About calculation of the ground-state energy of the helium atom

E V Baklanov¹,², P V Pokasov¹ and A V Taichenachev¹,²

¹Institute of Laser Physics SB RAS, Novosibirsk 630090, Russia
²Novosibirsk State University, Novosibirsk 630090, Russia

E-mail: baklanov.ev@gmail.com

Abstract. Two versions of the numerical calculation of the ground state energy of the helium atom are compared. First, the nonrelativistic Schrödinger equation with a fixed nucleus is solved, and then the perturbation theory is used. Another version solves this problem exactly. Comparison shows that the difference between the calculation results is 94 kHz.

1. Introduction

Precision spectroscopy of the helium atom plays an important role in the theory of three-particle problems. The energy levels of such a system are expressed as the sum of nonrelativistic energy, relativistic corrections, and radiative corrections that include the Lamb shift. The accuracy with which the energy levels of the nonrelativistic problem are found determines the volume of all subsequent calculations, that is, the corrections that must be taken into account. In this work, two versions of the numerical calculation of the ground state energy of the helium atom are compared. One traditional one, where first the nonrelativistic Schrödinger equation with a fixed nucleus is solved, and then, to take into account its motion, the perturbation theory is used in the small parameter \( m/M \) (the ratio of the electron mass to the nuclear mass) [1]. In another version [2], the same problem is solved exactly.

2. Perturbation theory

Let us first dwell on work [1]. The nonrelativistic Schrödinger equation for a helium atom with a fixed nucleus has the form (in atomic units):

\[
- \frac{1}{2} \Delta_1 \Psi - \frac{1}{2} \Delta_2 \Psi + \left( \frac{1}{r_{12}} - \frac{2}{r_2} - \frac{2}{r_1} \right) \Psi = E_0 \Psi,
\]

where the wave function \( \Psi = \Psi(r_1, r_2) \) depends on the coordinates of two electrons \( r_1 \) and \( r_2 \), \( r_i = |r_i| \), \( \Delta_i \) is the Laplacian acting on \( r_i \), \( r_{12} = |r_1 - r_2| \), the atomic nucleus is at the origin coordinates. \( E_0 \) - eigenvalue of energy for the ground state. This value was calculated by a number of authors. From work [1] we have:

\[
E_0 = -2.903724377034120.
\]

The ground state energy, expanded in powers of \( m/M \), is given in [1]:

\[
E_g = E_0 + (m/M)E_1 + (m/M)^2E_2,
\]

where \( E_1 = 3.06279384, E_2 = -3.692271 \). We will take the \( m/M \) value from [2]:

\[
M/m = 7294.299620097.
\]
This value with the required accuracy (the first six digits) coincides with the CODATA recommendation: \( \frac{M}{m} = 7294.29954142 \) (24) \[3\]. Substituting the value of \( \frac{m}{M} \) in (1), we get:

\[ E_g = -2.903304557748695. \]

### 3. Exact solution

In \[2\], a method was developed for calculating the nonrelativistic energy levels of a three-particle Coulomb system with arbitrary masses and charges. The Schrödinger equation for a system of three particles with Coulomb interaction is written as follows (in atomic units):

\[
- \sum_{i=1}^{3} \frac{1}{2M_i} \Delta_i \psi + \left( \frac{Z_1 Z_2}{r_{12}} + \frac{Z_2 Z_3}{r_{23}} + \frac{Z_3 Z_1}{r_{31}} \right) \psi = E \psi ,
\]

where \( M_i \) and \( Z_i \) - particle mass and charge, \( E \) - energy. For states with a total angular momentum equal to zero, the wave function does not depend on the angular variables, that is, \( \psi = \psi(r_{12}, r_{23}, r_{31}) \).

The coordinates \( r_{12}, r_{23}, r_{31} \) are not independent. This difficulty can be overcome by using the independent variables \( u, v, w \), defined as follows:

\[
 u = r_{12} - r_{23} + r_{31}, \quad v = r_{23} - r_{31} + r_{12}, \quad w = r_{31} - r_{12} + r_{23}.
\]

Variables \( u, v, w \) ranges from 0 to \( \infty \). The wave function is sought in the form:

\[
\psi = \exp(- (u + v + w)/2) \psi(u, v, w).
\]

The function \( \psi \) is expanded in a series in Laguerre polynomials:

\[
\psi(u, v, w) = \sum_{n,m,k=0}^{\infty} L_n(u)L_m(v)L_k(w) \psi_{nmk}.
\]

