

UNIVERSITÉ DE BOURGOGNE

M1 PROJECT

Calculating the Energy Levels of Helium

Student:

Diana AVETISYAN

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1 Introduction

The energy level structure of helium is a classic problem in quantum mechanics and was historically important in confirming of the correctness of quantum theory as well as in showing the demonstration of the Pauli principle.[1] It serves an excellent textbook example of the variational method, first-order perturbation theory and exchange symmetry [2][3].

In this project I will use the perturbation method to find the Hamiltonian of the helium atom using Octave, after showing some calculations and improving the existing code by adding also the second-order perturbations. Once Schrodinger equation had been solved for the Hydrogen atom, it was generally believed that the solution of the Helium atom would follow not long afterward. However, scientists have tried for decades to solve this three body problem without succeeding. Very accurate approximations were developed, but no exact solutions were found. As it turns out, even with the simplifications described above it is impossible to determine the eigenstates of the Helium atom. This situation is common in chemistry, as most of the problems we are interested in cannot be solved exactly [4]. Bohr's new theory is no longer suitable for helium atom, the main reasons are:

- Bohr's quantum theory does not take into account the exchange energy, which is a pure quantum effect.
- Bohr's theory does not take into account the spin of the electron. [5] In the table below I would like to introduce some results for the calculation of the ground state energy of the helium atom.

Method	Energy/ E_h	Ionization Energy/ E_h	Ionization Energy/ $kJ \times mol^{-1}$
<i>Perturbation calculations</i>			
Neglect of the interelectronic repulsion term	- 4.0000	2.000	5250
First-order perturbation theory	-2.7500	0.7500	1969
Second-order perturbation theory[6]	-2.9077	0.9077	2383
Thirteenth-order perturbation [7]	-2.903 724 33	0.903 724 33	2373
<i>Variational Calculations</i>			
$(1s)^2$ with $s = 1.6875$	-2.8477	0.8477	2226
Eckart [8]	-2.8757	0.8757	2299
Hartree- Fock [9]	2.861 68	0.8617	2262
Hylleraas, 10 parameters [10]	-2.903 63	0.903 63	2372
Pekeris, 1078 parameters [11]	-2.903 724 375	0.903 724 375	2373
<i>Experimental value</i>	-2.9033	0.9033	2373

So next we have gone ahead by adding second order corrections to the matrix represented in the article [1].

2 Theory

In the situation of Helium, we have two electrons – with coordinates r_1 and r_2 – orbiting a nucleus with charge $Z = 2$ located at the point R . Now, for the hydrogen atom we were able to ignore the motion of the nucleus by transforming to the center of mass. We then obtained a Schrodinger equation for a single effective particle – with a reduced mass that was very close to the electron mass – orbiting the origin. It turns out to be fairly difficult to transform to the center of mass when dealing with three particles, as is the case for Helium. However, because the nucleus is much more massive than either of the two electrons ($M_{Nuc} \approx 7000m_e$) it is a very good approximation to assume that the nucleus sits at the center of mass of the atom. In our case r_1 and r_2 measure the distance between each electron and the nucleus. Further we will only consider the motion of the electrons and ignore the motion of the nucleus. We will invent operators \hat{r}_1, \hat{r}_2 and associated momentum operators \hat{p}_1, \hat{p}_2 . The operators for a given particle 1 will be assumed to commute with all operators associated with any other particle 2:

$$[\hat{p}_i; \hat{p}_j] = [\hat{r}_i; \hat{r}_j] = [\hat{p}_i; \hat{r}_j] = [\hat{r}_i; \hat{p}_j] = \dots = 0 \quad (1)$$

Meanwhile, operators belonging to the same particle will obey the norm:

$$[\hat{p}_i; \hat{r}_i] = i\hbar \quad (2)$$

while all components belonging to different axes commute: In terms of these operators, we can quickly write the Hamiltonian for the Helium atom:

$$\hat{H} = \frac{\hat{p}_1^2}{2m_e} + \frac{\hat{p}_2^2}{2m_e} + \frac{Ze^2}{4\pi\epsilon_0} \frac{1}{\hat{r}_1} + \frac{Ze^2}{4\pi\epsilon_0} \frac{1}{\hat{r}_2} + \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\hat{r}_1 - \hat{r}_2|} \quad (3)$$

For the reason of simplicity we can express this Hamiltonian in the atomic units:

$$\hat{H} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} + V \quad (4)$$

There are a few possible ways to resolve the two electron interaction in the helium atom.

