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ORIGINAL PAPER

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

Artit Hutem · Sutee Boonchui

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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 $-54.416\,\text{eV}$, 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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A. Hutem · S. Boonchui (✉)
Forum for Theoretical and Computational Physics Department of Physics, Faculty of Science,
Kasetsart University, Bangkok 10900, Thailand
e-mail: fscistb@ku.ac.th

A. Hutem · S. Boonchui
Center of Excellence in Forum for Theoretical Science, Chulalongkorn University,
Bangkok 10330, Thailand

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

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

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

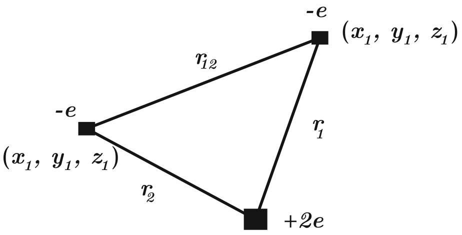

Fig. 1 Interparticle distances in the helium atom

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 $e^2/|\mathbf{r_1} - \mathbf{r_2}| \equiv e^2/\mathbf{r_{12}}$ were absent.

Because of the $e^2/\mathbf{r_{12}}$ 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

$$\psi(\mathbf{r_1}, \mathbf{r_2}) = \frac{1}{\sqrt{2}}[\psi_{100}(\mathbf{r_1})\psi_{nlm}(\mathbf{r_2}) \pm \psi_{100}(\mathbf{r_2})\psi_{nlm}(\mathbf{r_1})]. \tag{3}$$

We have, from the expectation value

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

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

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

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

$$\left\langle \frac{e^2}{r_{12}} \right\rangle = \int\limits_{\mathbf{r_2}} \int\limits_{\mathbf{r_1}} \psi^*(\mathbf{r_1}, \mathbf{r_2}) \frac{e^2}{|\mathbf{r_1} - \mathbf{r_2}|} \psi(\mathbf{r_1}, \mathbf{r_2}) d^3\mathbf{r_1} d^3\mathbf{r_2}. \tag{6}$$

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

$$\begin{aligned}\left\langle\frac{e^2}{r_{12}}\right\rangle &= \int\limits_{\mathbf{r_2}}\int\limits_{\mathbf{r_1}}(\psi_{100}^*(\mathbf{r_1})\psi_{nlm}^*(\mathbf{r_2}) \pm \psi_{100}^*(\mathbf{r_2})\psi_{nlm}^*(\mathbf{r_1}))\frac{e^2}{2|\mathbf{r_1}-\mathbf{r_2}|}\\ &\quad(\psi_{100}(\mathbf{r_1})\psi_{nlm}(\mathbf{r_2}) \pm \psi_{100}(\mathbf{r_2})\psi_{nlm}(\mathbf{r_1})d^3\mathbf{r_1}d^3\mathbf{r_2})\\ &= \frac{e^2}{2}\int\limits_{\mathbf{r_2}}\int\limits_{\mathbf{r_1}}[\psi_{100}^*(\mathbf{r_1})\psi_{nlm}^*(\mathbf{r_2})\psi_{100}(\mathbf{r_1})\psi_{nlm}(\mathbf{r_2})\\ &\quad\pm\psi_{100}^*(\mathbf{r_1})\psi_{nlm}^*(\mathbf{r_2})\psi_{100}(\mathbf{r_2})\psi_{nlm}(\mathbf{r_1})\\ &\quad\pm\psi_{100}^*(\mathbf{r_2})\psi_{nlm}^*(\mathbf{r_1})\psi_{100}(\mathbf{r_1})\psi_{nlm}(\mathbf{r_2})\\ &\quad+\psi_{100}^*(\mathbf{r_2})\psi_{nlm}^*(\mathbf{r_1})\psi_{100}(\mathbf{r_2})\psi_{nlm}(\mathbf{r_1})]\frac{d^3\mathbf{r_1}d^3\mathbf{r_2}}{|\mathbf{r_1}-\mathbf{r_2}|}\end{aligned} \tag{7}$$

