

# TIF320 Assignment 1

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## 1 Task 1

The goal of this task was to calculate the ground state energy and wave function of helium using the Hartree-Fock method. Here, the particle wave function is assumed to be a product of the two uncorrelated single-electron wave functions. By parameterization of the single-electron wave function with,

$$\Phi(r) = \sum_{p=1}^4 C_p \chi_p(r) \quad (1)$$

and applying the Hamiltonian, we acquire equation (2).

$$\left[ -\frac{1}{2} \nabla_1^2 - \frac{2}{r_1} + \sum_{r,s=1}^4 C_r C_s \int d^3 r_2 \chi_r(\mathbf{r}_2) \chi_s(\mathbf{r}_2) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right] \sum_{q=1}^4 C_q \chi_q(r) = E' \sum_{q=1}^4 C_q \chi_q(r) \quad (2)$$

From equation (2) we can multiply the equation with  $\chi_p \mathbf{r}_1$  and integration over  $\mathbf{r}_1$  gives equation (3).

$$\sum_{pq} \left( h_{pq} + \sum_{rs} C_r C_s Q_{prqs} \right) C_q = E' \sum_{pq} S_{pq} C_q \quad (3)$$

Where shorthand notations have been used for the different elements, see equation (4).

$$\begin{aligned} h_{pq} &= \langle \chi_p | -\frac{1}{2} \nabla^2 - \frac{2}{r} | \chi_q \rangle \\ Q_{prqs} &= \int d^3 r_1 d^3 r_2 \chi_p(\mathbf{r}_1) \chi_r(\mathbf{r}_2) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \chi_q(\mathbf{r}_1) \chi_s(\mathbf{r}_2) \\ S_{pq} &= \langle \chi_p | \chi_q \rangle \end{aligned} \quad (4)$$

By fixing  $C_r$  and  $C_s$ , equation (3) becomes a generalized eigenvalue problem in order to solve  $C_q$  which can be put into a self-consistency iteration. There we solve for  $C_q$  and then update  $C_r$  and  $C_s$  for each iteration to find the ground state, see equation (5) for the ground state equation,

$$E_G = 2 \sum_{pq} C_p C_q h_{pq} + \sum_{pqrs} Q_{prqs} C_p C_r C_s . \quad (5)$$

To calculate the shorthand elements of  $h_{pq}$ ,  $Q_{prqs}$  and  $S_{pq}$  we utilize Gaussian s-functions to find,

$$\chi(\mathbf{r}) = \exp(-\alpha_p r^2) \quad (6)$$

The algorithm is based on the Schrödinger equation of independent particles combined with a self-consistent iteration process. A particular choice of  $C_p$  is used to determine the terms in the Schrödinger

equation, and then the Schrödinger equation is solved to find the new  $C_p$ . This process is iteratively repeated until the energy eigenvalue is converged. See figure 1 where atomic units has been used.

Atomic units are defined as the unit system where the physical constants the reduced Planck constant  $\hbar$ , the elementary charge  $e$ , the Bohr radius  $a_0$  and the electron rest mass  $m_e$  are set to unity. Whenever the units a.u. are used in this report, the atomic base units are implied. E.g. for energy, the atomic base unit is  $1 E_h = 27.211 \text{ eV}$ .

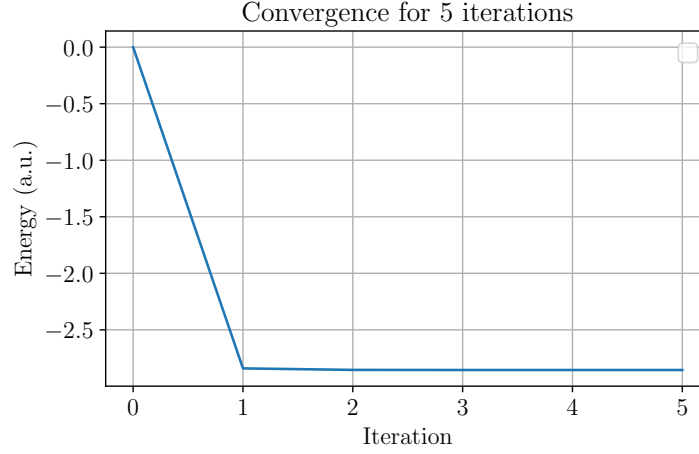


Figure 1: Energy convergence until  $\Delta E < 10^{-5}$ . Notice the quick convergence that requires only five iterations.

