

A1: Self-consistency and Density functional theory

Alfred Juhlin Onbeck

March 8, 2023

Introduction

By using the Hartree-Fock ansatz for the Helium atom which fulfills the antisymmetric requirement for fermions, we get wavefunction[2]

$$\Psi(\mathbf{r}_1, s_1; \mathbf{r}_2, s_2) = \phi(\mathbf{r}_1)\phi(\mathbf{r}_2)\frac{1}{\sqrt{2}}[\alpha(s_1)\beta(s_2) - \alpha(s_2)\beta(s_1)]. \quad (1)$$

From the Born-Oppenheimer approximation, the Hamiltonian for the helium atom becomes (using atomic units)

$$H_{\text{BO}} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} - \frac{2}{r_1} - \frac{2}{r_2}, \quad (2)$$

and then inserting our wavefunction and integrating it results in

$$\left[-\frac{1}{2}\nabla_1^2 - \frac{2}{r_1} + \int d^3r_2 |\phi(\mathbf{r}_2)|^2 \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right] \phi(\mathbf{r}_1) = E' \phi(\mathbf{r}_1). \quad (3)$$

Problem 1

Calculating the helium ground state with the Hartree-Fock method and a parametrisation for the wavefunction,

$$\Phi(\mathbf{r}) = \sum_p C_p \chi_p(\mathbf{r}), \quad \chi_p(\mathbf{r}) = e^{-\alpha_p r^2}. \quad (4)$$

The α_p values are constants and set to[2]

$$\begin{aligned} \alpha_1 &= 0.297104, \\ \alpha_2 &= 1.236745, \\ \alpha_3 &= 5.749982, \\ \alpha_4 &= 38.216677. \end{aligned}$$

Using the parametrisation of the wavefunction the Schrödinger eq. 3 becomes[2]

$$\left[-\frac{1}{2}\nabla_1^2 - \frac{2}{r_1} + \sum_{r,s=1}^4 C_r C_s \int d^3r_2 \chi_r(\mathbf{r}_2) \chi_s(\mathbf{r}_2) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right] \sum_{q=1}^4 C_q \chi_q(\mathbf{r}_1) = E' \sum_{q=1}^4 C_q \chi_q(\mathbf{r}_1). \quad (5)$$

By multiplying this eq. with $\chi_p(\mathbf{r})$, it leads to[2]

$$\sum_{pq} \left(h_{pq} + \sum_{rs} C_r C_s Q_{prqs} \right) C_q = E' \sum_{pq} S_{pq} C_q \quad (6)$$

with

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

Solving the integrals in h_{pq} , Q_{pqrs} , S_{pq} with $\chi_p(\mathbf{r}) = e^{-\alpha_p r^2}$ we get[2]

$$\begin{aligned} S_{pq} &= \int d^3 r e^{-\alpha_p r^2} e^{-\alpha_q r^2} = \left(\frac{\pi}{\alpha_p + \alpha_q} \right)^{3/2}, \\ T_{pq} &= -\frac{1}{2} \int d^3 r e^{-\alpha_p r^2} \nabla^2 e^{-\alpha_q r^2} = 3 \frac{\alpha_p \alpha_q \pi^{3/2}}{(\alpha_p + \alpha_q)^{5/2}}, \\ A_{pq} &= -\int d^3 r e^{-\alpha_p r^2} \frac{2}{r} e^{-\alpha_q r^2} = -\frac{4\pi}{\alpha_p + \alpha_q}, \\ Q_{pqrs} &= \frac{2\pi^{5/2}}{(\alpha_p + \alpha_q)(\alpha_r + \alpha_s) \sqrt{\alpha_p + \alpha_q + \alpha_r + \alpha_s}}. \end{aligned} \tag{7}$$

where $h_{pq} = T_{pq} + A_{pq}$. Let F_{pq} be the Fock operator which corresponds to

$$F_{pq} = h_{pq} + \sum_{rs} C_r C_s Q_{pqrs}, \tag{8}$$

and by solving the generalised eigenvalue problem

$$\text{FC} = \epsilon \text{SC}, \tag{9}$$

we get an improved wavefunction and with enough iterations should converge to the ground state. The total energy of state is not represented entirely by the eigenvalue ϵ but by[2]

$$E_0 = 2 \sum_{na} C_p C_q h_{pq} + \sum_{narc} Q_{pqrs} C_p C_q C_r C_s. \tag{10}$$

However, before solving eigenvalue problem or calculating the energy, the wavefunction must be normalized with

$$\sum_{pq} C_p S_{pq} C_q = 1, \tag{11}$$

which is done by

$$C_p \mapsto \frac{C_p}{\sqrt{\sum_{rq} C_r S_{rs} C_s}}. \tag{12}$$

We may now calculate the ground state by initially guessing C_p , normalizing before applying the fock operator or determining the energy, and then let C_p be the eigenvector corresponding to the lowest eigenvalue. This procedure is repeated until the energy converges, i.e the change in energy between two iterations is below $10^{-5} E_h$, and resulted in fig.

