REPULSIVE ELECTRON-ELECTRON INTERACTION AND NUCLEAR CHARGE SCREENING:-GROUND STATE OF TWO-ELECTRON ATOMS

BY

BONIFACE OTIENO NDINYA

A thesis submitted for the fulfillment of the requirements of the degree:
Doctor of Philosophy in Physics.

DEPARTMENT OF PHYSICS AND MATERIALS SCIENCE

MASENO UNIVERSITY

Abstract

The development of simple analytical methods for solving the first-order wave functions and the second-order energy for two-electron atoms has remained a major challenge of theoretical atomic physics. The failure to overcome this challenge has motivated progress in the variational-perturbation method which has yielded accurate approximations for second-order energy using arbitrary first-order trial wave functions. However, the main drawback of the variational-perturbation method is that, apart from determining optimal parameters to specify an nth-order wave function through sophisticated computing software, it fails to directly account for the mechanisms which cause nuclear charge screening usually introduced as one of the parameters.

The problem investigated in the present thesis is to obtain a simple analytical solution to the Schrödinger equation for two-electron atoms based on a model which formulates the role of the repulsive electron-electron interaction term in nuclear charge screening. The objectives of the study are:- First, to develop a model that specifies the direct role of the repulsive electron-electron interaction term in nuclear charge screening in two-electron atoms. Second, to determine analytically the first-order perturbed wave function for two-electron atoms. Third, to calculate the ground state energies of two-electron atoms based on the model, through application of perturbation theory to second-order approximation.

We have analyzed the repulsive electron-electron interaction between the two electrons to determine its role in nuclear charge screening and dynamics in two-electron atoms. The Hamiltonian governing the general dynamics of the system is composed of a component describing the stable state of the system under the anti-parallel orbit orientation and the other describing the binding energies treated as perturbation. The calculated ground state energies to first-order perturbation are far much better than those obtained within the independent electron approximation.

Finally, we have developed a simple analytical calculations for the first order perturbed wave functions for two-electron atoms in the model. The resulting first-order wave functions are applied to calculate second-order energy within the model. The calculated ground state energies to second-order perturbation agree exactly with those obtained in a perturbation scheme based explicitly on the Hartree-Fock approximation.

Chapter 1

1 Introduction

The two-electron atoms (or ions) consist of a nucleus of charge Ze and mass M and two electrons of mass m. We denote $\mathbf{r}_1$ and $\mathbf{r}_2$ as the relative coordinates of the two electrons with respect to the nucleus as show in figure 1 [1 − 4].

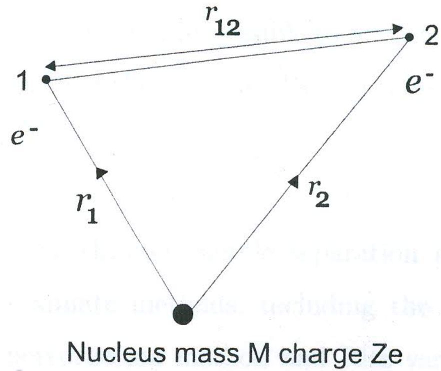

Figure 1: Coordinate system for two-electron atoms.

Each electron is then understood to experience an attractive Coulomb interaction with the nucleus and a repulsive Coulomb interaction with the other electron. The Hamiltonian governing the binding or dynamics of the two electrons is given in atomic units by [5 − 7]

$$H = -\frac{\nabla_1^2}{2} - \frac{\nabla_2^2}{2} - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} \tag{1.1a}$$

where

$$\nabla_i^2 = \frac{d^2}{dr_i^2} + \frac{2}{r_i}\frac{d}{dr_i} \qquad i = 1,2 \tag{1.1b}$$

is the Laplacian operator, Z is the atomic number, r_1 and r_2 are the electron distances from the nucleus and r_{12} is the distance between the electrons, defined by

$$r_1 = |\mathbf{r}_1| \quad ; r_2 = |\mathbf{r}_2| \quad ; r_{12} = |\mathbf{r}_1 - \mathbf{r}_2| \tag{1.1c}$$

