

Evaluation of Coulomb and exchange integrals for higher excited states of helium atom by using spherical harmonics series

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Abstract In this work we study the higher excited states of Helium Atom. The purpose is to evaluate Coulomb and exchange integral via spherical harmonics series. The Coulomb and exchange integrals energy shift is evaluated up to sixth order. This is the energy when the atom is perturbed by Coulomb potential between electrons. The energy levels obtained from both integrals are in agreement with the experimental data. For highly-excited states, the calculated energy approaches -54.416 eV, in agreement with the graphical results from the book by Powell and Crasemann [1].

Keywords Coulomb integral · Exchange integrals · Perturbation-theory · Addition theorem of spherical harmonics

1 Introduction

Modern physical theory rests upon the basic fact that matter is composed of relatively few types of elementary particles (electrons, positrons, protons, neutrons, etc.). Each type is characterized by a few properties, such as mass, charge, and intrinsic angular momentum or spin, which enter into the equations of the theory as invariable parameters. All electrons, for example, are intrinsically identical in every aspect.

Helium atom is a typical three-body system with strong correlated motion of two electrons influence by Coulomb potential. The numerical calculation of the energy

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levels and the wave functions of a helium atom is one of the most interesting and fundamental problems in the atomic physics. The perturbation method can be used to predict with a very high precision for energy values [2–4]. Scherr and Knight used 100-term trial functions to get extremely accurate approximations to the wave function correction up to sixth order and thus to the energy corrections up to thirteenth order [5,6]. The perturbation-theory series expansion for the He-atom energy can be proved to converge [7,8]. Baker et al. [9] calculated the energy corrections up to order of 401. Drake and Yan used linear variational functions containing r_{12} (Sect. 2) to calculate the ground-state energy and many excited-state energy of helium that are thought to be accurate to 1 part in 10^{14} or better [10,11]. These workers similarly calculated (Li) variational energy for the ground state and two excited states with 1 part in 10^9 accuracy or better [12–15] In 2002, Duan et al. [16–19] showed a new method to evaluate the energy levels of helium atom for a quantum three-body system, where the motion of the center of mass and the global rotation of the system are completely separated from the internal motion.

The plan of this paper is as follows. The helium atom has three-body system. We shall consider the nucleus to be at rest and place the origin of the coordinate system at the nucleus. We will explain the method in Sect. 2 and calculate the Coulomb integral and exchange integral. In Sect. 3, using the addition theorem of spherical harmonic [2] into the Coulomb integral and exchange integral to calculate total energy of each state. The discussion and conclusion are given in Sect. 4.

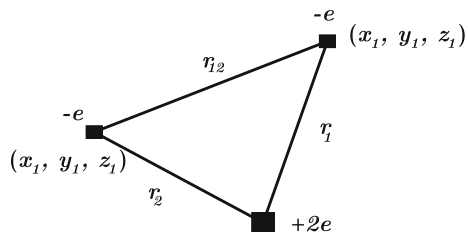
2 Basic theory

The helium atom has two electrons and a nucleus of charge $+2e$. We shall consider the nucleus to be at rest and place the origin of the coordinate system at the nucleus. The coordinate of two electrons 1 and 2 are (x_1, y_1, z_1) and (x_2, y_2, z_2) ; see Fig.1. If we take the nuclear charge to be $+Ze$ instead of $+2e$, we can treat heliumlike ions such as H^- , Li^+ , Be^{2+} The basic Hamiltonian is given by

$$\hat{H} = \frac{\hat{p}_1^2}{2m} + \frac{\hat{p}_2^2}{2m} - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|}, \tag{1}$$

$$\hat{H}_0 = \frac{\hat{p}_1^2}{2m} + \frac{\hat{p}_2^2}{2m} - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2}, \quad \hat{H}' = \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|}, \tag{2}$$

Fig. 1 Interparticle distances in the helium atom



where m is the mass of the electron, r_1 and r_2 are the distances of electrons 1 and 2 from the nucleus, and r_{12} is the distance from electrons 1 to 2. The first two terms are the operators for the electrons kinetic energy. The third and fourth terms are the potential energy of attraction between the electrons and the nucleus. The final term is the potential energy of interelectronic repulsion. Note that the potential energy of a system of interacting particles cannot be written as the sum of potential energy of the individual particles; the potential energy is a property of the system as a whole.

The Schrödinger equation involves six independent variables, three coordinates for each electron. In spherical coordinates, we obtain $\psi = \psi(r_1, \theta_1, \phi_1, r_2, \theta_2, \phi_2)$.

The operator $\hat{p}_1^2 \simeq -\hbar^2 \nabla_1^2$ is given by the Laplacian spherical coordinates with r_1, θ_1, ϕ_1 replacing r, θ, ϕ . The variable r_{12} is $r_{12} = [(x_1 - x_2)^2 + (y_1 - y_2)^2 + (z_1 - z_2)^2]^{1/2}$, and by using the relations between Cartesian and spherical coordinates, we can express r_{12} in terms of $r_1, \theta_1, \phi_1, r_2, \theta_2, \phi_2$. Suppose the $e^2/|\mathbf{r}_1 - \mathbf{r}_2| \equiv e^2/r_{12}$ were absent.

