the following form for the wave function:

$$\lim_{\rho\to\infty} u_l(\rho) \approx e^{-\rho}$$

$$\lim_{\rho\to 0} u_l(\rho) \approx \rho^{l+1}$$

Assume now that $u_l(\rho)$ is a product of the previous functions and $\xi(\rho)$, slowly varying near the bounds:

$$u_l(\rho) = N\rho^{l+1}\xi(\rho)e^{-\rho}$$

with N the normalization coefficient.

$\xi(\rho)$ has to satisfy

$$\left[\rho\frac{\partial^2}{\partial\rho^2} + 2(l+1-\rho)\frac{\partial}{\partial\rho} + (\rho_0 - 2(l+1))\right]\xi(\rho) = 0$$

This equation has no analytical solution then it is necessary to Taylor expand $\xi(\rho)$ as $\xi(\rho) = \sum_{j=0}^{\infty} a_j\rho^j$ that lead to the expression for the coefficients as:

$$a_{j+1} = \frac{2(j+l+1) - \rho_0}{(j+1)(j+2(l+1))}a_j$$

For $j \gg l+1$, $\xi(\rho) \approx a_0 e^{2\rho}$ that is non normalizable. To solve this problem, suppose that the serie can be truncated at $j = n_r$:

$$a_{n_r+1} = 0 \Leftrightarrow 2(n_r + l + 1) = \rho_0$$

Then, define the n quantum number as $n = n_r + l + 1$ that obeys to the conditions $l < n$ and $\rho_0 = 2n$ with n the principal quantum number, l the orbital number and n_r the number of nodes of the radial wave function [3].

Then the energy levels can also be back defined in function of χ like:

$$E_{n,l,m} = -\frac{\hbar^2}{2\mu}\chi^2 = E_1\frac{1}{n^2}$$

Note: All the wave function can be chosen as real functions because there is no energy loss or entanglement in that isolated system.

II. MANY ELECTRONS HYDROGENOID ATOM: HARTREE-FOCK APPROXIMATION

One way to treat N-body problem is first to observe the global Hamiltonian:

$$H = \sum_{i=1}^{N}\frac{p_i^2}{2m_i} + \sum_{j\neq i}V_{int}(|\overrightarrow{r_j} - \overrightarrow{r_i}|)$$

That can be reduces in Mass Center as:

$$H = H_0 + \sum_i V_i(r_i)$$

with $H_0 = \sum_i h_i = \sum_i \frac{p_i^2}{2\mu_i} + V_{2p-e}(r_i)$

and

$$V_i(r_i) = V_{e-e}(r_i) + V_H(r_i) + V_X(r_i) + V_{corr}(r_i)$$

with exchange potential:

$$V_{X_i}(r_i)\psi_i(|\overrightarrow{r_i}|) = \sum_j \int V_{e-e}(|\overrightarrow{r_j} - \overrightarrow{r}|)\psi_j^*(|\overrightarrow{r}|)\psi_i(|\overrightarrow{r}|)\mathrm{d}\overrightarrow{r}\psi_j(|\overrightarrow{r_i}|)$$

Note: Correlations and exchange potential are neglected [5], [6].

The sum over all interacting electrons can be expanded to space integral, considering the density probability for an electron to be at a relative distance from another electron $\eta(|\overrightarrow{r_i}|)$ as:

$$V_H(r_i) = \int V_{e-e}(|\overrightarrow{r_i} - \overrightarrow{r}|)\eta(|\overrightarrow{r}|)\mathrm{d}\overrightarrow{r}$$

However, this electric potential has to satisfy Gauss theorem and can be also expressed in a simpler equation is:

$$\triangle V_H(|\overrightarrow{r_i}|) = -4\pi\eta(|\overrightarrow{r_i}|)$$

A. Density Functional Theory at equilibrium: application to Helium atom

At equilibrium for an Helium atom in vacuum, its two electrons occupy 1s state. So its wave function in Mass Center Referential are both the $|1,0,0\rangle$ wave function. In this case, the density probability function becomes $\eta(|\overrightarrow{r_i}|) = |R_0(r_i)|^2$

The boundaries conditions are $V_H(0) = 0$ (continuum approximation of continuous wave function) and $V_H(\infty) = 1$ (one electron source with Gauss theorem applied to the full space) fix the integration constants.