$$\begin{aligned}\left\langle\frac{e^2}{r_{12}}\right\rangle &= \frac{e^2}{2}\int\limits_{\mathbf{r_2}}\int\limits_{\mathbf{r_1}}\left[|\psi_{100}(\mathbf{r_1})|^2|\psi_{nlm}(\mathbf{r_2})|^2 \pm \psi_{100}^*(\mathbf{r_1})\psi_{nlm}^*(\mathbf{r_2})\psi_{100}(\mathbf{r_2})\psi_{nlm}(\mathbf{r_1})\right.\\ &\quad\pm\psi_{100}^*(\mathbf{r_2})\psi_{nlm}^*(\mathbf{r_1})\psi_{100}(\mathbf{r_1})\psi_{nlm}(\mathbf{r_2})\\ &\quad\left.+|\psi_{100}(\mathbf{r_2})|^2|\psi_{nlm}(\mathbf{r_1})|^2\right]\frac{d^3\mathbf{r_1}d^3\mathbf{r_2}}{|\mathbf{r_1}-\mathbf{r_2}|}\end{aligned} \tag{8}$$

Consider the symmetry between $\mathbf{r_1}$ and $\mathbf{r_2}$, then Eq. (8) can be rewritten as

$$\begin{aligned}\left\langle\frac{e^2}{r_{12}}\right\rangle &= \int\limits_{\mathbf{r_2}}\int\limits_{\mathbf{r_1}}|\psi_{100}(\mathbf{r_1})|^2\cdot\frac{e^2}{|\mathbf{r_1}-\mathbf{r_2}|}\cdot|\psi_{nlm}(\mathbf{r_2})|^2d^3\mathbf{r_1}d^3\mathbf{r_2} \pm \mathrm{Re}\\ &\quad\int\limits_{\mathbf{r_2}}\int\limits_{\mathbf{r_1}}\psi_{100}^*(\mathbf{r_2})\psi_{nlm}^*(\mathbf{r_1})\cdot\frac{e^2}{|\mathbf{r_1}-\mathbf{r_2}|}\cdot\psi_{100}(\mathbf{r_1})\psi_{nlm}(\mathbf{r_2})d^3\mathbf{r_1}d^3\mathbf{r_2}.\end{aligned} \tag{9}$$

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

$$J = \int\limits_{\mathbf{r_2}}\int\limits_{\mathbf{r_1}}|\psi_{100}(\mathbf{r_1})|^2\cdot\frac{e^2}{|\mathbf{r_1}-\mathbf{r_2}|}\cdot|\psi_{nlm}(\mathbf{r_2})|^2d^3\mathbf{r_1}d^3\mathbf{r_2}. \tag{10}$$

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

$$K = \int\limits_{\mathbf{r_2}}\int\limits_{\mathbf{r_1}}\psi_{100}^*(\mathbf{r_2})\psi_{nlm}^*(\mathbf{r_1})\cdot\frac{e^2}{|\mathbf{r_1}-\mathbf{r_2}|}\cdot\psi_{100}(\mathbf{r_1})\psi_{nlm}(\mathbf{r_2})d^3\mathbf{r_1}d^3\mathbf{r_2}. \tag{11}$$

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

$$E = E_{100} + E_{nlm} + \varDelta E. \tag{12}$$

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

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

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

$$E = E_{100} + E_{nlm} + J \pm K. \tag{14}$$

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

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

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

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

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

$$J = \int\limits_{\mathbf{r_2}} \int\limits_{\mathbf{r_1}} |\psi_{100}(\mathbf{r_1})|^2 \cdot \frac{e^2}{|\mathbf{r_1} - \mathbf{r_2}|} \cdot |\psi_{nlm}(\mathbf{r_2})|^2 d^3\mathbf{r_1} d^3\mathbf{r_2}, \tag{17}$$