Because of the e^2/r_{12} term, the Schrödinger equation for helium cannot be separated in any coordinate system, and we must use approximation methods. The perturbation method separates the Hamiltonian Eq. (1) into two parts, \hat{H}_0 and \hat{H}' , where \hat{H}_0 is the Hamiltonian of an exactly solvable problem and \hat{H}' is the electron-electron interaction. Then, with the identity question ignored, the wave function would be just the product of two hydrogen atom wave functions with $Z = 1$ change into $Z = 2$. The total spin is constant, so the state is either singlet or triplet. The spatial part of the wave function for the important case where one of the electrons is in the ground state and the other in a higher excited states characterized by (nlm) is

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} [\psi_{100}(\mathbf{r}_1)\psi_{nlm}(\mathbf{r}_2) \pm \psi_{100}(\mathbf{r}_2)\psi_{nlm}(\mathbf{r}_1)]. \quad (3)$$

We have, from the expectation value

$$\langle f \rangle = \int \psi^*(x, t) \hat{f} \psi(x, t) dx \quad (4)$$

The next step is to evaluate the first-order perturbation correction to the energy.

$$\Delta E^{(1)} = \langle H' \rangle = \left\langle \frac{e^2}{r_{12}} \right\rangle \quad (5)$$

Let us define expectation values of \hat{H}' as

$$\left\langle \frac{e^2}{r_{12}} \right\rangle = \int \int_{\mathbf{r}_1, \mathbf{r}_2} \psi^*(\mathbf{r}_1, \mathbf{r}_2) \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \psi(\mathbf{r}_1, \mathbf{r}_2) d^3\mathbf{r}_1 d^3\mathbf{r}_2. \quad (6)$$

By substituting Eq. (3) into (5), we have

$$\begin{aligned}
 \left\langle \frac{e^2}{r_{12}} \right\rangle &= \int_{\mathbf{r}_2} \int_{\mathbf{r}_1} (\psi_{100}^*(\mathbf{r}_1)\psi_{nlm}^*(\mathbf{r}_2) \pm \psi_{100}^*(\mathbf{r}_2)\psi_{nlm}^*(\mathbf{r}_1)) \frac{e^2}{2|\mathbf{r}_1 - \mathbf{r}_2|} \\
 &\quad (\psi_{100}(\mathbf{r}_1)\psi_{nlm}(\mathbf{r}_2) \pm \psi_{100}(\mathbf{r}_2)\psi_{nlm}(\mathbf{r}_1)) d^3\mathbf{r}_1 d^3\mathbf{r}_2 \\
 &= \frac{e^2}{2} \int_{\mathbf{r}_2} \int_{\mathbf{r}_1} [\psi_{100}^*(\mathbf{r}_1)\psi_{nlm}^*(\mathbf{r}_2)\psi_{100}(\mathbf{r}_1)\psi_{nlm}(\mathbf{r}_2) \\
 &\quad \pm \psi_{100}^*(\mathbf{r}_1)\psi_{nlm}^*(\mathbf{r}_2)\psi_{100}(\mathbf{r}_2)\psi_{nlm}(\mathbf{r}_1) \\
 &\quad \pm \psi_{100}^*(\mathbf{r}_2)\psi_{nlm}^*(\mathbf{r}_1)\psi_{100}(\mathbf{r}_1)\psi_{nlm}(\mathbf{r}_2) \\
 &\quad + \psi_{100}^*(\mathbf{r}_2)\psi_{nlm}^*(\mathbf{r}_1)\psi_{100}(\mathbf{r}_2)\psi_{nlm}(\mathbf{r}_1)] \frac{d^3\mathbf{r}_1 d^3\mathbf{r}_2}{|\mathbf{r}_1 - \mathbf{r}_2|} \tag{7}
 \end{aligned}$$

$$\begin{aligned}
 \left\langle \frac{e^2}{r_{12}} \right\rangle &= \frac{e^2}{2} \int_{\mathbf{r}_2} \int_{\mathbf{r}_1} [|\psi_{100}(\mathbf{r}_1)|^2 |\psi_{nlm}(\mathbf{r}_2)|^2 \pm \psi_{100}^*(\mathbf{r}_1)\psi_{nlm}^*(\mathbf{r}_2)\psi_{100}(\mathbf{r}_2)\psi_{nlm}(\mathbf{r}_1) \\
 &\quad \pm \psi_{100}^*(\mathbf{r}_2)\psi_{nlm}^*(\mathbf{r}_1)\psi_{100}(\mathbf{r}_1)\psi_{nlm}(\mathbf{r}_2) \\
 &\quad + |\psi_{100}(\mathbf{r}_2)|^2 |\psi_{nlm}(\mathbf{r}_1)|^2] \frac{d^3\mathbf{r}_1 d^3\mathbf{r}_2}{|\mathbf{r}_1 - \mathbf{r}_2|} \tag{8}
 \end{aligned}$$

Consider the symmetry between \mathbf{r}_1 and \mathbf{r}_2 , then Eq. (8) can be rewritten as

$$\begin{aligned}
 \left\langle \frac{e^2}{r_{12}} \right\rangle &= \int_{\mathbf{r}_2} \int_{\mathbf{r}_1} |\psi_{100}(\mathbf{r}_1)|^2 \cdot \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \cdot |\psi_{nlm}(\mathbf{r}_2)|^2 d^3\mathbf{r}_1 d^3\mathbf{r}_2 \pm \text{Re} \\
 &\quad \int_{\mathbf{r}_2} \int_{\mathbf{r}_1} \psi_{100}^*(\mathbf{r}_2)\psi_{nlm}^*(\mathbf{r}_1) \cdot \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \cdot \psi_{100}(\mathbf{r}_1)\psi_{nlm}(\mathbf{r}_2) d^3\mathbf{r}_1 d^3\mathbf{r}_2. \tag{9}
 \end{aligned}$$

The first term on the right-hand sides of Eq. (9) are *Coulomb integral* [2–4] written as

$$J = \int_{\mathbf{r}_2} \int_{\mathbf{r}_1} |\psi_{100}(\mathbf{r}_1)|^2 \cdot \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \cdot |\psi_{nlm}(\mathbf{r}_2)|^2 d^3\mathbf{r}_1 d^3\mathbf{r}_2. \tag{10}$$