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

So the new effective one electron potential is given by:

$$V_i(r_i) = V_{e-e}(r_i) + V_H(r_i)$$

The goal is now to solve the Schrödinger equation using this new potential. For this, we will Use Numerov Integration method.

III. NUMEROV METHOD

The objective of Numerov method is to solve the Schrodinger equation. In this case, only the radial equation will be treated because spherical harmonics are considered as well known and tabulated.

A. Numerov method theory

The first step to develop the Numerov algorithm is to write the Schrodinger equation in the following form [7]:

$$\frac{\partial^2 u_l(\rho)}{\partial\rho^2} + Q(\rho)u_l(\rho) = S(\rho)$$

with $Q(\rho)$ and $S(\rho)$, two continuous known functions. in a first time, set $S(\rho) = 0$

The Numerov method consists in local derivative expansion of the wave-function using Taylor series at order 4.

$$u_l(\rho + \delta) = \sum_{j=0}^{4} \frac{\delta^j}{j!} \frac{\partial^j}{\partial \rho^j} u_l(\rho) + O(\delta^5)$$

Then, compare with the Taylor expansion for $u_l(\rho - \delta)$ and vanish the odd terms. Because second order derivative is known, express fourth order in terms of second order's derivatives:

$$\frac{\partial^2 u_l(\rho + \delta)}{\partial \rho^2} + \frac{\partial^2 u_l(\rho - \delta)}{\partial \rho^2} - 2\frac{\partial^2 u_l(\rho)}{\partial \rho^2} = \delta^2 \frac{\partial^4 u_l(\rho)}{\partial \rho^4}$$

Compare again with the second order derivative taken at $\rho - \delta$ and insert it in initial expansion to get:

$$T_1 u_l(\rho + \delta) = -T_2 u_l(\rho - \delta) + T_3 u_l(\rho)$$

with
$T_1 = (1 + \frac{\delta^2}{12} Q(\rho + \delta))$ $T_2 = (1 + \frac{\delta^2}{12} Q(\rho - \delta))$
$T_3 = 2(1 - \frac{5\delta^2}{12} Q(\rho))$

If $S(\rho) \neq 0$, add S_1, S_2, S_3 on the right side with

$$S_1 = \frac{\delta^2}{12} S(\rho + \delta), \ S_2 = \frac{\delta^2}{12} S(\rho - \delta), \ S_3 = \frac{10\delta^2}{12} S(\rho)$$

To perform the integration, the two first values have to be set hardly. Because the Schrödinger equation is of the form: $S[\rho] u_l(\rho) = 0$ with $S[\rho]$ the Schrödinger operator, the associated wave function $u_l(\rho)$ does not depend on the scale of the space in which the equation is solved.

Consequently, the first hardly set value of the wave function does not affect the final expression of the function because its impact is canceled by normalization.

There is two ways to perform the integration: outward from zero to infinity and inward from infinity to zero. The wave function minimizes the difference between both of these methods.

IV. ALGORITHM

In order to get the most simple potential in the program, the Rydberg Unity is used and the Schrodinger equation is also transformed into:

$$(-\frac{\partial^2}{\partial \rho^2} + \frac{l(l+1)}{\rho^2} - \frac{2Z}{\rho} + V_H(\rho) - E) u_l(\rho) = 0$$

Note: Z is the number of nuclei in the nuclei.

A. Hydrogen atom

In this first case, Hartree potential is null and the we identify: $Q(\rho) = -\left[\frac{l(l+1)}{\rho^2} - \frac{2}{\rho} - E \right]$ and $S(\rho) = 0$ to apply Numerov method.

The aim is to find the eigen energy of the hydrogen atom for a given quantum configuration defined by the two quantum numbers n and l that fixes the number of nodes and orbital momentum of the associated wave function.

The first step is to find the eigen energy. Because we are interested in bounded states, the starting energy is set as positive $+1 Ryd$ and then decrease linearly with a 10^{-2} energy step until the associated wave function has n_r or $n_r + 1$ nodes. This defines an energy range containing the researched eigen energy.