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]:

$$\frac{1}{|\mathbf{r_1} - \mathbf{r_2}|} = \sum_{l'=0}^{\infty} \sum_{m'=-l'}^{l'} \left(\frac{4\pi}{2l' + 1} \right) \cdot \frac{r_<^{l'}}{r_>^{l'+1}} \, Y_{l'm'}(\Omega_1) Y_{l'm'}^{*}(\Omega_2), \tag{18}$$

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

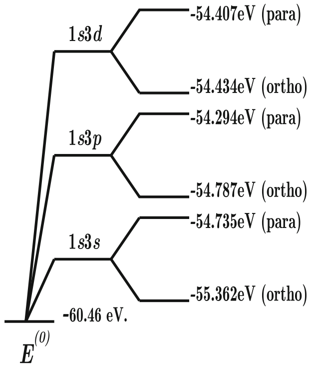

Fig. 2 Schematic energy level diagram for higher excited state configurations of helium atom

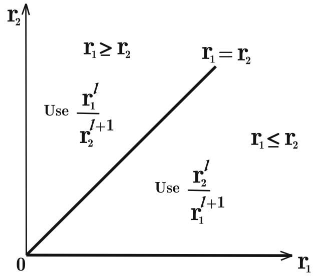

Fig. 3 The graph shows the relation between individual electrons and atomic nuclei

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

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

$$Y_{00}(\Omega_1)\left(\frac{r_<^{l'}}{r_>^{l'+1}}\right) Y_{l'm'}(\Omega_1) Y_{l'm'}^*(\Omega_2) r_2^2 R_{nl}^2(r_2) Y_{lm}^*(\Omega_2) Y_{lm}(\Omega_2) \tag{19}$$

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

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

$$\int_{r_2}\int_{r_1} dr_1 dr_2 r_1^2 R_{10}^2(r_1) r_2^2 R_{nl}^2(r_2) \left(\frac{r_<^{l'}}{r_>^{l'+1}}\right) \tag{20}$$

We define the new variable C_i so that

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

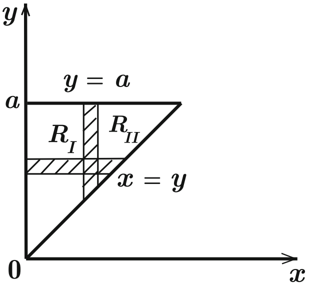

Fig. 4 Showing the area of double integrals

Substituting the definition [2]

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

into Eq. (21), we have

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

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

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

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

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

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

$$\int_{R_I} f(x, y)\, dxdy = \int_0^a \int_0^y f(x, y)\, dxdy, \tag{25}$$

$$\int_{R_{II}} f(x, y)\, dxdy = \int_0^a \int_x^a f(x, y)\, dydx. \tag{26}$$

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

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

Equation (23) is hence transformed to

$$\begin{aligned} C_{l_1'} &= \int_0^\infty \int_0^{r_2} r_2^2 \cdot \frac{r_1^{l'+2}}{r_2^{l'+1}} R_{nl}^2(r_2) R_{10}^2(r_1) dr_1 dr_2 \\ &= \int_0^\infty \int_{r_1}^\infty r_2^2 \cdot \frac{r_1^{l'+2}}{r_2^{l'+1}} R_{nl}^2(r_2) R_{10}^2(r_1) dr_1 dr_2 \end{aligned} \tag{28}$$

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

$$\begin{aligned} J = e^2 \sum_{l'=0}^{\infty} \sum_{m'=-l'}^{l'} \left(\frac{C_{l'}}{2l'+1}\right) \iint_{\Omega_2 \Omega_1} Y_{l'm'}^*(\Omega_2) Y_{1m}^*(\Omega_2) Y_{1m}(\Omega_2) \\ \left\{ \int_{\Omega_1} \frac{Y_{00}^*(\Omega_1)}{Y_{00}(\Omega_1)} \cdot Y_{l'm'}(\Omega_1) d\Omega_1 \right\} d\Omega_2 \end{aligned} \tag{30}$$