The second term on the right-hand sides of Eq. (9) are *Exchange integral* [2–4] written as

$$K = \int_{\mathbf{r}_2} \int_{\mathbf{r}_1} \psi_{100}^*(\mathbf{r}_2)\psi_{nlm}^*(\mathbf{r}_1) \cdot \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \cdot \psi_{100}(\mathbf{r}_1)\psi_{nlm}(\mathbf{r}_2) d^3\mathbf{r}_1 d^3\mathbf{r}_2. \tag{11}$$

We consider just $(1s)(nl)$. We write the energy of this state as

$$E = E_{100} + E_{nlm} + \Delta E. \quad (12)$$

In first-order perturbation theory, ΔE is obtained by evaluating the expectation value of e^2/r_{12} . We can write

$$\left\langle \frac{e^2}{r_{12}} \right\rangle = (J \pm K). \quad (13)$$

By substituting Eq. (13) back into Eq. (12), we obtain total energy of helium atom

$$E = E_{100} + E_{nlm} + J \pm K. \quad (14)$$

The **lower energy** level is, therefore,

$$E_t = E_{100} + E_{nlm} + (J - K), \quad (15)$$

and is triply degenerate(-) it is called a **triplet** [4]. The **higher energy** level,

$$E_t = E_{100} + E_{nlm} + (J + K), \quad (16)$$

is non-degenerate, and is therefore a **singlet** [4], as is the ground state (Table 1).

The physical interpretation for this is as follows: In the singlet (Eq. (16)) case the spatial function is symmetric and the electrons have a tendency to come close to each other. Therefore, the effect of the electrostatic repulsion is more serious; hence, a higher energy results. In the triplet (Eq. (15)) case, the spatial function is antisymmetric and the electrons tend to avoid each other. Helium in spin-singlet states is known as **parahelium**, while helium in spin-triplet states is known as **orthohelium**. See Fig. 2. for a schematic energy level diagram of the helium atom.

3 Numerical results of the Coulomb integral and exchange integral

The Coulomb integral and exchange integral for higher excited states of Helium Atom is calculated by using Spherical Harmonics Series. We use mathematica program in the calculation of energy.

3.1 Calculation of the Coulomb integral

The Coulomb integral can be written as

$$J = \int_{\mathbf{r}_2} \int_{\mathbf{r}_1} |\psi_{100}(\mathbf{r}_1)|^2 \cdot \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \cdot |\psi_{nlm}(\mathbf{r}_2)|^2 d^3\mathbf{r}_1 d^3\mathbf{r}_2, \quad (17)$$

Table 1 The total energy of the helium atom in higher excited state

| Spectral term | Calculated | Experimental [19] | % Difference |
|---------------------|-------------------|-------------------|--------------|
| 1s2s ¹ S | -55.4050425240055 | -58.3624572424563 | 5.33781 |
| 1s3s ¹ S | -54.7346592339410 | -56.0579202431514 | 2.41759 |
| 1s4s ¹ S | -54.5535138464768 | -55.2491296415375 | 1.27511 |
| 1s5s ¹ S | -54.4870842912034 | | |
| 1s6s ¹ S | -54.4573420862175 | | |
| 1s7s ¹ S | -54.4421110706479 | | |
| 1s8s ¹ S | -54.4335251863824 | | |
| 1s2s ³ S | -57.7936735237756 | -59.1581011131610 | 2.36086 |
| 1s3s ³ S | -55.3623828666753 | -56.2604609645120 | 1.62218 |
| 1s4s ³ S | -54.8081410245632 | -55.3634244356412 | 1.01314 |
| 1s5s ³ S | -54.6151609247315 | | |
| 1s6s ³ S | -54.5307576125461 | | |
| 1s7s ³ S | -54.4880803922891 | | |
| 1s8s ³ S | -54.4642075785788 | | |
| 1s2p ¹ P | -53.8789727573545 | -57.7604441467894 | 7.20406 |
| 1s3p ¹ P | -54.2937581108941 | -55.8915139004001 | 2.94287 |
| 1s4p ¹ P | -54.3691766078874 | -55.1922689600000 | 1.51396 |
| 1s5p ¹ P | -54.3930976624178 | | |
| 1s6p ¹ P | -54.4030752736124 | | |
| 1s7p ¹ P | -54.4079840937083 | | |
| 1s8p ¹ P | -54.4106831400724 | | |
| 1s2p ³ P | -55.7367968297516 | -58.0143534226402 | 4.08627 |
| 1s3p ³ P | -54.7869695366753 | -55.9717377584023 | 2.16250 |
| 1s4p ³ P | -54.5698827364966 | -55.2361266080000 | 1.22090 |
| 1s5p ³ P | -54.4941966213751 | | |
| 1s6p ³ P | -54.4610710235423 | | |
| 1s7p ³ P | -54.4443148339112 | | |
| 1s8p ³ P | -54.4349393578153 | | |
| 1s3d ¹ D | -54.4073461968324 | -55.9043256000000 | 2.75143 |
| 1s4d ¹ D | -54.4115360143487 | -55.1854601120000 | 1.42235 |
| 1s5d ¹ D | -54.4135541023456 | | |
| 1s6d ¹ D | -54.4145386574369 | | |
| 1s7d ¹ D | -54.4150632320963 | | |
| 1s8d ¹ D | -54.4153655047746 | | |
| 1s3d ³ D | -54.4342486382376 | -55.9047828800000 | 2.70149 |
| 1s4d ³ D | -54.4258864312197 | -55.1879867210000 | 1.40025 |
| 1s5d ³ D | -54.4215435764179 | | |
| 1s6d ³ D | -54.4193543215431 | | |

