

DFT algorithm for calculating the ground-state energy of the He atom

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- The aim of this project is to implement and analyze the DFT algorithm based on the KS scheme in order to calculate the ground-state energy $E_{\text{gs}} = E[\rho_{\text{gs}}] \approx -2.877 E_h$ of the He atom.
- My main focus today is in explaining in details the algorithm that drives the ground-state calculations in the case of the He atom.
- Technically, the implementation is given in the Julia programming language and is based on the one provided in Fortran 90.

1 Description of the algorithm

- The objective of DFT is to calculate the ground-state energy $E_{\text{gs}} = E[\rho_{\text{gs}}]$ by relying on the KS scheme, making guesses iteratively on the ground-state electron density ρ_{gs} . Those guesses then get progressively more accurate at each iteration.
- The given implementation relies on integrating the KS differential equations on a grid. At the core of our problem is the radial coordinate r from which every quantity depends, and because the finite difference method is employed, only a finite range of N samples for r is allowed in the range $r_{\text{min}} < r < r_{\text{max}}$. For this reason, r is represented as an array of length N in the program.
- Technically, all quantities that are a function of r will also be defined on the same grid. This means that $\rho_{\text{gs}}(r)$, $V_H(r)$, etc... are going to be arrays of fixed size given by the number of samples N .

1.1 Bootstrap of the self-consistent loop

- After initializing the ground-state density ρ_{gs} to a first guess, which can be any, the algorithm proceeds by calculating all further guesses of the density inside the self-consistent loop.
- Specifically, this self-consistent loop will run until the difference between subsequent energies E_n are lower than an arbitrarily small threshold value ε chosen upfront.
- The condition for convergence is that $|E_n - E_{n-1}| < \varepsilon$, where n is the index of the current iteration. The index n starts from 1, considering that initially $E_0 \neq E_1$, for any two energy values arbitrarily chosen in order to bootstrap the loop.
- At this point we are now ready to carry out the main calculations for the potentials that are needed to solve the KS Schrödinger equation.

1.2 Hartree potential V_H

- Once the loop has been bootstrapped, then we get into the core of the self-consistent algorithm. The first step is calculating numerically the Hartree potential V_H by solving the differential equation

$$\ddot{U}_H(r) = -\frac{\rho_{\text{gs}}(r)}{r}, \quad \text{with } U_H(r_{\text{min}}) = 0, U_H(r_{\text{max}}) = 1,$$

and then obtaining the potential by means of

$$V_H(r) = \frac{U_H(r)}{r} + \alpha, \quad \text{with } \alpha = \frac{2 - U_H(r_{\text{max}})}{r_{\text{max}}}.$$

1.3 Exchange and correlation potentials V_x, V_c

- Next, the exchange potential is obtained from the following formula,

$$V_x(r) = \left[-\frac{3\rho_{\text{gs}}(r)}{4\pi^2 r^2} \right]^{1/3},$$

while the correlation potential has a parametrised form obtained by means of a variable known as r_s ,

$$V_c(r_s) = \begin{cases} e_c \frac{1 + \frac{7}{6}\beta_1\sqrt{r_s} + \frac{4}{3}\beta_2 r_s}{1 + \beta_1\sqrt{r_s} + \beta_2 r_s}, & \text{if } r_s \geq 1 \\ A\ln(r_s) + B - \frac{A}{3} + \frac{2}{3}Cr_s\ln(r_s) + (2D - C)\frac{r_s}{3}, & \text{if } 0 < r_s < 1 \end{cases}$$

where $e_c = A\ln(r_s) + B + Cr_s\ln(r_s) + Dr_s$ and $r_s = \left(\frac{3r^2}{\rho_{\text{gs}}} \right)^{1/3}$.