- Non-Interacting electron approximation. In this model the interaction between the electrons is ignored, as a result the error is not negligible. $E_{experiment} = -79 \text{ eV}$ and calculated this way, $E_{1s1s} = -108.8 \text{ eV}$.

- The other way is to use our hydrogenic functions to calculate matrix elements of this and get an H_1 , an E_1 . And the third step would be to get the exact answer by doing an infinitely difficult calculation. The other method requires taking into account the interaction between electrons. I will discuss about the variational method combined with the perturbation theory.

2.1 Non-Interacting Electron Approximation

For Helium, the first thing we notice is that the Hamiltonian becomes separable if we neglect the electron-electron repulsion term:

$$H_0 = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} = H_1 + H_2 \quad (5)$$

Thus, if we neglect the interaction between the electrons, the Hamiltonian reduces to the sum of two hydrogenic atom Hamiltonians (with $Z = 2$). The separability of the Hamiltonian allows us to immediately write the energies:

$$E_{n_1, n_2} = E_{n_1} + E_{n_2} = \frac{Z^2}{2n_1^2} + \frac{Z^2}{2n_2^2} \quad (6)$$

If we calculate the value in atomic units we can find:

$$E_{11} = \frac{Z^2}{2} + \frac{Z^2}{2} = 4 \text{ a.u.} = 108.8 \text{ eV} \quad (7)$$

Well, we can determine the ground state energy of Helium by removing one electron to create He^+ and then removing the second to create He^{2+} . As it turns out, the first electron takes 24.6 eV to remove and the second takes 54.4 eV to remove, which means the correct ground state energy is 79.0 eV. So our non-interacting electron picture is larger by 30 eV, which is a lot of energy. To understand how much energy that is, a typical covalent chemical bond is worth about 5 eV of energy [4].

2.2 Interacting Electron Approximation Using First Order Perturbation Theory

We use perturbation theory to approach the analytically unsolvable helium atom Schrödinger equation by focusing on the Coulomb repulsion term that

makes it different from the simplified Schrödinger equation that we have just solved analytically. The electron-electron repulsion term is conceptualized as a correction, or perturbation, to the Hamiltonian that can be solved exactly, which is called a zero-order Hamiltonian. The perturbation term corrects the previous Hamiltonian to make it fit the new problem.

$$H = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{|r_1 - r_2|} \quad (8)$$

The expression for the first-order correction to the energy is:

$$E^1 = \langle \psi^0 | \hat{H} | \psi^0 \rangle = \int \psi^{0*} E^1 \psi^0 d\tau \quad (9)$$

Equation 9 is a general expression for the first-order perturbation energy, which provides an improvement or correction to the zero-order energy. Hence, E^1 is the average interaction energy of the two electrons calculated using wavefunctions that assume there is no interaction.

The solution to (Equation 5) is the product of two single-electron hydrogen wavefunctions (scaled by the increased nuclear charge) since H_0 can be separated into independent functions of each electron (i.e., Separation of Variables).

$$|\psi^0\rangle = |\varphi_{1s}(r_1)\varphi_{1s}(r_2)\rangle \quad (10)$$

So the integral in Equation 9 is:

$$E^1 = \int \int \varphi_{1s}(r_1)\varphi_{1s}(r_2) \frac{1}{|r_1 - r_2|} \varphi_{1s}(r_1)\varphi_{1s}(r_2) d\tau_1 d\tau_2 \quad (11)$$

where the double integration symbol represents integration over all the spherical polar coordinates of both electrons $r_1, \theta_1, \varphi_1, r_2, \theta_2, \varphi_2$. The evaluation of these six integrals is lengthy. When the integrals are done, the result is $E^1 = +34.0 \text{ eV} \approx 1.249 \text{ a.u.}$ so that the total energy calculated using our second approximation method, first-order perturbation theory, is:

$$E = -74 \text{ eV} \approx -2.719456 \text{ a.u.} \quad (12)$$

The new approximate value for the binding energy represents a substantial (30%) improvement over the zero-order energy. It takes thirteenth-order perturbation theory to compute an energy for helium that agrees with experiment to within the experimental uncertainty. Interestingly, while we have

improved the calculated energy so that it is much closer to the experimental value, we learn nothing new about the helium atom wavefunction by applying the first-order perturbation theory to the energy above. He need to expand the wavefunctions to first order perturbation theory, which requires more effort.