In $(1.1a)$ the nucleus is taken to be infinitely massive, and relativistic effects are ignored. The Schrödinger equation for the two-electron atoms is

$$\left(-\frac{\nabla_1^2}{2} - \frac{\nabla_2^2}{2} - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}\right)\Psi = E\Psi \tag{1.2}$$

where Ψ is the eigenfunction and E the corresponding eigenvalue of the Hamiltonian $(1.1a)$. It has proved impossible to find an analytical solution to (1.2), due to the presence of the electron-electron repulsive interaction term

$$H' = \frac{1}{r_{12}}, \tag{1.3}$$

which prevents solutions through simple separation of variables $[8-10]$. However, many approximate methods, including the perturbation theory method, variational perturbation method and Ritz variation method, have been used to give a reasonable calculation of the correlation effect between two electrons in the system [11].

In standard quantum mechanics textbooks $[1-10]$ and in some other research literature $[11-15]$, the ground state of two-electron atoms is treated as an elementary application of the perturbation method. The method starts by neglecting the electron-electron repulsive interaction term (1.3) in (1.2), i.e., the independent electron model. The Schrödinger equation (1.2) reduces to

$$\left(-\frac{\nabla_1^2}{2} - \frac{\nabla_2^2}{2} - \frac{Z}{r_1} - \frac{Z}{r_2}\right)\Psi^{(0)}\left(\mathbf{r}_1, \mathbf{r}_2\right) = E^{(0)}\Psi^{(0)}\left(\mathbf{r}_1, \mathbf{r}_2\right), \tag{1.4}$$

which may be solved independently for the two one-particle hydrogen-like equations [1, 2, 5]. The unperturbed wave function becomes

$$\Psi^{(0)}(\mathbf{r}_1, \mathbf{r}_2) = \frac{Z^3}{\pi} \exp(-Z(r_1 + r_2)) \tag{1.5}$$

and its corresponding energy eigenvalue is given by

$$E^{(0)} = -Z^2 \tag{1.6}$$

Thus for Helium atom (Z=2), the ground state energy $E^{(0)} = -4.0000\, a.u.$, about 37.76% lower than the experimental value $E^{(ex)} = -2.9037\, a.u.$. Hence, the independent electron model gives the unperturbed ground state energy lower than the experimental values because the electron-electron repulsive interaction term (1.3), whose effect is clearly to raise the energy levels, has been neglected.

The effect of the neglected electron-electron repulsive interaction term H' on the ground state energy can be estimated using Rayleigh-Schrödinger perturbation theory [1, 2, 5]. The first-order perturbation energy $E^{(1)}$ is readily evaluated with the results

$$\begin{aligned} E^{(1)} &= \langle \Psi^{(0)} | r_{12}^{-1} | \Psi^{(0)} \rangle \\ &= \frac{5}{8} Z \end{aligned} \tag{1.7}$$

The ground state energy to first-order perturbation becomes

$$\begin{aligned} E &= E^{(0)} + E^{(1)} \\ &= -Z^2 + \frac{5}{8} Z \end{aligned} \tag{1.8}$$

This gives for Helium atom (Z=2) $E = -2.7500\, a.u.$, about 5.29% higher than the experimental value $E^{(ex)} = -2.9037\, a.u.$. Further improvements on the ground state energy was achieved by addition of the second-order and higher-order perturbation energies [11, 12, 13].

The second-order perturbation energy is given by

$$E^{(2)} = \langle \Psi^{(0)} | H' - E^{(1)} | \Psi^{(1)} \rangle \tag{1.9}$$

where $\Psi^{(1)}$ is the first-order perturbed wave function which can be obtained by solving the equation [14, 15]

$$\left(H^{(0)} - E^{(0)}\right) \Psi^{(1)} + \left(H' - E^{(1)}\right) \Psi^{(0)} = 0 \tag{1.10}$$