The optimal values for the  $\alpha_p$  were given and an initial guess of equal  $C_p$  was made. The algorithm was constructed to find the ground state energy and was run until the energy change was less than  $10^{-5} \text{ eV}$ . This gave a value of

$$\begin{aligned} E_0(5 \text{ iterations}) &= -2.85515991 \text{ a.u.} \\ E_0(50 \text{ iterations}) &= -2.85516038 \text{ a.u.} , \end{aligned}$$

after five iterations and 50 iterations respectively where a.u. stands for the Hartree atomic units. The energy convergence with 5 iterations is shown in Figure 1. The goal of the exercise was

$$E_0(\text{goal}) = -2.85516038 \text{ a.u.} ,$$

with which our solution agrees to the 9th decimal place. The wave functions for both the 5th and 50th iteration are shown in Figure 2 and look nearly identical.

## 2 Task 2

The Poisson equation,  $\nabla^2 \Psi = \sigma(x)$ , can be solved numerically by a combination of grid-discretization and application of the finite differences method. After implementing the algorithm in the assignment, this was tested with the ground state energy for hydrogen by exploiting the radial symmetry which gives

$$\frac{d^2}{dr^2} U_0(r) = -\frac{u^2(r)}{r} = -\frac{4\pi r^2 \psi_{1s}^2}{r} , \quad (7)$$

where the last step uses the equality  $u(r) = \sqrt{4\pi r} \psi(r)$ . As a discretized version, this equation is

$$\frac{d^2}{dr^2} U_0(r_i) = \frac{U_{i-1} - 2U_i + U_{i+1}}{\Delta r^2} = -\frac{u^2(r_i)}{r_i} = f_i , \quad (8)$$

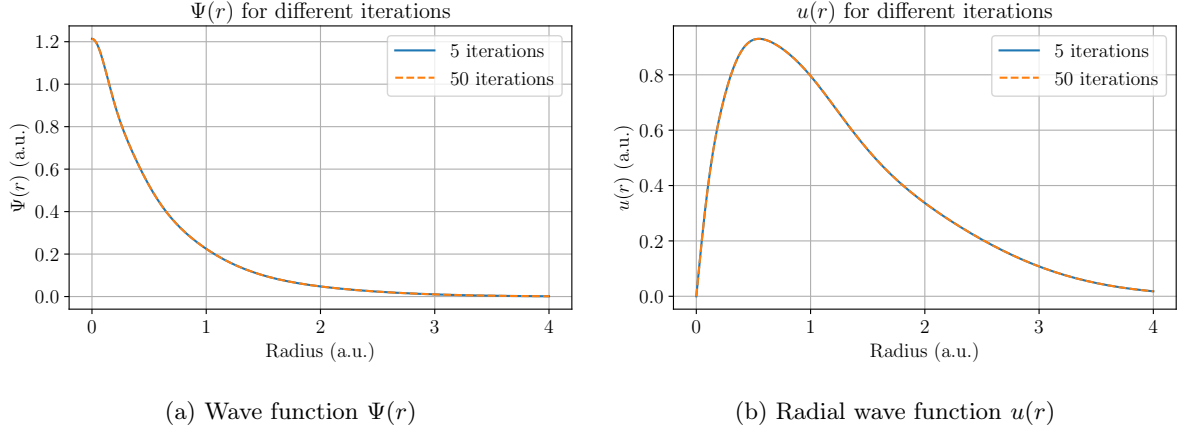


Figure 2: Wave function for the 5th and 50th iteration. Because both are nearly identical, the wave function after 50 iterations is drawn with a dashed line.

with the boundary conditions  $U_0(0) = U_0(r_{\max}) = 0$ . This was solved numerically as the solution of  $\mathbf{U}_0$  in the matrix equation  $A\mathbf{U}_0 = \mathbf{f}$  with

$$A = \frac{1}{\Delta r^2} \begin{pmatrix} 1 & 0 & 0 & \dots \\ 1 & -2 & 1 & 0 & \dots \\ 0 & 1 & -2 & 1 & 0 & \dots \\ \dots & & & & & \\ \dots & & 0 & 1 & -2 & 1 \\ \dots & & & 0 & 0 & 1 \end{pmatrix}, \quad \mathbf{f} = \begin{pmatrix} 0 \\ f_1 \\ f_2 \\ \dots \\ f_{n-1} \\ 0 \end{pmatrix} \quad (9)$$

and  $r_0 = 0$ .