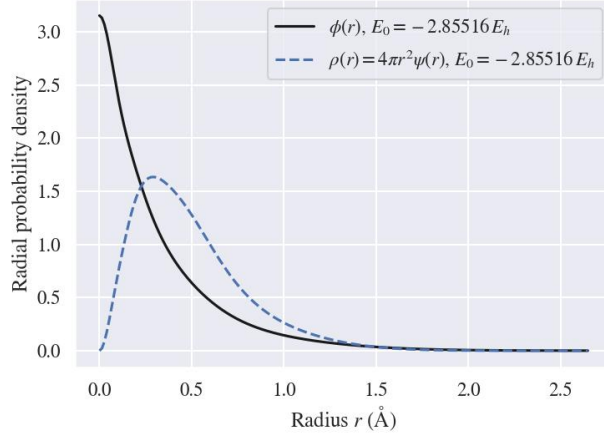


Figure 1: Wavefunction and radial electron pdf of the helium atom, with ground state energy $E_0 \approx -2.855 E_h$.

Problem 2

Solving Poisson's equation for the Hartree potential V_H , which represents the electrostatic potential from the charge distribution $n(\mathbf{r}) = \sum_n |\psi_n(\mathbf{r})|^2 = 2|\psi(\mathbf{r})|^2$. Poisson's equation is the following

$$\nabla^2 V_H(\mathbf{r}) = -4\pi n(\mathbf{r}), \quad (13)$$

and if the potential is only radially-dependent it can be written as

$$\frac{d^2}{dr^2} U(r) = -4\pi r n_s(r), \quad (14)$$

where $U(r) = rV_H/2$. Let $u(r) = \sqrt{4\pi n_s(r)}r$, then

$$\frac{d^2}{dr^2} U(r) = -\frac{u^2(r)}{r}. \quad (15)$$

This 2nd order differential equation can be solved by assigning a maximum radius r_{max} , dividing $R \in [0, r_{max}]$ in N discrete pieces, and substituting the derivative with

$$\frac{d^2 f(r_i)}{dr^2} = \frac{f(y_{i+1}) - 2f(y_i) + f(y_{i-1}))}{h^2}, \quad (16)$$

where h is the spacing between the grid points. The boundary conditions we will be using are $U(0) = 0$, $U(r_{max}) = 1$, and solving eq. 16 linear algebraically, i.e. N grid points turns to a NN matrix D ,

$$\frac{1}{h^2} D \mathbf{U} = \mathbf{b}, \quad (17)$$

where $D_{ii} = -2$, $D_{i,i-1} = 1$, $D_{i,i+1} = 1$, and the rest are 0 (with a couple of exceptions, the indices are $0 \leq i \pm 1 \leq N-1$ and $i = 0, 1, \dots, N-1$), and $b_0 = b_{N-1} = 0$, $b_i = -u_i^2/r_i$. To verify

that the method is working we will test it on the hydrogen atoms charge density, after solving eq. 17 for \mathbf{U} , it results in a potential identical to the Hartree potential

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

and can be seen in fig. 2.

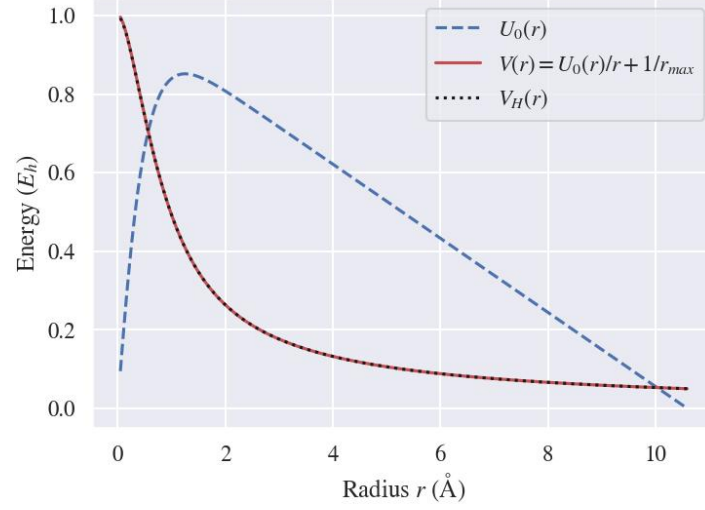


Figure 2: Comparison of the potential from finite difference method solution of the Poisson equation and the Hartree potential.