Considering the properties of the Laguerre polynomials and the normalization condition

\[
\int_{0}^{\infty} dx e^{-x} L_n(x)L_{n'}(x) = \delta_{nn'},
\]

in \[2\], an exact recurrence relation was obtained for the coefficients \( \psi_{nmk} \). This relationship is an infinite system of linear equations for finding the eigenvectors \( \psi_{nmk} \) and eigenvalues of energy \( E \):

\[
\sum_{n'=0}^{\infty} \langle n \, m \, k | C | n' \, m' \, k' \rangle \, \psi_{nmkr} = E \sum_{n'=0}^{\infty} \langle n \, m \, k | R | n' \, m' \, k' \rangle \, \psi_{nmkr},
\]

where \( \langle n \, m \, k | C | n' \, m' \, k' \rangle \) and \( \langle n \, m \, k | R | n' \, m' \, k' \rangle \) known matrix elements. Each coefficient \( \psi_{nmk} \) is determined by three numbers, which is not very convenient for numerical solution of equations. Therefore, to each triple \( n, m, k \) we associate the index \( i \), which ranges from 0 to \( \infty \). This correspondence is established as follows. The number \( p = n + m + k \) is entered, where \( p = 0, 1, \ldots \). For a fixed \( p \), the numbers \( i \) are ordered as follows. First, \( n \) changes from 0 to \( p \), then (for a fixed \( n \) \( m \) changes from 0 to \( p-n \), while \( k = p-n-m \). Thus, we have:
\[ \sum_{j=0}^{\infty} C_{ji} \psi_i = E \sum_{j=0}^{\infty} R_{ji} \psi_i. \]

In work [2] this system was solved for the energy \( E \) by the method of successive approximations. A convergent sequence of energy values was obtained with an increase in the number of solved equations. In the case of a helium atom, the masses and charges of the particles are as follows:

\[
M_1 = 1, \quad M_2 = 1, \quad M_3 = M, \\
Z_1 = -1, \quad Z_2 = -1, \quad Z_3 = 2,
\]

where \( M \) is the mass of the nucleus of a helium atom in atomic units. For the ground state energy, the following value was obtained:

\[ E = -2.903304557734390. \]

4. Comparison of calculation results
The difference between the exact \( E \) and the approximate \( E_g \) values of the energy of the ground state of the helium atom is the error in calculating \( E_g \):

\[ E - E_g = 0.000000000014305. \]

The results of calculations of \( E \) and \( E_g \) coincide with an accuracy of \( 10^{-10} \), which confirms the high accuracy of both methods. Taking into account that the atomic frequency unit is equal to 6579683920.50 MHz [3], we have

\[ E - E_g = 0.094 \text{ MHz}. \]

5. Conclusion
The comparison shows that the difference between the two results of calculating the ground state energy of the helium atom is about 100 kHz. However, it should be noted that work [2] was carried out in 2000, when the computing power was significantly lower than at present. The motivation for this article is related to our studies [4, 5], where we focus on 10 kHz accuracy in the study of resonant stimulated Raman scattering on the \( 2^3S-1^1S \) transition of the helium atom (62.6 nm).
The pump field frequency is close to the frequency of the $^{2\text{I}}\text{P} - ^{2\text{I}}\text{S}$ transition (1083 nm), and the stimulated scattering frequency is close to the frequency of the $^{2\text{I}}\text{P} - ^{1\text{S}}\text{S}$ transition (59.1 nm). The $^{2\text{I}}\text{S}-^{1\text{I}}\text{S}$ transition has a small radiative width, which is determined by the lifetime of the $^{2\text{I}}\text{S}$ state (7900 s). In [4], the possibility of measuring the frequency of the forbidden $^{2\text{I}}\text{S}-^{1\text{I}}\text{S}$ transition with an accuracy of 10 kHz was shown. Measuring the $^{2\text{I}}\text{S}-^{1\text{I}}\text{S}$ transition frequency with this precision will provide additional information for testing quantum electrodynamics. For example, you can measure the Lamb shift of the $^{2\text{I}}\text{S}$ level and compare it with the theoretical value (~5 GHz). The work [5] shows the possibility of creating a frequency standard based on the $^{2\text{I}}\text{S}-^{1\text{I}}\text{S}$ forbidden transition. The standard is needed to measure frequencies in the region of extreme ultraviolet radiation, and possibly X-ray radiation. This is relevant for research in chemistry and biochemistry, which are currently widely carried out using synchrotron radiation.

The study was carried out with the financial support of the Russian Foundation for Basic Research within the framework of scientific project No. 20-02-00068

6. References
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