By solving equation (7) we should obtain the Hartree-potential which enables a comparison of the code accuracy. By running with a 1D-grid size, or grid spacing, of  $\Delta r = 0.005 \text{ a.u.}$  and  $n = 2000$  points a good agreement with the exact Hartree-potential

$$V_{H,\text{exact}} = \frac{1}{r} - \left(1 + \frac{1}{r}\right) e^{-2r} \quad (10)$$

could be found, which can be observed in Figure 3. This agreement strongly indicates that the correct method has been used, as it corresponds strongly to the exact solution.

### 3 Task 3

The Kohn-Sham equation is in nature similar to the solution of task 2 by utilizing the same grid-discretization and then the finite difference method to obtain an eigenvalue.

The Kohn-Sham equation for hydrogen (radial Schrödinger equation) is

$$\left(-\frac{1}{2} \frac{d^2}{dr^2} - \frac{1}{r}\right) u(r) = E u(r). \quad (11)$$

This is solved numerically by finding the lowest energy eigenvalue  $E_0$  and the corresponding eigenvector of the equation  $M\mathbf{u} = E\mathbf{u}$  with

$$M = -\frac{1}{2}A + V \quad (12)$$

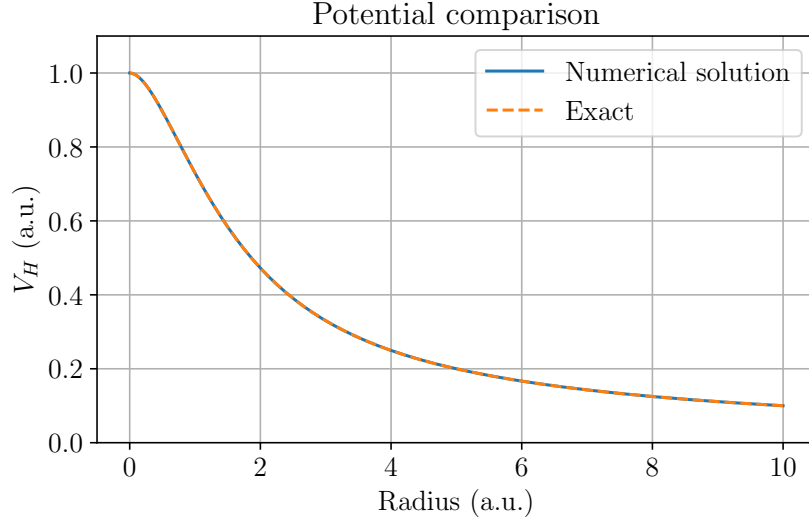


Figure 3: Comparison of the exact and the numerically solved Hartree-potential. Notice the close agreement with the exact solution.

where  $A$  is taken from eq. 9 and  $\text{diag}(V)$  is a matrix with the potential  $V(r_i) = -1/r_i$  on the diagonal. To account for the boundary conditions (by not including them), the first and last rows and columns in  $M$  are set to 0 and then  $u(r_0) = u(r_{\max}) = 0$  after solving the eigenvalue equation. In particular in this task

$$M = \begin{pmatrix} 0 & 0 & 0 & \dots & 0 & 0 \\ 0 & +\frac{1}{\Delta r^2} - \frac{1}{r_1} & -\frac{1}{2\Delta r^2} & \dots & 0 & 0 \\ 0 & -\frac{1}{2\Delta r^2} & +\frac{1}{\Delta r^2} - \frac{1}{r_2} & -\frac{1}{2\Delta r^2} & \dots & 0 \\ 0 & \dots & \dots & \dots & \dots & 0 \\ 0 & \dots & -\frac{1}{2\Delta r^2} & +\frac{1}{\Delta r^2} - \frac{1}{r_{n-2}} & -\frac{1}{2\Delta r^2} & 0 \\ 0 & \dots & 0 & -\frac{1}{2\Delta r^2} & +\frac{1}{\Delta r^2} - \frac{1}{r_{n-1}} & 0 \\ 0 & 0 & 0 & \dots & 0 & 0 \end{pmatrix}. \quad (13)$$