However, in the case where the electron-electron repulsive interaction term (1.3), is treated as a perturbation, analytical solutions of the homogenous differential equation (1.10) have not been found. Faced with this situation, there has been increasing recognition of the fact, that one can often get satisfactory variational approximation to the *individual terms* in the perturbation series, i.e, variational perturbation method [16, 17, 18]. The second-order perturbation energy is obtained using variational perturbation method by varying the functional

$$F_1[\Psi_1^t] = 2\langle \Psi_1^t | H' - E^1 | \Psi^{(0)} \rangle + \langle \Psi_1^t | H^{(0)} - E^{(0)} | \Psi_1^t \rangle \tag{1.11}$$

which, because of the completeness of the eigenfunction of $H^{(0)}$, gives the variational principle for $E^{(2)}$ [14]. The first-order trial wave function Ψ_1^t may be chosen from either the Hylleraas type of basis function or the configuration interaction method or a hybrid of both methods [11, 14]. For example, in previous works, Hylleraas and Midtdal [19], Schwartz [20] and Knight and Scherr [21] have calculate numerically the second-order perturbation energy of two-electron atoms, to obtain

$$E^{(2)} = -0.15766625\, a.u. \tag{1.12}$$

The ground state energy to second-order perturbation becomes

$$E = -Z^2 + \frac{5}{8} - 0.157666 \tag{1.13}$$

Thus, for Helium atom, the ground state energy become $E = -2.907666\,a.u.$, which is $0.003942a.u.$ lower than the experimental value $E^{(ex)} = -2.9037\,a.u.$. Addition of higher-order perturbation energies using variational perturbation method have led to the ground state energy for two-electron atoms similar to the experimental values, for example, the works of Knight and Scherr [21, 22] and Midtdal [23].

The main challenge of treating the electrons as entirely independent, i.e., the independent electron model, is that, it does not seem possible that in an atom of finite size, we can have two electrons infinitely separated from each other to justify zero repulsive interaction, i.e., each electron moves in the fully unscreened field of the nucleus. This explains why the ground state energies to first-order perturbation in this approximation are generally poor. The vast improvement achieved through the addition of higher-order perturbation energy terms using variational perturbation method is mainly attributed to the inclusion of nuclear charge screening effects as one of the arbitrary parameters in the trial wave functions. But the variational method does not directly account for the mechanisms which cause nuclear charge screening.

This thesis is an effort to address the apparent contradiction of having two electrons infinitely separated in an atom of finite size, by developing an alternative model of the quantum theory of the two-electron atoms; this formulates the nuclear charge screening in terms of electron-electron repulsive interaction and determines its direct role in the dynamics of the atom. The ground state configuration with the two electrons equidistant from the nucleus and in *anti-parallel* orbit orientation gives the ground state energy for helium to be $-3.06\,a.u.$ which is about 5.5% lower than the experimental value. Application of first-order perturbation gives the ground state energy $E = -2.84\,a.u.$ which is about 2% higher than the experimental value. We proceed to evaluate the ground state energy to second-order perturbation within the model by first solving the first-order perturbation equation (1.10) analytically for the first-order perturbed wave function $\Psi^{(1)}$ and then applying the resulting function in (1.9) to calculate the second-order perturbation energy $E^{(2)}$. The direct calculation of the first-order perturbed wave function and second-order perturbation energy is a major achievement of the thesis. Part of the results have been published in refereed journals [24, 25].

1.1 Statement of the problem

The problem was to obtain a simple analytical solution to the Schrödinger equation for two-electron atoms based on a model which formulates the nuclear charge screening in terms of electron-electron repulsive interaction and determines its direct role in the dynamics of the atom. The ground state energies to second-order perturbation approximation of the two-electron atoms will be calculated using analytically determined first-order perturbed wave functions.

1.2 Objectives of the study

The objectives of the study are

1. To develop a model that specifies the direct role of the electron-electron repulsive interaction in determining nuclear charge screening in two-electron atoms.

2. To determine analytically the first-order perturbed wave function for two-electron atoms.

3. To calculate ground state energies of two-electron atoms based on the model, through application of perturbation theory to second-order approximation.