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

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

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

$$J = \frac{59 Z e^2}{243 a_0} = 13.22 \text{ eV}. \tag{33}$$

3.2 Calculation of the exchange integral

The exchange integral can be written as

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

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

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

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

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

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

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

Substituting the definition [2]

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

into Eq. (37), we have

$$K = \frac{e^2}{3}\int_0^\infty\int_0^{r_2} r_2^2\frac{r_1^3}{r_2^2}R_{10}(r_2)R_{21}(r_2)R_{10}(r_1)R_{21}(r_1)dr_1dr_2$$
$$+\frac{e^2}{3}\int_0^\infty\int_{r_2}^\infty r_1^2\frac{r_2^3}{r_1^2}R_{10}(r_2)R_{21}(r_2)R_{10}(r_1)R_{21}(r_1)dr_1dr_2 \tag{38}$$

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

$$K_{1a} = \frac{e^2}{3}\int_0^\infty\int_0^{r_2} r_2^2\frac{r_1^3}{r_2^2}R_{10}(r_2)R_{21}(r_2)R_{10}(r_1)R_{21}(r_1)dr_1dr_2. \tag{39}$$

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

$$k_{2a} = \frac{e^2}{3}\int_0^\infty\int_{r_2}^\infty r_1^2\frac{r_2^3}{r_1^2}R_{10}(r_2)R_{21}(r_2)R_{10}(r_1)R_{21}(r_1)dr_1dr_2. \tag{40}$$

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

$$K_{1a} = \frac{e^2}{3}\int_0^\infty\int_{r_1}^\infty r_1^2\frac{r_2^3}{r_1^2}R_{10}(r_2)R_{21}(r_2)R_{10}(r_1)R_{21}(r_1)dr_2dr_1. \tag{41}$$

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

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

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

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

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)

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

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

$In := R10[r1\_] := 2(\frac{z}{a0})^{\frac{3}{2}} E^{-\frac{zr1}{a0}}$
$In := R30[r1\_] := 2(\frac{z}{3a0})^{\frac{3}{2}} (1 - \frac{2zr1}{3a0} + \frac{2z^2r1^2}{27a0}) E^{-\frac{zr1}{3a0}}$
$In := R10[r2\_] := 2(\frac{z}{a0})^{\frac{3}{2}} E^{-\frac{zr2}{a0}}$
$In := R30[r2\_] := 2(\frac{z}{3a0})^{\frac{3}{2}} (1 - \frac{2zr2}{3a0} + \frac{2z^2r2^2}{27a0}) E^{-\frac{zr2}{3a0}}$
$In := J3A[r2\_] := \int_{r2}^{\infty} r1(R10[r1])^2 dr1$
$In := J3A[r2]$
$Out := ConditionExpression[(\frac{e^{-\frac{2r2z}{a0}} z(a0+2r2z)}{a0^2}), Re[\frac{z}{a0}] > 0]$
$In := J2A[r2\_] := (\frac{e^{-\frac{2r2z}{a0}} z(a0+2r2z)}{a0^2})$
$In := J1A = \int_0^{\infty} r2^2(R30[r2])^2(J2A[r2])dr2$
$Out := ConditionExpression[\frac{269z}{32768a0}, Re[\frac{z}{a0}] > 0]$
$In := JA = (\frac{269z}{32768a0})$
$Out := \frac{269z}{32768a0}$
$In := J3B[r2\_] := \int_0^{r2} r1^2(R10[r1])^2 dr1$
$In := J3B[r2]$
$Out := (1 - \frac{\exp - \frac{2r2z}{a0}(a0^2+2a0r2z+2r2^2z^2)}{a0^2})$
$In := J2B[r2] := (1 - \frac{\exp - \frac{2r2z}{a0}(a0^2+2a0r2z+2r2^2z^2)}{a0^2})$
$In := J1B = \int_0^{\infty} r2(R30[r2])^2(J2B[r2])dr2$
$Out := ConditionExpression[\frac{2991z}{32768a0}, Re[\frac{z}{a0}] > 0]$
$In := JB = (\frac{2991z}{32768a0}, Re[\frac{z}{a0}])$
$Out := \frac{2991z}{32768a0}$
$In := J = JA + JB$
$Out := \frac{815z}{8192a0}$