The starting energy has to be set higher than the maximum value of the concerned potential. For Hydrogen potential, this maximum is zero and for Hartree-added potential, it could be positive. However Hartree potential converges to 1 at the origin so it defines the upper limit in both cases.

To increase energy accuracy, there are two methods:
1) Mid point method reducing linearly the interval until minimum energy accuracy. Here, the limit is set at $10^{-8} Ryd$. The final energy is taken at the middle of the last energy range.
2) Secant method using the difference between the logarithmic derivative of the outward and inward wave function. If this difference vanishes, both wave functions are equal and the "good" energy is found.

Note: Secant method needs a matching point to evaluate the logarithmic derivative ratio and is the fastest method. However Mid point method is the strongest.

A shot test of Secant method has been done during this project. However the result diverges all the time. The most possible source of this fatal error is surely an error in the main code. However, time restrictions did not allow to purchase in this way. That's why Mid point method will be used because of its high stability.

The link between inward and outward integrated wave function is done at ρ_0 by normalization with respect to its value at this point. This matching point ρ_0 is taken at $Q(\rho_0) = 0$ which means that the wave function "crosses" the potential barrier so it never vanishes because of its exponential behavior.

Then the final wave function is: $\psi_{final}(\rho) = \psi_{outward}(\rho)$ if $\rho < \rho_0$ and $\psi_{final}(\rho) = \psi_{inward}(\rho)$ if $\rho > \rho_0$
The last step is to normalize the final wave function to 1.

B. Hartree potential

Hartree potential is defined from Poisson equation. Inserting $V_H(\rho) = \frac{C_H(\rho)}{\rho}$ in three dimensional Poisson equation and using the source $\eta(\rho) = -\frac{|u_l(\rho)|^2}{4\pi \rho^2}$ we get the differential equation:

$$\frac{\partial^2}{\partial \rho^2} C_H(\rho) = -\frac{|u_l(\rho)|^2}{\rho} = -4\rho e^{-2\rho}$$

In Numerov terms, we identify $Q(\rho) = 0$ and $S(\rho) = -4\rho e^{-2\rho}$

Then, proceed to simple integration.

Note: Applying boundaries conditions to $C_H(\rho)$ gives the following analytical solution: $C_H(\rho) = 1 - (\rho + 1)e^{-2\rho}$ because Hartree potential vanishes at infinity and is finite at the origin. Moreover, integrating this potential over all space sends the source charge considered by Gauss theorem.

C. Helium atom

To get the Helium wave functions, the program is the same than for Hydrogen atom. However, the Hartree potential in introduced into the $Q(\rho)$ term. Be careful that this new potential can get positive values so starting energy should be upper than than the maximum of the potential.

V. RESULTS AND INTERPRETATION

A. Hydrogen atom

The first point to check is the eigen energies that should follow Rydberg's rule. Table I represents the eigen energies computed for three first quantum numbers.

n	l	energy
1	0	-0.999934010505677
2	0	-0.2499917654855347
2	1	-0.2500000047683716
3	0	-0.11110867023468016
3	1	-0.11111111164093015
3	2	-0.11111111164093015

Table I

NUMERICAL ENERGY VALUES FOR THREE FIRST QUANTUM NUMBERS

The difference between theoretical expectations and numerical results is of the order of 10^{-5} that is greater than energy accuracy imposed in the program. This is a mark of the divergence of the method during the integration. Here we can observe the impact of finite integration on integration path and then, on eigen energies.

Then, check the match between the eigen wave functions for Hydrogen ground state. In figure 1 we compare theoretical expectations with respect to numerical solution for 1s state.
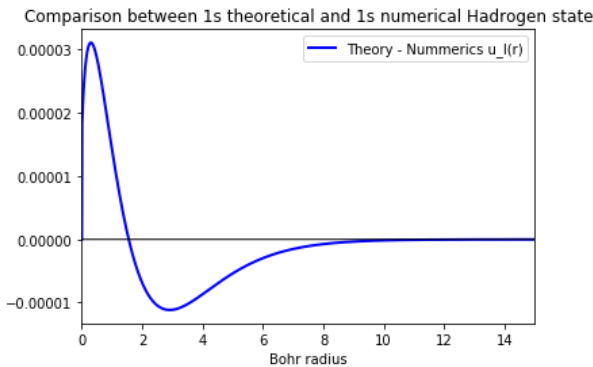
Figure 1. Comparison between theoretical wave function and Numerov applied numerical solution with respect to radial coordinate for Hydrogen 1s state

The existence of null value shows a shift and an amplitude difference between the two functions. This is due to the finite length of integration that leads to a quite well normalization on this interval and a small uncertainty on energy definition. The error is 4 order of magnitude smaller than the radial wave function amplitude. This is satisfying.