With a grid spacing of  $\Delta r = 0.005 \text{ a.u.}$  and a number of grid points  $n = 2000$ , the numerical method was employed by solving the radial Schrödinger equation for hydrogen. This gave the results in Figure 4 where the solution is compared to the known exact radial wavefunction

$$u_{\text{exact}}(r) = 2re^{-r}. \quad (14)$$

The resulting ground state energy is  $-0.5000 \text{ a.u.}$ , which differs compared to the exact value of  $-0.4998 \text{ a.u.}$  with roughly  $0.04 \%$  [1].

## 4 Task 4

The procedures used in task 2 and 3 are now applied to helium instead of hydrogen. The Kohn-Sham equation in radial coordinates for helium is

$$\left[ -\frac{1}{2} \frac{d^2}{dr^2} - \frac{2}{r} + V_H(r) + V_x(r) + V_c(r) \right] u(r) = \varepsilon u(r). \quad (15)$$

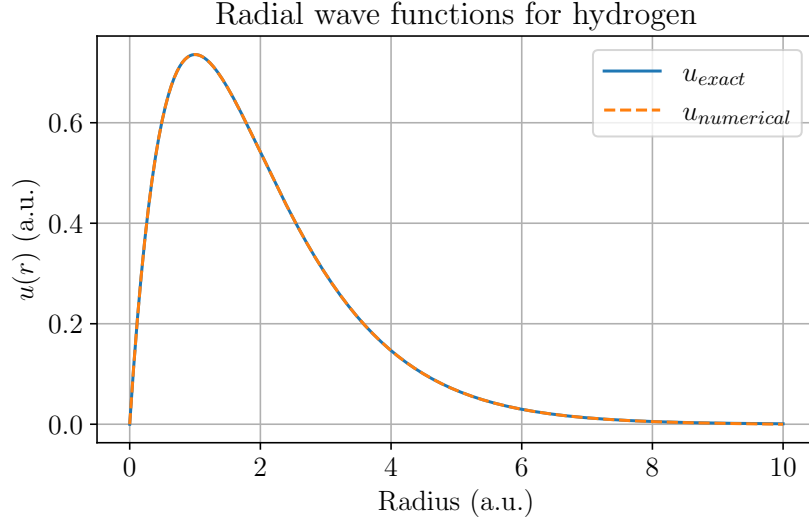


Figure 4: Comparison of the exact hydrogen wave function to the numerical solution with the finite differences method.

Similar to task 3 this equation is solved for  $u(r)$  and  $\varepsilon$  numerically using the finite difference method. The eigenvalues and eigenvectors of  $M$  (equation 13) with

$$V(r_i) = -\frac{2}{r_i} + V_H(r_i) \quad (16)$$

are calculated numerically. The energy eigenvalue is then calculated through

$$E_0 = 2\varepsilon - 2 \int dr u^2(r) \left[ \frac{1}{2} V_H(r) + V_x(r) + V_c(r) - \varepsilon_x(r) - \varepsilon_c(r) \right]. \quad (17)$$

Here,  $V_H$  is taken as the solution of the matrix equation used in task 2 with an initial guess of

$$u(r) = 2re^{-r}. \quad (18)$$

$V_x$  and  $V_c$  are not considered in this task. Then the found eigenvector  $u(r)$  of  $M$  is used as a new initial guess for  $V_H$ . This algorithm is then repeated until the energy changes less than  $10^{-5}$  eV.

To find a sufficient grid precision, then the whole procedure is repeated with changing grid parameters. First,  $r_{\max}$  is increased (with  $\Delta r = 0.1$  a.u.) and then  $\Delta r$  is decreased. Both are done until the energy is converged to the energy with a change of less than  $10^{-4}$  eV. A finer grid could not be taken because of limitations on the computing resources. The convergence of the energy eigenvalue  $E_0$  with respect to  $r_{\max}$  and  $\Delta r$  is shown in Figure 5 and resulted in  $r_{\max} = 10.125$  a.u. and  $\Delta r = 0.0056$  a.u. .