Problem 3

The eigenvalue, differential problem will be solved using linear algebra and finite differences. Similarly to the previous problem the region of interest $R \in [0, r_{max}]$ will be divided into N discrete pieces. The Kohn-Sham equation in radial coordinates is

$$\left[-\frac{1}{2} \frac{d^2}{dr^2} + V(r)_{\text{eff}} \right] u(r) = \varepsilon u(r). \quad (18)$$

Using finite differences the differential term can be substituted as in eq. 16 and $r \rightarrow r_i$ we get the linear algebra equation of

$$\mathbf{D}\mathbf{r} = \varepsilon\mathbf{r}, \quad (19)$$

with $\mathbf{r} = [r_1 \ r_2 \ \dots r_{N-1}]$ and the matrix elements in \mathbf{D}

$$\begin{aligned} D_{i,i} &= 1/h^2 + V(r_i), \\ D_{i,i-1} &= -1/(2h^2), \quad \text{if } i > 0, \\ D_{i,i+1} &= -1/(2h^2), \quad \text{if } i < N-1. \end{aligned}$$

Note that this excludes the first and last grid point. To verify that the solution to the eigenvalue problem is working correctly we will try solving the radial Schrödinger equation for the hydrogen atom ($V_{\text{eff}} = -1/r$)

$$\left(-\frac{1}{2} \frac{d^2}{dr^2} - \frac{1}{r} \right) u(r) = E u(r), \quad (20)$$

to compare with the analytical solution. The solution from finite difference method compared with the theoretical solution is seen in fig. 3, and there visually no difference from the wavefunctions and a minor inaccuracy for the ground state energy.

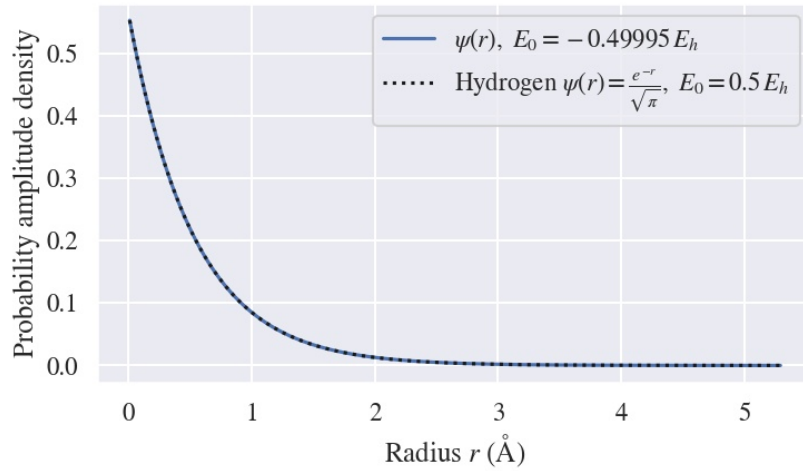


Figure 3: Solution of the Kohn-Sham equation compared with the analytical solution of the hydrogen ground state.

Problem 4

Determining the ground state of helium using the Kohn-Sham equation, without exchange-correlation terms and no self-interaction in the Hartree potential V_H ,

$$\left[-\frac{1}{2} \frac{d^2}{dr^2} - \frac{2}{r} + V_H(r) \right] u(r) = \varepsilon u(r), \quad (21)$$

with $V_H(r) = V_{sH}(r)$ when there is no self-interaction. In order to solve eq. 21 we first need the potential $V_H(r)$ which is obtained by guessing the charge density and then solving the Poisson eq. as in Problem 2. This now lets us solve the Kohn-Sham eq. to get a new wavefunction and one step closer to convergence. The iterative process is stopped when the change in energy is less than $10^{-5} E_h$. In fig. 4 we see the converged solution and its ground state energy.