The nest point to check is the behavior of the wave function for different quantum numbers and its orthogonality properties. Table II shows the scalar product between different wave function having the same orbital momenta.

Wave functions	Scalar product
1s-2s	5.915324734084773e-11
1s-3s	-5.759003851325721e-12
2p-3p	1.62020593958428926e-10

Table II

ORTHOGONALITY OF THE WAVE FUNCTIONS HAVING THE SAME ORBITAL MOMENTA FOR HYDROGEN ATOM THREE FIRST QUANTUM NUMBERS

The orthogonality properties are respected and the residual value can be attributed to finite range integration.

B. Hartree Potential

To get Hartree potential, we use 1s wave function performed by Hydrogen Numerov program. Take care on calculating first the global charge carried by 1s wave function by integrating it over all space in Hartree units. This induces a scale transformation of the laplacian and the differential equation becomes:

$$\frac{\partial^2}{\partial \rho^2} C_H(\rho) = -4 \frac{|u_l(\rho)|^2}{\rho}$$

with $u_l(\rho)$ the reduced radial wave function in Rydberg units.

Then, integrate the source using Numerov method with $Q(\rho) = 0$ and $S(\rho) = -4\frac{|u_l(\rho)|^2}{\rho}$

The integrated reduced Hartree potential with respect to radial coordinate and the real Hartree potential are available in appendix figure 10 and 11. The boundaries are correctly respected.

The figure 2 compares theoretical expectations for Hartree potential with respect to Numerical solution. The order of magnitude of the difference is also small compared to the potential value (~ 1).
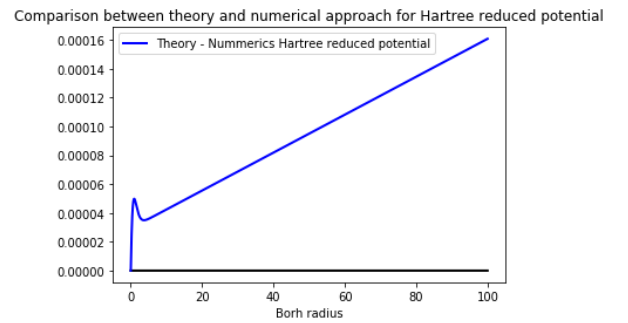

Figure 2. Comparison between theory and numerical approach for Hartree reduced potential applied to Helium atom with one electron source

The linear part of the error curve shows that the numerical potential does not converge to 1 but to the integration of the source. This integration is derived from numerical Schrödinger equation solution. In this case, numerical errors add up. The difference between theoretical source and numerical performed source is 0,000160873912 that correspond to the final value of the error (read at infinity).

The last point of this curve represents the difference between the theoretical total charge and the integration of the source over all space. Numerically, this difference is worth 0,000160873912 that correspond to the final value of the error read at infinity.

The linear part is the limited expansion of the difference between two decreasing expressions taken at infinity.

The behavior of the curve near the origin is a superposition of linear part (described previously) and integration of the difference between theoretical and numerical 1s wave function.