Table 1 continued

| Spectral term | Calculated | Experimental [19] | % Difference |
|---------------------|-------------------|-------------------|--------------|
| 1s7d ³ D | -54.4181667827563 | | |
| 1s8d ³ D | -54.4174749665374 | | |
| 1s4f ¹ F | -54.4189244597897 | | |
| 1s5f ¹ F | -54.4159400013254 | | |
| 1s6f ¹ F | -54.4159582013456 | | |
| 1s7f ¹ F | -54.4159709138162 | | |
| 1s8f ¹ F | -54.4159792752935 | | |
| 1s4f ³ F | -54.4191486578456 | | |
| 1s5f ³ F | -54.4161203653457 | | |
| 1s6f ³ F | -54.4160847564789 | | |
| 1s7f ³ F | -54.4160593395956 | | |
| 1s8f ³ F | -54.4164240923064 | | |
| 1s5g ¹ G | -54.4159995887897 | | |
| 1s6g ¹ G | -54.4159996143478 | | |
| 1s7g ¹ G | -54.4159996261728 | | |
| 1s8g ¹ G | -54.4159997043236 | | |
| 1s5g ³ G | -54.4160007956426 | | |
| 1s6g ³ G | -54.4160008567534 | | |
| 1s7g ³ G | -54.4160009189475 | | |
| 1s8g ³ G | -54.4160009570744 | | |
| 1s6h ¹ H | -54.4159999984201 | | |
| 1s7h ¹ H | -54.4159999988620 | | |
| 1s8h ¹ H | -54.4159999997917 | | |
| 1s6h ³ H | -54.4160000029215 | | |
| 1s7h ³ H | -54.4160000034795 | | |
| 1s8h ³ H | -54.4160000039854 | | |
| 1s7i ¹ I | -54.4159999999956 | | |
| 1s8i ¹ I | -54.4159999999969 | | |
| 1s7i ³ I | -54.4160000000080 | | |
| 1s8i ³ I | -54.4160000000130 | | |

and using the addition theorem of spherical harmonics [2]:

$$\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} = \sum_{l'=0}^{\infty} \sum_{m'=-l'}^{l'} \left(\frac{4\pi}{2l'+1} \right) \cdot \frac{r_{<}^{l'}}{r_{>}^{l'+1}} Y_{l'm'}(\Omega_1) Y_{l'm'}^*(\Omega_2), \quad (18)$$

where $r_{>}$ ($r_{<}$) is the larger (smaller) of r_1 and r_2 respectively. Thus a different expansion is presented for each region see Fig. 3. $r_{>}$ is the vector indicating the position of

Fig. 2 Schematic energy level diagram for higher excited state configurations of helium atom

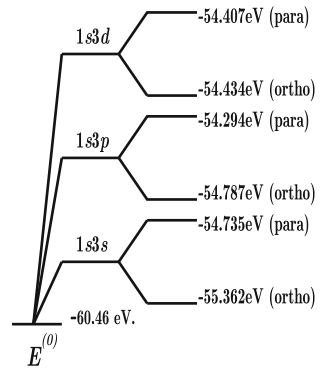
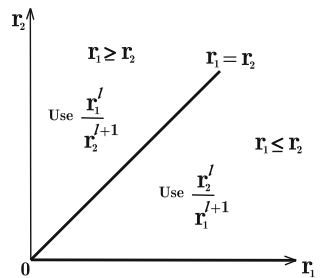


Fig. 3 The graph shows the relation between individual electrons and atomic nuclei



the electron far away from the nucleus. $r_<$ is the vector indicating the position of the electron near the nucleus.

Substituting Eq. (18) back into Eq. (17) yields

$$J = e^2 \sum_{l'=0}^{\infty} \sum_{m'=-l'}^{l'} \left(\frac{4\pi}{2l'+1} \right) \int \int \int \int_{\Omega_2 \Omega_1 r_2 r_1} dr_1 dr_2 d\Omega_1 d\Omega_2 r_1^2 R_{10}^2(r_1) Y_{00}^*(\Omega_1) Y_{00}(\Omega_1) \left(\frac{r_{<}^{l'}}{r_{>}^{l'+1}} \right) Y_{l'm'}(\Omega_1) Y_{l'm'}^*(\Omega_2) r_2^2 R_{nl}^2(r_2) Y_{lm}^*(\Omega_2) Y_{lm}(\Omega_2) \quad (19)$$

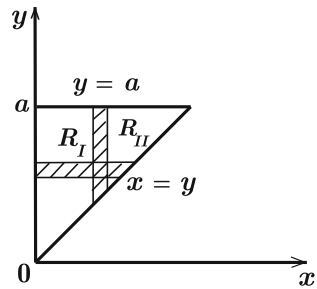
Substituting $Y_{00}(\Omega_1)Y_{00}^*(\Omega_1) = (4\pi)^{-1/2}$ into Eq. (19) gives

$$J = e^2 \sum_{l'=0}^{\infty} \sum_{m'=-l'}^{l'} \left(\frac{1}{2l'+1} \right) \int \int_{\Omega_2 \Omega_1} d\Omega_1 d\Omega_2 Y_{l'm'}(\Omega_1) Y_{l'm'}^*(\Omega_2) Y_{lm}^*(\Omega_2) Y_{lm}(\Omega_2) \int \int_{r_2 r_1} dr_1 dr_2 r_1^2 R_{10}^2(r_1) r_2^2 R_{nl}^2(r_2) \left(\frac{r_{<}^{l'}}{r_{>}^{l'+1}} \right) \quad (20)$$