3 Estimation of the Ground State Energy

3.1 Analytical Calculation

Firstly, I have analytically calculated the ground state energy of the helium. For that I had some basic preliminary steps to complete. I have estimated the basis in bra-ket notation for two electrons.

$$\psi_{n_1, l_1, m_{l_1}}(r_1, \theta_1, \phi_1) = \langle r_1 \theta_1 \phi_1 | n_1 l_1 m_{l_1} \rangle = |n_1 l_1 m_{l_1}\rangle \quad (13)$$

$$\psi_{n_2, l_2, m_{l_2}}(r_2, \theta_2, \phi_2) = \langle r_2 \theta_2 \phi_2 | n_2 l_2 m_{l_2} \rangle = |n_2 l_2 m_{l_2}\rangle \quad (14)$$

As we have independent probability for electrons 1 and 2 to be in a particular states, the probability of the resulted state will multiplied, consequently:

$$\psi(1, 2) = \psi_{n_1, l_1, m_{l_1}} \psi_{n_2, l_2, m_{l_2}} = |n_1 l_1 m_{l_1} n_2 l_2 m_{l_2}\rangle \quad (15)$$

Next what I had to do is the calculation of the normalization factor. For that case I first calculated the He^+ reduced radial wavefunction.

$$P_{nl}(r) = \sqrt{\frac{2(n-l-1)!}{n^2(n+l)!}} \left(\frac{4r}{n}\right)^{l+1} e^{-2r/n} L_{n-l-1}^{2l+1}(4r/n) \quad (16)$$

where $L_p^a(r)$ are the generalized p-th order Laguerre polynomials. In our case we have n=1, l=0, as a result:

$$L_0^1 = 1 \quad (17)$$

Afterwards I substituted this result and integrated the modulus squared over r from 0 to infinity using integration by parts.

$$P_{1s}(r) = \sqrt{\frac{2}{1}} 4r e^{-2r} = \int_0^\infty |P_{1s}(r)|^2 = \int_0^\infty 32r^2 r^{-4r} dr \quad (18)$$

$$= 32 \left(-r_2 \frac{e^{-4r}}{4} \Big|_0^\infty + \int_0^\infty \frac{2r}{4} e^{-4r} dr \right) = 32 \left(-r \frac{e^{-4r}}{8} \Big|_0^\infty + \int_0^\infty \frac{e^{-4r}}{8} dr \right) \quad (19)$$

$$= 32 \times \frac{e^{-4r}}{32} \Big|_0^\infty = 1 \quad (20)$$

So this is a proof that $P_{1s}(r)$ is normalized. Next I went along with calculating the first element of the Hamiltonian matrix.

$$\langle n_1 s \ n_2 s | V | n_3 s \ n_4 s \rangle = \int d^3 r_1 d^3 r_2 P_{n_1 s}(r_1) P_{n_2 s}(r_1) \frac{1}{|r_1 - r_2|} P_{n_3 s}(r_2) P_{n_4 s}(r_2) \quad (21)$$

In order to find the first element of the matrix I had to estimate the following variables:

$$P_{n_1 s}(r_1) = 4\sqrt{2} r_1 e^{-2r_1} \quad (22)$$

$$P_{n_2 s}(r_2) = 4\sqrt{2} r_2 e^{-2r_2} \quad (23)$$

$$P_{n_3 s}(r_1) = 4\sqrt{2} r_1 e^{-2r_1} \quad (24)$$

$$P_{n_4 s}(r_2) = 4\sqrt{2} r_2 e^{-2r_2} \quad (25)$$

I substituted them in the integral (12):

$$I = 1024 \int_0^\infty d^3 r_1 d^3 r_2 r_1^2 e^{-4r_1} \frac{1}{|r_1 - r_2|} r_2^2 e^{-4r_2} \quad (26)$$

$$= 1024 \int_0^\infty d^3 r_1 r_1^2 e^{-4r_1} \left(\int_0^\infty d^3 r_2 r_2^2 e^{-4r_2} \frac{1}{|r_1 - r_2|} \right) \quad (27)$$