C. Helium atom

In the case of Helium atom, the electron interacts with two protons Coulomb potential and Hartree potential. To check the behavior of the wave function, we introduce the analytical Hartree potential into global potential. This is possible only for ground state because of DFT definition so we are allowed to check only $1s^2$ state. The figure 3 shows the wave functions for Hydrogen atom and Helium atom.
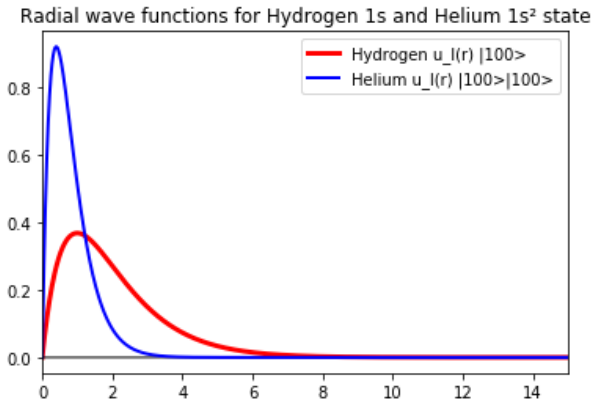
Figure 3. Hydrogen 1s and Helium 1s wave functions with respect to radial coordinate

This situation suggests that electrons are closer to the nuclei and with a restricted dispersion. This is coherent with noble gas behavior and semi-screening effect due to Hartree approach. This is also coherent with an electron in two proton potential screened by a diffused single electron.

D. Strength of Numerov method

By construction, Numerov method is a fourth order combination of Taylor expansion of the function to integrate. This expansion includes a second order average of the second member of the associated second order differential equation. Then, the accuracy of the integration takes into account the local curvature of the second member.

Consequently, the concerned function has to be twice continuously derivable !

A higher order expansion would add four correction terms and the time needed to perform it will be multiplied by four at least. The correction being of order four in integration step, the gain seems to be small for a "slowly varying" function with respect to the integration step.

This fourth order expansion is also very efficient to solve second order differential equation of the form $\left[\frac{\partial^2}{\partial \rho^2} + Q(\rho)\right] u_l(\rho) = S(\rho)$ only if the $Q(\rho)$ associated operator is completely known and purely multiplicative. Moreover, the second member has to be smooth enough with respect to $u_l(\rho)$. Otherwise, the fast oscillations cannot be taken into account and the result will look like an "averaged" function with respect to the expected function.

VI. CONCLUSION

Hydrogen atom is analytically well known. It's properties are fully defined by the three quantum numbers n,l,m. Hartree mean-field method neglects exchange and correlations between electrons and restricts the study to ground state electrons interactions using density functional theory. However its expectations are coherent with physical meaning of stable many-electrons atom.

Numerov expansion to sixth order is the most performing expansion for second degree differential equations. A higher order expansion will cost a lot of time of calculation relatively to the accuracy gain.

The application of the Numerov method on Hydrogen and Helium atom shows a 10^{-6} accuracy with respect to theoretical expectations. Moreover, the computing time is of the order of a few seconds. It is still acceptable.

Finally, we recover the expected behavior for Hydrogen atom and Helium atom electrons. Screening effect without exchange leads to stabilize the atom however it restricts our exploration to ground state for Helium atom.

VII. OPENING

My approach is limited to Hartree approach of Hydrogen atom. It could be interesting to expand this work to two interacting Hydrogen atom and explore the influence of the overlap of the electronic wave functions to stabilize Hydrogen links. This could lead to develop a physical explanation for the Di-Hydrogen molecule stability.

During this project, a cycle in "convergence dimmer program" (see appendix) has appear. It could be interesting to explore the cycling values of that kind of approach to develop a "range reducer program" faster than Mid Point method.