1.3 Significance of the study

The calculation for the ground state energy of two-electron atoms are normally based on correlated wave functions using variational or variational-perturbation methods. However, neither the variational method nor the variational-perturbation method permits one to express analytically the ground state energy of the two-electron atoms. However, it is widely believed that there are distinct advantages to viewing problems of physics within the framework of simple analytical models. In the present thesis, we develop an alternative model of the quantum theory of the two-electron atoms and obtain analytically the first-order perturbed wave function and the second-order perturbation energy. The development of an appropriate quantum mechanical model for two-electron atoms, which leads to analytic solutions of Schrödinger equation, will provide a clear understanding of the dynamics within two-electron atoms, thereby leading to far reaching applications to studies of the multi-electron atoms. The general analytical structure of the wave functions is an important guideline in the choice of the trial wave functions for the variational calculations. The trial wave function chosen with the correct analytic structure has been shown to be very efficient in giving variational energies of a very high level of accuracy.

Chapter 2

2 Literature review

The theoretical description of ground state energy of two-electron atoms has been a subject intensively investigated since the advent of quantum mechanics. Unlike the solutions for the one-electron atom, the solution for the eigenfunctions Ψ and energy eigenvalues E of (1.2) cannot be expressed in closed analytic form. Therefore various approximation methods namely the perturbation method, Ritz variational method and Hylleraas variational perturbation method have been applied to obtain approximate solution to (1.2) [1, 2, 10, 11].

The perturbation method and variational perturbation method have been discussed in section 1.

The variational method with elaborate trial wave function, have also been applied to calculate the non-relativistic ground state energy of two-electron atoms. The method starts by guessing a parametrized form of a trial wave-function Ψ_α, where $\alpha = (\alpha_1, \alpha_2, \ldots\ldots, \alpha_m)$ denotes a set of variational parameters. The variational parameters are then optimized in accordance with the *variational principle* and the energy expectation value of a variational wave-function provides an upper bound to the true ground state energy E [2, 5], i.e.,

$$\frac{\int \Psi_\alpha^\star \, H \, \Psi_\alpha \, d\tau}{\int \Psi_\alpha^2 \, d\tau} \geq E, \tag{2.1}$$

In the one-parameter variational approach, a simple trial wave function for the ground state of two-electron atoms is expressed in terms of the independent electron model wave function (1.5) as

$$\begin{aligned}\Psi_{tr} &= \Phi(r_1, r_2)\\ &= \frac{Z_e^3}{\pi} e^{-Z_e(r_1+r_2)} \end{aligned}\tag{2.2}$$

where Z_e is the effective charge which incorporates nuclear charge screening and is considered as a variational parameter. The mean energy $E_{tr} = E(Z_e)$ is given by [2, 5]

$$E(Z_e) = -Z_e^2, \tag{2.3}$$

the minimum being reached for an effective charge

$$Z_e = Z - \frac{5}{16} \tag{2.4}$$

The calculated ground state energy for Helium atom is $E(Z_e) = -2.8477a.u.$, higher than the experimental value $E^{(ex)} = -2.9037\,a.u.$ by about 2.27%. This gives an improved results, compared to $E = -2.7500\,a.u.$ obtained in the independent electron method up to first-order perturbation (1.8). Thus, the variational results (2.3) corresponding to the effective charge Z_e (2.4), is lower and hence more accurate than the ground state energy to first-order perturbation (1.8) [1, 5].

Great progress has been made in the variation approach by including more parameters in the trial wave function that are suitable for numerical evaluation, leading to very accurate values of the non-relativistic ground state energy of the two-electron atoms. In his pioneering work, Hylleraas adopted a trial wave function of the form [16]

$$\Phi(\mathbf{r}_1, \mathbf{r}_2) = e^{-\kappa s} \sum_{l,m,n=0}^{N} c_{l,2m,n} s^l u^m t^n. \tag{2.5}$$

where

$$s = r_1 + r_2; \qquad t = r_1 - r_2; \qquad u = r_{12}, \tag{2.6}$$

the coefficients $c_{l,2m,n}$ are linear variational parameters and κ is a non-linear variational parameter similar to the effective charge Z_e used in the simple one-parameter trial wave function (2.2) and the number N determines the maximum number of terms. The Hylleraas approach, which accounts explicitly for the correlations between the motion of the two electron through the variable $u = r_{12}$, has been very successful in getting accurate values for the ground state energy E of two-electron atoms. For example, with a 6-parameter trial wave function

$$\Psi(s,t,u) = (c_0 + c_1 u + c_2 t^2 + c_3 s + c_4 s^2 + c_5 u^2)\exp(-\frac{1}{2}\kappa s), \qquad (2.7)$$

of the form (2.5), Hylleraas [16] obtained numerically, the ground state energy of Helium atom as $E^{(0)} = -2.90324a.u.$ which differs from the experimental value by only $-0.00048au$. Since then several improved Hylleraas-type trial wave functions have been extensively studied in the literature; for example, the works of Pekeris [26], Wang and Guan [27], Drake *et al* [28] and Korobov [29] who obtained accurate values for the ground state energy of Helium atom.