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

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

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

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

4 Conclusion

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

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

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

For the state 1s3p, we get

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

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

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

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

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

For the state 1s4f, we have

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

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

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

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

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

For the state 1s6h, we obtain

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

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

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

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

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

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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References

1. J.L. Powell, B. Crasemann, *Quantum Mechanics* (Addison-Wesley, Reading, Mss, 1961), pp. 456–458
2. H. Eyring, J. Walter, G.E. Kimball, *Quantum Chemistry* (Wiley, United State of America, 1944), p. 369
3. T.-Y. Wu, *Quantum Mechanics* (World Scientific Publishing Co Pte Ltd, Singapore, 1986), pp. 332–337
4. D. Park, *Introduction to the Quantum Theory* (Dover, New York, 2005), pp. 486–500
5. C.W. Scherr, R.E. Knight, Two-electron atoms II. A perturbation study of some excited states. Rev. Mod. Phys. **35**, 431 (1963)
6. C.W. Scherr, R.E. Knight, Two-electron atoms III. A sixth-order perturbation study of the 11S ground state. Rev. Mod. Phys. **35**, 436 (1963)
7. F.C. Sanders, C.W. Scherr, Perturbation study of some excited states of two-electron atoms. Phys. Rev. **181**, 84 (1969)
8. R. Ahlrichs, Convergence of the $1/Z$ expansion. Phys. Rev. A **5**, 605 (1972)
9. J.D. Baker, D.E. Freund et al., Radius of convergence and analytic behavior of the $1/Z$ expansion. Phys. Rev. A **41**, 1247 (1990)
10. G.W.F. Drake, Z.-C. Yan, Energies and relativistic corrections for the Rydberg states of helium: variational results and asymptotic analysis. Phys. Rev. A **46**, 2378 (1992)
11. B. Zhou, C.D. Lin, A hyperspherical close-coupling calculation of photoionization from the He atom, $Li+$ and $C4+$ ions. II. Between the $N = 2$ and $N = 3$ thresholds. J. Phys. B **26**, 2575 (1993)
12. G.W.F. Drake, Z.-C. Yan, Variational eigenvalues for the S states of helium. Chem. Phys. Lett. **229**, 486 (1994)
13. G.W.F. Drake, Z.-C. Yan, Eigenvalues and expectation values for the 1s22s 2S, 1s22p 2P, and 1s23d 2D states of lithium. Phys. Rev. A **52**, 3711 (1995)
14. M. Viviani, Transformation coefficients of hyperspherical harmonic functions of an A-body system. Few-body systems **25**, 177 (1998)

15. T.A. Herm, D. Green, Alternative sets of hyperspherical harmonics satisfying cusp conditions through frame transformations. J. Math. Phys. **40**, 2162 (1999)
16. Z.Q. Ma, Sci. Chin. A **43**, 1093 (2000)
17. X.Y. Gu, B. Duan et al., Conservation of angular momentum and separation of global rotation in a quantum N-body system. Phys. Lett. A **281**, 168 (2001)
18. B. Duan et al., Energy levels in D waves for a helium atom. Phys. Rev. A **64**, 012102 (2001)
19. B. Duan et al., Numerical calculation of energies of some excited states in a helium atom. Eur. Phys. J. D **19**, 9–12 (2002)
20. M.R. Spiegel, *Mathematical Handbook of Formulas and Tables* (McGrw-Hill, Singapre, 1999), p. 122