Next we consider two different cases in order to split the integral. For the first case, we have $r_1 > r_2$, in this case the integration goes from 0 to r_1 . In the case $r_1 < r_2$ the integral goes from r_1 to infinity. Those conditions appear due to the modulus $|r_1 - r_2|$. As a result we can split the integral in the brackets into two parts:

$$\frac{1}{r_1} \int_0^{r_1} r_2^2 e^{-4r_2} dr_2 + \int_{r_1}^\infty r_2 e^{-4r_2} dr_2 \quad (28)$$

Using the integration by parts several times:

$$I_1 = \frac{1}{r_1} \left(-\frac{r_2^2 e^{-4r_1}}{4} \Big|_0^{r_1} - \int_0^{r_1} -\frac{r_2 e^{-4r_2}}{2} dr_2 \right) \quad (29)$$

$$= \frac{1}{r_1} \left(-\frac{r_2^2 e^{-4r_2}}{4} + \frac{1}{2} \left(\frac{(-r_2 e^{-4r_2})}{4} + \int_0^{r_1} \frac{e^{4r_2}}{4} \right) \Big|_0^{r_1} \right) \quad (30)$$

$$= \frac{1}{r_1} \left(-\frac{r_2^2 e^{-4r_2}}{4} - \frac{(-r_2 e^{-4r_2})}{8} + \frac{e^{4r_2}}{32} \right) \Big|_0^{r_1} \quad (31)$$

I have also implemented analogical calculations for the second member of the sum, and similarly I got:

$$I_2 = \frac{(4r_1 + 1)e^{-4r_1}}{16} \quad (32)$$

Next I summed up the terms:

$$I_1 + I_2 = \frac{1 - (2r_1 + 1)e^{-4r_1}}{32r_1} \quad (33)$$

Next I started calculating the I:

$$I = 1024 \int_0^\infty dr_1 r_1^2 e^{-4r_1} \left(\frac{1 - (2r_1 + 1)e^{-4r_1}}{32r_1} \right) \quad (34)$$

$$= \frac{1024}{32} \left(\int_0^\infty r_1 e^{-4r_1} dr_1 - \int_0^\infty (2r_1^2 + r_1) e^{-8r_1} dr_1 \right) \quad (35)$$

Next I denoted the members of the sum as X and Y:

$$X = -\frac{r_1 e^{-4r_1}}{4} \Big|_0^\infty + \int_0^\infty \frac{e^{-4r_1}}{4} = \left(-\frac{r_1 e^{-4r_1}}{4} - \frac{e^{-4r_1}}{16} \right) \Big|_0^\infty = \frac{1}{16} \quad (36)$$

By doing similar calculations for Y we get:

$$Y = \frac{3}{128} \quad (37)$$

$$I = 32|X - Y| = 32 \left| \frac{1}{16} - \frac{3}{128} \right| = \frac{5}{4} \quad (38)$$

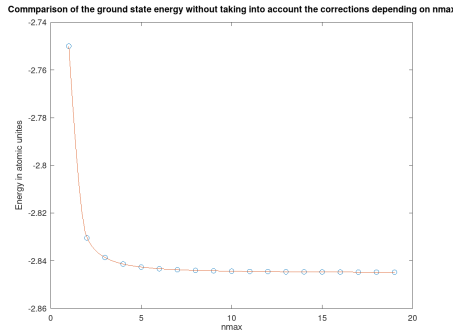
3.2 Numerical Simulations

As a first step, I have plotted the first element of the Hamiltonian matrix, which as a result is the ground state energy of helium atom without second order corrections depending on n_{\max} . Before getting to this plot I have diagonalized the Hamiltonian matrix and stored the first element in an according array, afterwards I plotted the values and used the piecewise interpolation to have a visible convergence to a certain value.