We define the new variable C_i so that

$$C_{l'} = \int \int_{r_2 r_1} dr_1 dr_2 r_1^2 R_{10}^2(r_1) r_2^2 R_{nl}^2(r_2) \left(\frac{r_{<}^{l'}}{r_{>}^{l'+1}} \right). \quad (21)$$

Fig. 4 Showing the area of double integrals



Substituting the definition [2]

$$\left(\begin{matrix} r'_1 < \\ r'_2 > \end{matrix} \right) = \begin{cases} \frac{r'_1}{r'^{l'+1}_2} & \text{for } r_1 < r_2 \\ \frac{r'_2}{r'^{l'+1}_1} & \text{for } r_1 > r_2 \end{cases}$$

into Eq. (21), we have

$$C_{l'} = \int_0^\infty \int_0^{r_2} r_2^2 \cdot \frac{r_1^{l'+2}}{r_2^{l'+1}} R_{nl}^2(r_2) R_{10}^2(r_1) dr_1 dr_2 + \int_0^\infty \int_{r_1}^\infty r_1^2 \cdot \frac{r_2^{l'+2}}{r_1^{l'+1}} R_{nl}^2(r_2) R_{10}^2(r_1) dr_1 dr_2 \quad (22)$$

The first term on the right-hand sides of Eq. (22) are $C_{l'_1}$ written as

$$C_{l'_1} = \int_0^\infty \int_0^{r_2} r_2^2 \cdot \frac{r_1^{l'+2}}{r_2^{l'+1}} R_{nl}^2(r_2) R_{10}^2(r_1) dr_1 dr_2 \quad (23)$$

The second term on the right-hand sides of Eq. (22) are $C_{l'_2}$ written as

$$C_{l'_2} = \int_0^\infty \int_{r_1}^\infty r_1^2 \cdot \frac{r_2^{l'+2}}{r_1^{l'+1}} R_{nl}^2(r_2) R_{10}^2(r_1) dr_1 dr_2 \quad (24)$$

Let us consider Fig. 4. The area integrals of the region R_I, R_{II} are

$$\int_{R_I} f(x, y) dx dy = \int_0^a \int_0^y f(x, y) dx dy, \quad (25)$$

$$\int_{R_{II}} f(x, y) dx dy = \int_0^a \int_x^a f(x, y) dy dx. \quad (26)$$

when

$$R_I : 0 \leq x \leq y, 0 \leq y \leq a$$

$$R_{II} : 0 \leq x \leq a, x \leq y \leq a.$$

Following the Double Integral method in Ref. [20], Eq. (25) can change the order of the integrated hazard. There is value in the Eq. (26), we have

$$\int_0^a \int_0^y f(x, y) dx dy = \int_0^a \int_x^a f(x, y) dy dx. \tag{27}$$

Equation (23) is hence transformed to

$$C_{l'} = \int_0^\infty \int_0^{r_2} r_2^2 \cdot \frac{r_1^{l'+2}}{r_2^{l'+1}} R_{nl}^2(r_2) R_{10}^2(r_1) dr_1 dr_2$$

$$= \int_0^\infty \int_{r_1}^\infty r_2^2 \cdot \frac{r_1^{l'+2}}{r_2^{l'+1}} R_{nl}^2(r_2) R_{10}^2(r_1) dr_1 dr_2 \tag{28}$$

Equation (23) is compared with that of the Eq. (28). It is found that the value of r_1 and r_2 relation is $r_1 \leftrightarrow r_2$. Equation (23) has to be transformed into Eq. (28) in order to get the Coulomb integral done. Inserting Eq. (22) into (20) the Coulomb integral is written as

$$J = e^2 \sum_{l'=0}^\infty \sum_{m'=-l'}^{l'} \left(\frac{C_{l'}}{2l'+1} \right) \iint_{\Omega_2 \Omega_1} Y_{l'm'}(\Omega_1) Y_{l'm'}^*(\Omega_2) Y_{lm}^*(\Omega_2) Y_{lm}(\Omega_2) \tag{29}$$

We consider the first excited state(1s2p) of helium $n = 2, l = 1, m = \pm 1, 0$ into Eq. (29), yields

$$J = e^2 \sum_{l'=0}^\infty \sum_{m'=-l'}^{l'} \left(\frac{C_{l'}}{2l'+1} \right) \iint_{\Omega_2 \Omega_1} Y_{l'm'}^*(\Omega_2) Y_{1m}^*(\Omega_2) Y_{1m}(\Omega_2)$$

$$\left\{ \int_{\Omega_1} \frac{Y_{00}^*(\Omega_1)}{Y_{00}(\Omega_1)} \cdot Y_{l'm'}(\Omega_1) d\Omega_1 \right\} d\Omega_2 \tag{30}$$

Using properties of the orthonormality relations of spherical harmonics into Eq. (30), we have

$$J = e^2 C_{l'} \tag{31}$$

By substituting Eq. (22) into (31), we have

$$J = e^2 \left\{ \int_0^\infty r_2 R_{21}^2(r_2) \left[\int_0^{r_2} r_1^2 R_{10}^2(r_1) dr_1 \right] dr_2 + \int_0^\infty r_2^2 R_{21}^2(r_2) \left[\int_{r_2}^\infty r_1 R_{10}^2(r_1) dr_1 \right] dr_2 \right\} \quad (32)$$

Substituting Eq. (32) into Mathematica program, will the value of the Coulomb integral so that

$$J = \frac{59Ze^2}{243a_0} = 13.22 \text{ eV}. \quad (33)$$

3.2 Calculation of the exchange integral

The exchange integral can be written as

$$K = e^2 \int_{r_2} \int_{r_1} \psi_{100}^*(\mathbf{r}_2) \psi_{nlm}^*(\mathbf{r}_1) \cdot \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \cdot \psi_{100}(\mathbf{r}_1) \psi_{nlm}(\mathbf{r}_2) d^3 \mathbf{r}_1 d^3 \mathbf{r}_2 \quad (34)$$