The resulting energy eigenvalue is

$$E_0(\text{Task 4}) = -2.862 \text{ a.u.},$$

with the corresponding wave function shown in Figure 6.

## 5 Task 5

Building on task 4, we now add the second term in equation (15), the so-called exchange contribution

$$V_x = \varepsilon_x + n(r) \frac{d\varepsilon_x}{dn}, \quad (19)$$

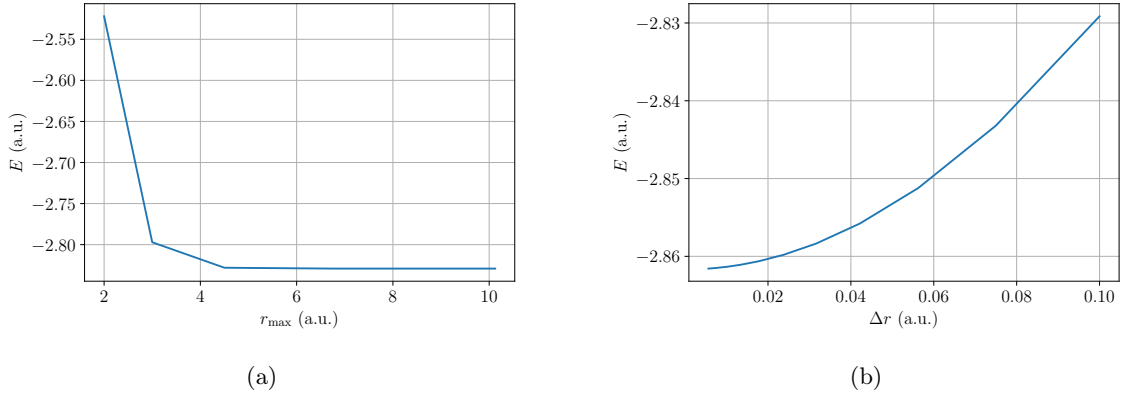


Figure 5: Progression of the energy while changing the radial discretization in task 4. Dependency of the energy of the grid spacing and grid size.

where  $n(r) = u^2(r)/2\pi r^2$  and

$$\varepsilon_x = -\frac{3}{4} \left( \frac{3n}{\pi} \right)^{1/3}. \quad (20)$$

This adds a potential contribution that originates from having more than one electron in the atom. Since the two electrons are identical, an exchange interaction between electrons with opposite spin is enabled. Furthermore, the so-called self interaction is now accounted for by using  $V_H = 2V_{sH}$ , which is a mathematical construct that would cancel out if the exchange-correlation functional would be exact. The grid parameters  $r_{\max}$  and  $\Delta r$  are taken to be the same as in task 4 after convergence.

The resulting energy eigenvalue is

$$E_0(\text{Task 5}) = -2.724 \text{ a.u.},$$

with the corresponding wave function shown in Figure 6. Notice that this is further away from the experimental value stated in Thijssen of  $-2.903 \text{ a.u.}$  compared to task 4 where no exchange-correlation term was added [2].

## 6 Task 6

The final step is now to add the last term, the so-called correlation term, which now gives us equation (15). This correlation comes once again from having more than one electron in the atom and so the positions are in some ways correlated. The correlation term is added as

$$V_c = \varepsilon_c + n(r) \frac{d\varepsilon_c}{dn}, \quad (21)$$

with

$$\varepsilon_c(r_s) = \frac{\gamma}{1 + \beta_1 \sqrt{r_s} + \beta_2 r_s}, \quad r_s \geq 1 \quad (22)$$

$$\varepsilon_c(r_s) = A \ln r_s + B + C r_s \ln r_s + D r_s, \quad r_s < 1, \quad (23)$$