1.4 Solving the Schrödinger equation

- Once we know all the potentials, then we can construct the full effective potential V_{eff} ,

$$V_{\text{eff}}(r) = V_{\text{nuc}} + V_H + V_x + V_c,$$

where V_{nuc} is the nuclear potential, taken from the Coulombic interaction,

$$V_{\text{nuc}}(r) = -\frac{Z}{r}, \quad \text{with } Z = 2.$$

- The next step is calculating the energies E_{eff} associated to the effective potential and the eigenfunctions ϕ of the spherically-symmetric Schrödinger equation for hydrogenoid atoms by enforcing Dirichlet-type homogeneous boundary conditions,

$$-\frac{1}{2}\ddot{\phi}(r) + V_{\text{eff}}(r)\phi(r) = E_{\text{eff}}\phi(r), \quad \text{with } \phi(r_{\text{min}}) = \phi(r_{\text{max}}) = 0.$$

1.5 Making a guess on the ground-state density ρ_{gs}

- Out of all the possible eigenvalues E_{eff} associated to the effective potential, the one associated to the ground state (the most negative one) $E_{\text{eff},0}$ is extracted together with its associated eigenfunction ϕ_0 .
- At this point the normalization condition is enforced,

$$\int_{r_{\min}}^{r_{\max}} |\phi_0(r)|^2 dr = 1.$$

The guess for the ground-state density ρ_{gs} is then calculated by squaring the modulus of the ground-state normalised eigenfunction ϕ_0 and then multiplying by a factor of 2 due to the degeneracy,

$$\rho_{\text{gs}}(r) = 2|\phi_0(r)|^2.$$

1.6 Total energy E_n for the current iteration

- The total energy E_n for the current iteration is obtained from the ground-state effective energy $E_{\text{eff},0}$ corrected by the Hartree, exchange and correlation energies E_H, E_x, E_c ,

$$E_n = 2E_{\text{eff},0} - E_H - \frac{E_x - E_c}{2},$$

where the energy E is calculated from the integration of the respective potential with the current guess of the ground-state density ρ_{gs} ,

$$E = \int_{r_{\text{min}}}^{r_{\text{max}}} V(r) \rho_{\text{gs}}(r) dr.$$

- The loop then terminates if convergence has been achieved, otherwise it restarts. If there is convergence, then the program returns the current guess for the ground-state energy $E_{\text{gs}} = E_n$.

2 Results of the calculations

By running the calculations with 4096 points, having a step of approximately $\mu \approx 0.012$, convergence is obtained at $E = -2.877 E_h$.