Substituting the addition theorem of spherical harmonics series into Eq. (34), we finally obtain the exchange integral as

$$K = e^2 \sum_{l'=0}^\infty \sum_{m'=-l'}^{l'} \left(\frac{4\pi}{2l'+1} \right) \int_{r_2} \int_{r_1} d^3 \mathbf{r}_1 d^3 \mathbf{r}_2 \psi_{100}^*(\mathbf{r}_2) \psi_{nlm}^*(\mathbf{r}_1) \left(\frac{r_{<}^{l'}}{r_{>}^{l'+1}} \right) Y_{l'm'}(\Omega_1) Y_{l'm'}^*(\Omega_2) \psi_{100}(\mathbf{r}_1) \psi_{nlm}^*(\mathbf{r}_2). \quad (35)$$

We consider the first excited state(1s2p) of helium $n = 2, l = 1, m = \pm 1, 0$ into Eq. (35), yields

$$K = e^2 \sum_{l'=0}^\infty \sum_{m'=-l'}^{l'} \left(\frac{4\pi}{2l'+1} \right) \int_{r_2} \int_{r_1} d^3 \mathbf{r}_1 d^3 \mathbf{r}_2 \psi_{100}^*(\mathbf{r}_2) \psi_{21m}^*(\mathbf{r}_1) \left(\frac{r_{<}^{l'}}{r_{>}^{l'+1}} \right) Y_{l'm'}(\Omega_1) Y_{l'm'}^*(\Omega_2) \psi_{100}(\mathbf{r}_1) \psi_{21m}^*(\mathbf{r}_2). \quad (36)$$

We consider the wave function to be $\psi_{2,1,-1}(\mathbf{r}) = R_{2,1}(r)Y_{1,-1}(\Omega)$ and using properties of the orthonormality relations of spherical harmonics into Eq. (36), we get

$$K = \frac{e^2}{3} \int_{r_2} r_2^2 R_{10}(r_2) R_{21}(r_2) \left\{ \int_{r_1} r_1^2 R_{10}(r_1) R_{21}(r_1) \left(\frac{r_{<}^{l'}}{r_{>}^{l'+1}} \right) dr_1 \right\} dr_2. \quad (37)$$

Substituting the definition [2]

$$\left(\begin{matrix} r'_{<} \\ r'_{>} \end{matrix} \right) = \begin{cases} \frac{r'_1}{r'_1+1} & \text{for } r_1 < r_2 \\ \frac{r'_2}{r'_2+1} & \text{for } r_1 > r_2 \end{cases}$$

into Eq. (37), we have

$$K = \frac{e^2}{3} \int_0^\infty \int_0^{r_2} r_2^2 \frac{r_1^3}{r_2^2} R_{10}(r_2) R_{21}(r_2) R_{10}(r_1) R_{21}(r_1) dr_1 dr_2 + \frac{e^2}{3} \int_0^\infty \int_{r_2}^\infty r_1^2 \frac{r_2^3}{r_1^2} R_{10}(r_2) R_{21}(r_2) R_{10}(r_1) R_{21}(r_1) dr_1 dr_2 \tag{38}$$

The first term on the right-hand sides of Eq. (38) are K_{1a} written as

$$K_{1a} = \frac{e^2}{3} \int_0^\infty \int_0^{r_2} r_2^2 \frac{r_1^3}{r_2^2} R_{10}(r_2) R_{21}(r_2) R_{10}(r_1) R_{21}(r_1) dr_1 dr_2. \tag{39}$$

The second term on the right-hand sides of Eq. (38) are K_{2a} written as

$$k_{2a} = \frac{e^2}{3} \int_0^\infty \int_{r_2}^\infty r_1^2 \frac{r_2^3}{r_1^2} R_{10}(r_2) R_{21}(r_2) R_{10}(r_1) R_{21}(r_1) dr_1 dr_2. \tag{40}$$

From Eq. (39) used change the order of the integrated, we obtain K_{1a} rewritten as

$$K_{1a} = \frac{e^2}{3} \int_0^\infty \int_{r_1}^\infty r_1^2 \frac{r_2^3}{r_1^2} R_{10}(r_2) R_{21}(r_2) R_{10}(r_1) R_{21}(r_1) dr_2 dr_1. \tag{41}$$

It is easy to see that $K_{1a} = K_{2a}$. The exchange integral Eq. (38) can therefore be rewritten as

$$K = \frac{2e^2}{3} \int_0^\infty r_2^3 R_{10}(r_2) R_{21}(r_2) \left\{ \int_{r_2}^\infty R_{10}(r_1) R_{21}(r_1) dr_1 \right\} dr_2. \tag{42}$$

Substituting $m = 0, 1$ into Eq. (35), we get the exchange integral like Eq. (42). Substituting Eq. (42) into Mathematica program (see Sect. 3.3), will the value of the exchange integral so that

$$K = \frac{112Z e^2}{6561a_0} = 0.94 \text{ eV}. \tag{43}$$

3.3 The calculation of mathematica program

Calculation of the energy of the Coulomb integral and exchange integral ($\frac{e^2}{a_0}$ unit) Case

1. Evaluation of the Coulomb integral (1s3s)

$$J = e^2 \left\{ \int_0^\infty r_2 R_{30}^2(r_2) \left[\int_0^{r_2} r_1^2 R_{10}^2(r_1) dr_1 \right] dr_2 + \int_0^\infty r_2^2 R_{30}^2(r_2) \left[\int_{r_2}^\infty r_1 R_{10}^2(r_1) dr_1 \right] dr_2 \right\}, \quad (44)$$

where $l' = 0, l = 0, n = 3$. The calculation is as follows.