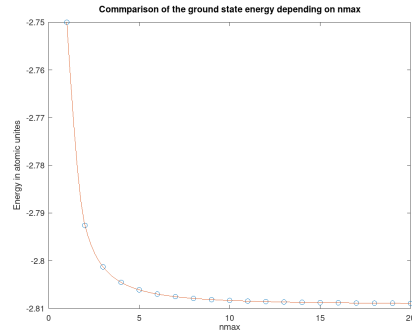
After calculating the first element of the Hamiltonian matrix, I proceeded with adding second order perturbation corrections depending on the n_{\max} .

$$E_1 = E_0 - \sum_{p=1}^{n_{\max}} \frac{|\langle \psi_1 | V | \psi_p \rangle|^2}{E_p - E_1} \quad (39)$$

where $E_0 = -\frac{2}{n_1^2} - \frac{2}{n_2^2}$, where the n_1 and n_2 are the quantum numbers of the state. As can be seen from the graph, the more we add the corrections the more the energy reaches a specific value, it's visible that for the case $n_{\max} = 8$ to $n_{\max} = 11$ there is not much difference, so the convergence of the graph is visible ≈ 2.81 . The convergence also means that the higher the n_{\max} the less is the impact of the state on the ground state energy, which means that we get closer to the continuum states, so the electron is no longer bounded to the nucleus.



(a) First element of the diagonalized Hamiltonian depending on the n_{\max}



(b) Dependence of the Helium ground state energy depending on the n_{\max}

4 Calculation of the First and Second Excited State Energies

Before starting the main task I had a short exercise to complete by diagonalizing the Hamiltonian matrix and the matrix for the second state, consisting of $H(2,2)$, $H(3,2)$, $H(2,3)$ and $H(3,3)$. I accomplished that by using the `diag(H)` syntax in Octave code. For the eigenvalues I got -2.1241 and -2.0364. Which are consequently the diagonal elements of the diagonalized matrix.

First I have divided the wavefunction into a symmetrical and antisymmetrical parts:

$$\psi_+ = \langle 1s2s | + \langle 2s1s | \quad (40)$$

$$\psi_- = \langle 1s2s | - \langle 2s1s | \quad (41)$$

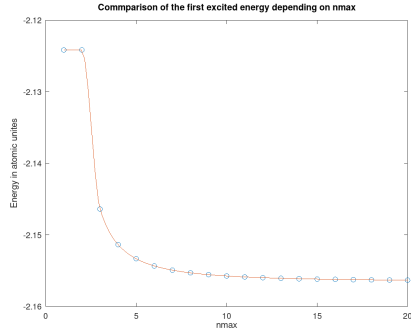
By doing this we also take into account not only the direct but also the exchange contribution which is a purely quantum effect:

$$E_{1s2s} \approx E_{1,2}^0 + J \pm K \quad (42)$$

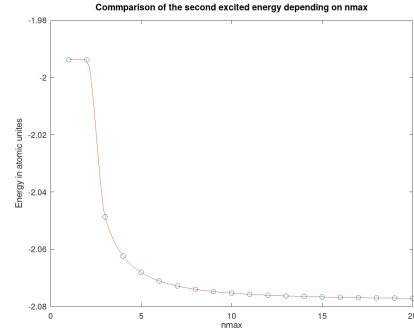
Where the $+$ gives the singlet energy and the $-$ gives the triplet energy. The experimental values are -2.1604 ± 0.0146 atomic units [13]. -2.1559 and -2.1397 for the antisymmetrical and symmetrical parts accordingly. In my code I have substituted the following formula:

$$- \frac{|\langle \psi_m(0) | V | \psi_b(0) \rangle|^2}{E_p - E_m} = - \frac{|\langle 1s2s | V | \psi_b \rangle \pm \langle 2s1s | V | \psi_b \rangle|^2}{E_p - E_m} \quad (43)$$

Here we also did the iteration for the state p , starting from $i=3$ to n_max , and afterwards adding the ground state correction for the symmetrical part, as for the antisymmetrical part it is 0.



(a) The graph for the first excited energy



(b) The graph for the second excited energy

5 Conclusion

The He atom is an example of a realistic system than can be quantitatively understood using the methods learned in an introductory quantum mechanics course. Taking advantage of the power of computer software to make such calculations possible adds new dimensions to learning. Of course, in order to be effective the programming must be straightforward enough to not detract from concentrating on the physics. This problem nicely fits within these constraints.

By comparing the ground state energy, I got approximately $\approx 3\%$ error. For the first excited state I got $\approx 0.88\%$ (antisymmetrical) error and $\approx 1.6\%$ error for the symmetrical part. So by comparing the simulation values with experimental values I got quite small errors, as well as the graphs can be nicely explained within the theory of quantum mechanics and atomic physics.

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