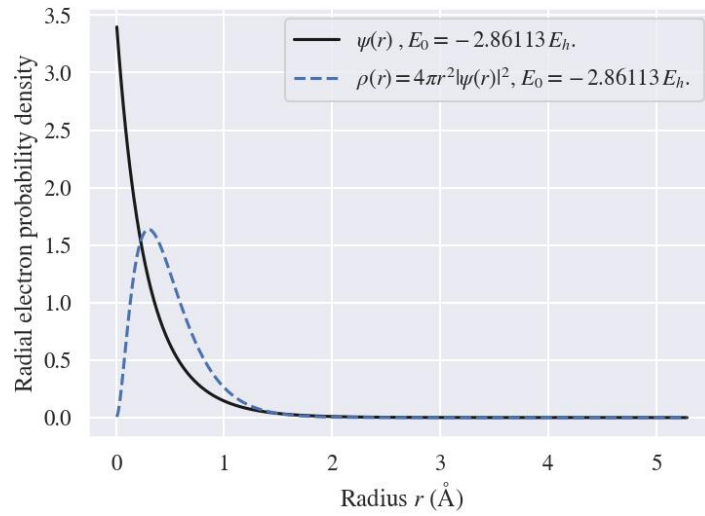


Figure 4: Wavefunction and radial electron probability density for the converged solution of the helium atom.

In order to not waste computation time but also reach the correct energy, r_{max} should be swept over and choose the value when the ground state energy has converged and similarly done to the density of grid points. In fig. 5 the convergence tests for r_{max} and grid density is seen. Resulting from the tests, appropriate values for $r_{max} = 30 \text{ Å}$ and grid points $N = 1000$.

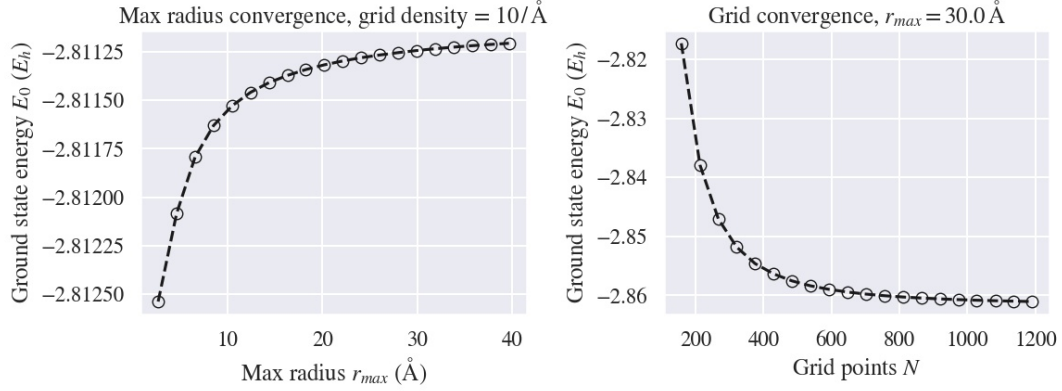


Figure 5: Convergence of r_{max} and number of grid points.

Problem 5 & 6

Solving Kohn-Sham equation with exchange contributions and with both exchange, correlation contributions. With exchange contributions the ground state energy is $E_0 = -2.270886 E_h$, with both exchange and correlation contributions the ground state energy is $E_0 = -2.83029 E_h$, and without either the ground state energy is $E_0 = -2.84835 E_h$. In fig. 6 the wavefunctions and $u(r)$ for the three different potentials can be seen with very little difference for the wavefunctions but an apparent difference in $u(r)$.

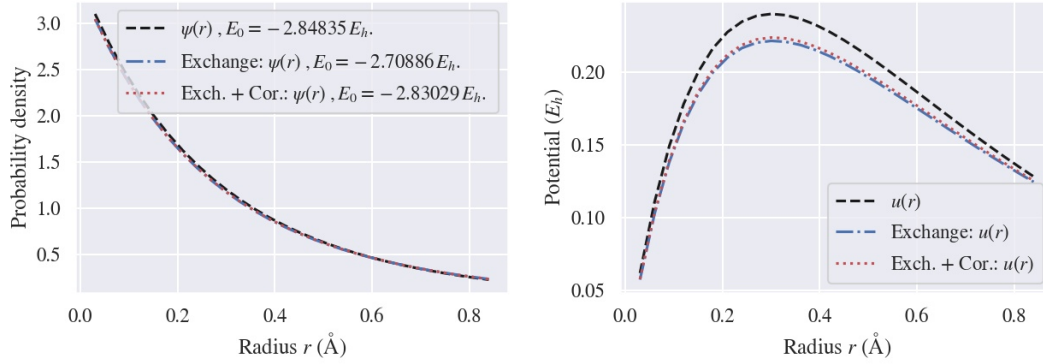


Figure 6: Wavefunction and potential $u(r)$ for solving Kohn-Sham with exchange, both exchange and correlations contributions, and without any contributions.

References

- [1] G. Wahnström, P. Sundell, and M. Petisme (2014-01-24), *Self-consistency and the density-functional theory*.
- [2] J. M. Thijssen (1999), *Computational Physics* - Cambridge University Press.