$$In := R10[r1_] := 2\left(\frac{z}{a_0}\right)^{\frac{3}{2}} E^{-\frac{zr1}{a_0}}$$

$$In := R30[r1_] := 2\left(\frac{z}{3a_0}\right)^{\frac{3}{2}} \left(1 - \frac{2zr1}{3a_0} + \frac{2z^2r1^2}{27a_0^2}\right) E^{-\frac{zr1}{3a_0}}$$

$$In := R10[r2_] := 2\left(\frac{z}{a_0}\right)^{\frac{3}{2}} E^{-\frac{zr2}{a_0}}$$

$$In := R30[r2_] := 2\left(\frac{z}{3a_0}\right)^{\frac{3}{2}} \left(1 - \frac{2zr2}{3a_0} + \frac{2z^2r2^2}{27a_0^2}\right) E^{-\frac{zr2}{3a_0}}$$

$$In := J3A[r2_] := \int_{r2}^\infty r1 (R10[r1])^2 dr1$$

$$In := J3A[r2]$$

$$Out := ConditionExpression\left[\left(e^{-\frac{2r2z}{a_0}} z(a_0 + 2r2z)\right), \operatorname{Re}\left[\frac{z}{a_0}\right] > 0\right]$$

$$In := J2A[r2_] := \left(\frac{e^{-\frac{2r2z}{a_0}} z(a_0 + 2r2z)}{a_0^2}\right)$$

$$In := J1A = \int_0^\infty r2^2 (R30[r2])^2 (J2A[r2]) dr2$$

$$Out := ConditionExpression\left[\frac{269z}{32768a_0}, \operatorname{Re}\left[\frac{z}{a_0}\right] > 0\right]$$

$$In := JA = \left(\frac{269z}{32768a_0}\right)$$

$$Out := \frac{269z}{32768a_0}$$

$$In := J3B[r2_] := \int_0^{r2} r1^2 (R10[r1])^2 dr1$$

$$In := J3B[r2]$$

$$Out := \left(1 - \frac{\exp\left(-\frac{2r2z}{a_0}\right) (a_0^2 + 2a_0r2z + 2r2^2z^2)}{a_0^2}\right)$$

$$In := J2B[r2] := \left(1 - \frac{\exp\left(-\frac{2r2z}{a_0}\right) (a_0^2 + 2a_0r2z + 2r2^2z^2)}{a_0^2}\right)$$

$$In := J1B = \int_0^\infty r2 (R30[r2])^2 (J2B[r2]) dr2$$

$$Out := ConditionExpression\left[\frac{2991z}{32768a_0}, \operatorname{Re}\left[\frac{z}{a_0}\right] > 0\right]$$

$$In := JB = \left(\frac{2991z}{32768a_0}, \operatorname{Re}\left[\frac{z}{a_0}\right]\right)$$

$$Out := \frac{2991z}{32768a_0}$$

$$In := J = JA + JB$$

$$Out := \frac{815z}{8192a_0}$$

Case 2. Evaluation of the exchange integral (1s3s)

$$K = 2e^2 \int_0^\infty r_2^2 R_{10}(r_2) R_{30}(r_2) \left\{ \int_{r_2}^\infty r_1 R_{10}(r_1) R_{30}(r_1) dr_1 \right\} dr_2 \quad (45)$$

where $l' = 0, l = 0, n = 3$. The calculation is as follows.

$$\begin{aligned}
 In &:= R10[r1_] := 2\left(\frac{z}{a0}\right)^{\frac{3}{2}} E^{-\frac{zr1}{a0}} \\
 In &:= R30[r1_] := 2\left(\frac{z}{3a0}\right)^{\frac{3}{2}} \left(1 - \frac{2zr1}{3a0} + \frac{2z^2r1^2}{27a0}\right) E^{-\frac{zr1}{3a0}} \\
 In &:= R10[r2_] := 2\left(\frac{z}{a0}\right)^{\frac{3}{2}} E^{-\frac{zr2}{a0}} \\
 In &:= R30[r2_] := 2\left(\frac{z}{3a0}\right)^{\frac{3}{2}} \left(1 - \frac{2zr2}{3a0} + \frac{2z^2r2^2}{27a0}\right) E^{-\frac{zr2}{3a0}} \\
 In &:= K3[r2_] := \int_{r2}^{\infty} r1 R10[r1] R30[r1] dr1 \\
 In &:= K3[r2] \\
 Out &:= ConditionalExpression\left[\frac{\exp\left(-\frac{4r2z}{3a0}\right)z(81a0^3+108a0^2r2z-216a0r2^2z^2+32r2^3z^3)}{432\sqrt{3}a0^4}\right] \\
 In &:= K2[r2_] := \left(\frac{\exp\left(-\frac{4r2z}{3a0}\right)z(81a0^3+108a0^2r2z-216a0r2^2z^2+32r2^3z^3)}{432\sqrt{3}a0^4}\right) \\
 In &:= K1 = \int_0^{\infty} r2^2 R10[r2] R30[r2] K2[r2] dr2 \\
 &:= ConditionalExpression[((189z)/(65536a0)) \\
 In &:= K = \left(\frac{189z}{65536a0}\right) \\
 Out &:= \left(\frac{189z}{65536a0}\right)
 \end{aligned}$$