$$(24)$$

where the constants are given in the exercise and

$$r_s = \left( \frac{3}{4\pi n} \right)^{1/3}. \quad (25)$$

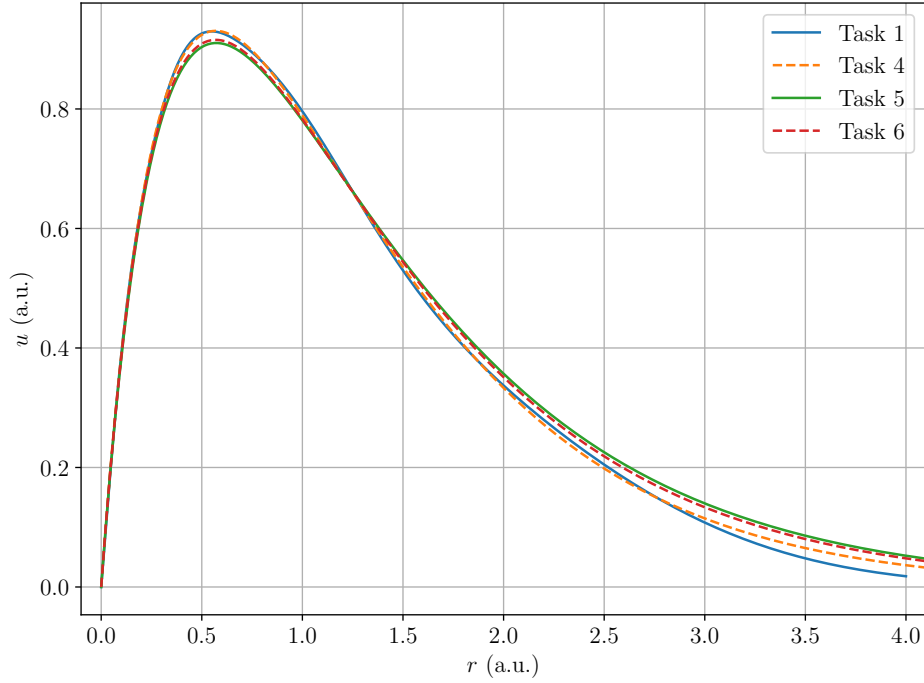


Figure 6: The radial wave functions calculated in task 1, 4, 5 and 6. Observe the lower peaks of task 5 and 6 and slower convergence to zero compared to task 1 and 4.

The resulting energy eigenvalue is

$$E_0(\text{Task 6}) = -2.834 \text{ a.u.},$$

with the corresponding wave function shown in Figure 6.

In figure 6 the differences in the wave function between task 5 and task 6 are barely visible while differences to task 1 and 4 are more clearly seen. This is expected due to the introduction of the exchange-correlation terms, and the small difference between the latter two is expected as the combined exchange-correlation term is small compared to the other potential [3]. The wave function when including the exchange-correlation functional show a slightly lower peak and a slower convergence to zero compared to the case with out this term. This is believed to be due to the fact that the distance to the nucleus affects the electron exchange-correlation, something that is not taken into account without this term. When the distance grows larger, the correlation between the electrons should however decrease but the probability due to the exchange-correlation means that the probability for electrons further away from the nucleus should increase, something that can be observed in figure 6. This effect, that Hartree-Fock fails to include all repulsion can be seen in the later stages where it goes quickly to zero meanwhile a less steep curve could be expected.

When comparing the energy eigenvalues obtained in the various tasks in table 1, none of the used methods correspond to the experimental values in more than one decimal places. The results from task 1 and task 4 are the closest to the experimental value. From task 6, the value is an improvement from task 5 with a 0.12 a.u. difference. However, the original task 4 without any corrections is still better with a margin of 0.021 a.u. and a 0.048 a.u. distance to the experimental value.

Table 1: Resulting energy eigenvalues of the ground state of helium using different simulation methods. LCG stands for linear combination of Gaussian wave functions, FD stands for finite differences, X stands for the exchange potential and XC stands for the exchange-correlation potential.

Task	Method	Energy $E_0$ (a.u.)
1	LCG	-2.855
4	FD	-2.862
5	FD + X	-2.724
6	FD + XC	-2.834
	experimental	-2.903

## References

- [1] Pieter Kok. 13.6: The hydrogen atom, 11 2021. URL [https://phys.libretexts.org/Bookshelves/Quantum\\_Mechanics/Advanced\\_Quantum\\_Mechanics\\_\(Kok\)/13%3A\\_The\\_Schr%C3%B6dinger\\_Equation/13.6%3A\\_The\\_Hydrogen\\_Atom](https://phys.libretexts.org/Bookshelves/Quantum_Mechanics/Advanced_Quantum_Mechanics_(Kok)/13%3A_The_Schr%C3%B6dinger_Equation/13.6%3A_The_Hydrogen_Atom).
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