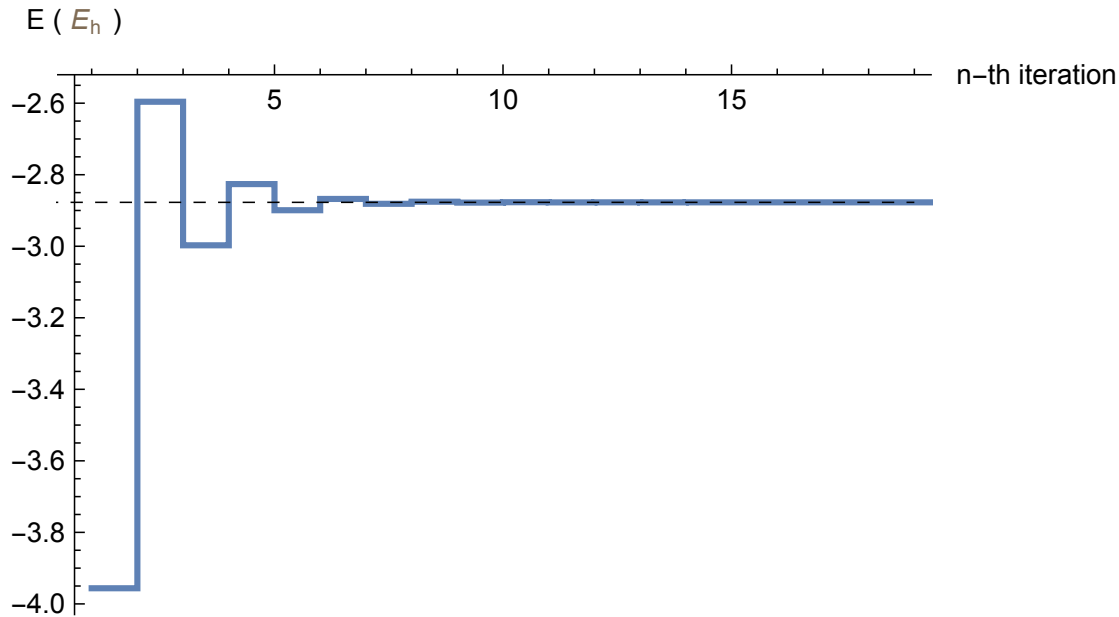


Figure 1. Convergence of the total energy E_n at the n -th iteration.

3 Considerations on the algorithm

- No interpolation and error corrections are used in the code.
- The integrals are evaluated by means of a dense grid of evenly-spaced points, the separation of which is referred to as μ . This means that every function of r is also represented by a grid of values evaluated at the different points r_0, r_1, r_2 , etc...
- Schrödinger's differential equation is solved by the use of Verlet integration. This means that $\ddot{\psi}(r) = f(r)$ is solved by setting the initial conditions for $\psi(r_0), \psi(r_1)$ and then calculating

$$\psi(r_{i+1}) = 2\psi(r_i) - \psi(r_{i-1}) + f(r)\mu^2,$$

if f is the non-Laplacian term of the Schrödinger equation.

- The ground-state energy is a monotonic decreasing function of the number N of samples chosen. Basically, the smaller the step, the lower the energy is. We see it is converging to $E \approx -2.8777 E_h$.

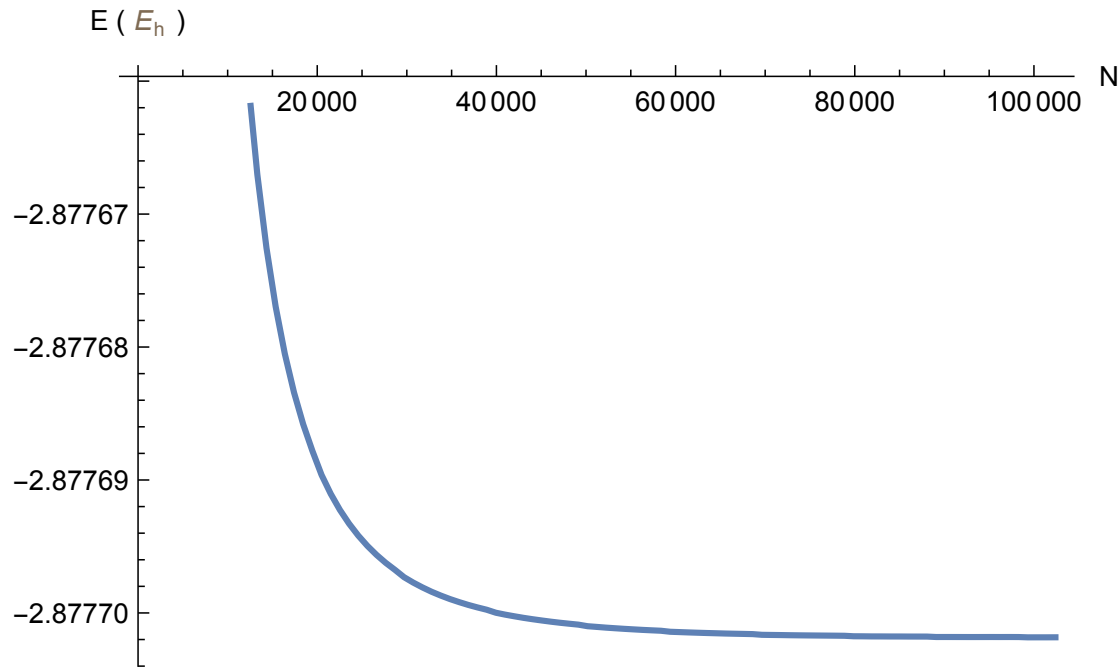


Figure 2. Ground-state energy of He as a function of the samples N .