4 Conclusion

For the state 1s3s, we obtain the Coulomb integral and exchange integral as follows:

$$\begin{aligned}
 J &= e^2 \left\{ \int_0^{\infty} r_2 R_{30}^2(r_2) \left[\int_0^{r_2} r_1^2 R_{10}^2(r_1) dr_1 \right] dr_2 \right. \\
 &\quad \left. + \int_0^{\infty} r_2^2 R_{30}^2(r_2) \left[\int_{r_2}^{\infty} r_1 R_{10}^2(r_1) dr_1 \right] dr_2 \right\}, \tag{46}
 \end{aligned}$$

$$K = 2e^2 \int_0^{\infty} r_2^2 R_{10}(r_2) R_{30}(r_2) \left\{ \int_{r_2}^{\infty} r_1 R_{10}(r_1) R_{30}(r_1) dr_1 \right\} dr_2. \tag{47}$$

For the state 1s3p, we get

$$\begin{aligned}
 J &= e^2 \left\{ \int_0^{\infty} r_2 R_{31}^2(r_2) \left[\int_0^{r_2} r_1^2 R_{10}^2(r_1) dr_1 \right] dr_2 \right. \\
 &\quad \left. + \int_0^{\infty} r_2^2 R_{31}^2(r_2) \left[\int_{r_2}^{\infty} r_1 R_{10}^2(r_1) dr_1 \right] dr_2 \right\}, \tag{48}
 \end{aligned}$$

$$K = \frac{2}{3} e^2 \int_0^{\infty} r_2^3 R_{10}(r_2) R_{31}(r_2) \left\{ \int_{r_2}^{\infty} R_{10}(r_1) R_{31}(r_1) dr_1 \right\} dr_2. \tag{49}$$

For the state 1s3d, we obtain the Coulomb integral and exchange integral as follows:

$$J = e^2 \left\{ \int_0^\infty r_2 R_{32}^2(r_2) \left[\int_0^{r_2} r_1^2 R_{10}^2(r_1) dr_1 \right] dr_2 + \int_0^\infty r_2^2 R_{32}^2(r_2) \left[\int_{r_2}^\infty r_1 R_{10}^2(r_1) dr_1 \right] dr_2 \right\}, \quad (50)$$

$$K = \frac{2}{5} e^2 \int_0^\infty r_2^4 R_{10}(r_2) R_{32}(r_2) \left\{ \int_{r_2}^\infty \frac{1}{r_1} R_{10}(r_1) R_{32}(r_1) dr_1 \right\} dr_2. \quad (51)$$

For the state 1s4f, we have

$$J = e^2 \left\{ \int_0^\infty r_2 R_{43}^2(r_2) \left[\int_0^{r_2} r_1^2 R_{10}^2(r_1) dr_1 \right] dr_2 + \int_0^\infty r_2^2 R_{43}^2(r_2) \left[\int_{r_2}^\infty r_1 R_{10}^2(r_1) dr_1 \right] dr_2 \right\}, \quad (52)$$

$$K = \frac{2}{7} e^2 \int_0^\infty r_2^5 R_{10}(r_2) R_{43}(r_2) \left\{ \int_{r_2}^\infty \frac{1}{r_1^2} R_{10}(r_1) R_{43}(r_1) dr_1 \right\} dr_2. \quad (53)$$

For the state 1s5g, we obtain the Coulomb integral and exchange integral as follows:

$$J = e^2 \left\{ \int_0^\infty r_2 R_{54}^2(r_2) \left[\int_0^{r_2} r_1^2 R_{10}^2(r_1) dr_1 \right] dr_2 + \int_0^\infty r_2^2 R_{54}^2(r_2) \left[\int_{r_2}^\infty r_1 R_{10}^2(r_1) dr_1 \right] dr_2 \right\}, \quad (54)$$

$$K = \frac{2}{9} e^2 \int_0^\infty r_2^6 R_{10}(r_2) R_{54}(r_2) \left\{ \int_{r_2}^\infty \frac{1}{r_1^3} R_{10}(r_1) R_{54}(r_1) dr_1 \right\} dr_2. \quad (55)$$

For the state 1s6h, we obtain

$$J = e^2 \left\{ \int_0^\infty r_2 R_{65}^2(r_2) \left[\int_0^{r_2} r_1^2 R_{10}^2(r_1) dr_1 \right] dr_2 + \int_0^\infty r_2^2 R_{65}^2(r_2) \left[\int_{r_2}^\infty r_1 R_{10}^2(r_1) dr_1 \right] dr_2 \right\}, \quad (56)$$

$$K = \frac{2}{11} e^2 \int_0^\infty r_2^7 R_{10}(r_2) R_{65}(r_2) \left\{ \int_{r_2}^\infty \frac{1}{r_1^4} R_{10}(r_1) R_{65}(r_1) dr_1 \right\} dr_2. \quad (57)$$

For the state $1s7i$, we obtain the Coulomb integral and exchange integral as follows:

$$J = e^2 \left\{ \int_0^\infty r_2 R_{76}^2(r_2) \left[\int_0^{r_2} r_1^2 R_{10}^2(r_1) dr_1 \right] dr_2 + \int_0^\infty r_2^2 R_{76}^2(r_2) \left[\int_{r_2}^\infty r_1 R_{10}^2(r_1) dr_1 \right] dr_2 \right\}, \quad (58)$$

$$K = \frac{2}{13} e^2 \int_0^\infty r_2^8 R_{10}(r_2) R_{76}(r_2) \left\{ \int_{r_2}^\infty \frac{1}{r_1^5} R_{10}(r_1) R_{76}(r_1) dr_1 \right\} dr_2. \quad (59)$$

For highly-excited states, the calculated energy approach -54.416 eV, in agreement with the graphical results from the book by Powell and Crasemann [1] ($1s3s$, $1s3p$, $1s3d$, $1s4s$, $1s4p$, $1s4d$, $1s4f$).

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