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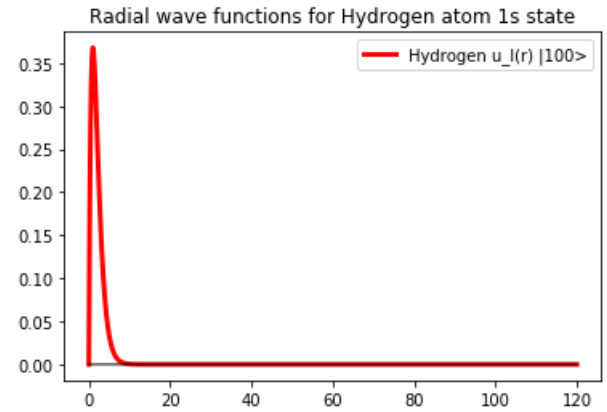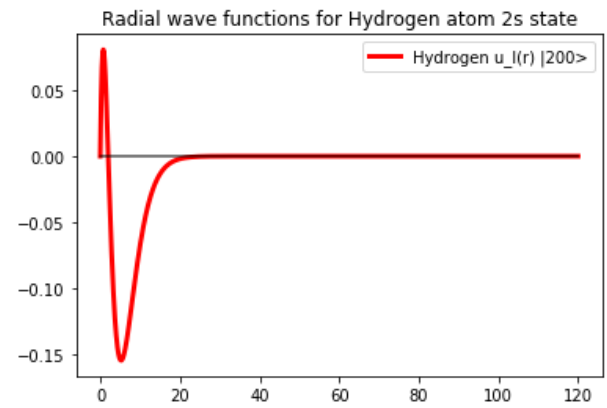
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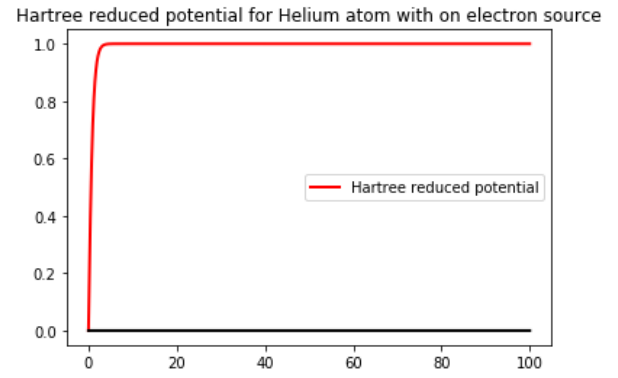
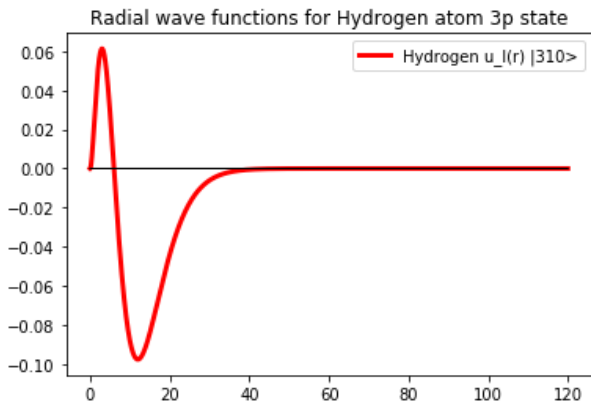Figure 10. Reduced Hartree potential integrated by Numerov method with respect to radial coordinate.
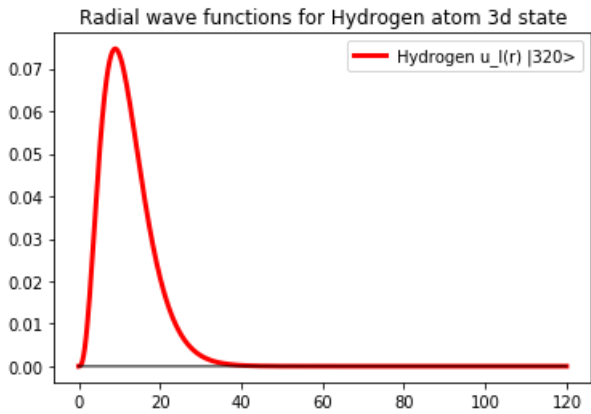

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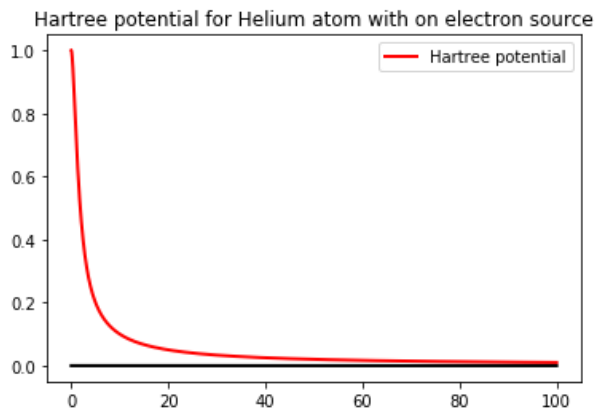

Figure 9. 3d Hydrogen wave function

Figure 11. Hartree potential integrated by Numerov method with respect to radial coordinate