Table 2.1. The historical data concerning the improvement of the ground state energy of Helium atom using variational method. Here N is the number of basis functions.

Scientist	Year	N	E(a.u.)
Hylleraas [16]	1929	6	-2.9032
Pekeris [26]	1958	6	-2.903724377
Wang and Guan [27]	2001	168	-2.9037161
Drake [28]	2002	2114	-2.903724377034119596
Korobov [29]	2002	2200	-2.903724377034119598296

The historical data, concerning the improvement of the ground state energy of Helium atom using variational method, is given in Table 2.1. The non-relativistic ground state energy of the two-electron atoms obtained by Pekeris

[26] using improved Hylleraas-type trial wave function are given in Table 2.2 for H^- to Ne^{8+}.

Table 2.2. The non-relativistic ground state energy of the two-electron atoms (H^- to Ne^{8+}) obtained by Pekeris.

Atom	Z	$E^{(exa)}$
H^-	1	-0.52775101
He	2	-2.903724377
Li^+	3	-7.2799134
Be^{2+}	4	-13.655566
B^{3+}	5	-22.030972
C^{4+}	6	-32.406247
N^{5+}	7	-44.781445
O^{6+}	8	-59.156595
F^{7+}	9	-75.531712
Ne^{8+}	10	-93.906806

We note in Table 2.2, that the ground state energy value obtained by Pekeries [26] for Helium atom is similar to the experimental value; thus, in this thesis, we will refer to this values as the exact energy $E^{(exa)}$.

The accurate Hylleraas-type trial wave functions determined by Rayleigh-Ritz variational method have been used to calculate expectation values of various operators, oscillator strengths and transition probabilities [11, 16, 26]. However, in many cases of practical interest, it is convenient to use less accurate, but more tractable wave function, which does not involve explicitly the interelectronic coordinate r_{12}. It is then natural to use the ground state trial wave functions which are expansions in Legendre polynomials,

$$\Psi(r_1, r_2) = \frac{1}{4\pi} \sum_{l=0}^{\lambda} F_l(r_1, r_2) P_l(\cos\theta), \tag{2.8a}$$

where the subscript l refers to the *relative* partial waves [5, 11, 30]. This approach is known as the configuration interaction (CI) method. If we set $\lambda = 0$ in (2.8a) so that the trial wave function is restricted to the pure s wave ($l = 0$), only radial correlation between the position of the two electrons are introduced in the wave function. In this way, a radial limit for the ground state energy is approached when an increasing number of parameters are included in the function $F_0(r_1, r_2)$. For example, in Helium atom, the radial limit is $-2.87903\, a.u.$ which differs from the experimental value by $-0.02469\, a.u.$ [5, 31]. This difference is due to the radial and angular correlations distributed among the higher relative partial waves in the expansion of (2.8a).

The simplest choice of the functions $F_l(r_1, r_2)$ in (2.8a) is given by

$$F_l(r_1, r_2) = \sum_{m \leq n} A^{(l)}_{mn} r_1^l r_2^l (r_1^m r_2^n + r_1^n r_2^m)\, e^{-\alpha(r_1+r_2)/2}, \tag{2.8b}$$

where $m + n \leq \mu$, α is a non-linear variational parameter and the coefficient $A^{(l)}_{lm}$ are linear variational parameters . These yield an upper limit of $E = -2.90227\, a.u.$ for the ground state energy of Helium atom with $\lambda = 3$ and 15 parameter in each relative partial wave [31, 32].

In previous works, several simple trial wave functions, that contain only a few variational parameters and are products of hydrogenic one-electron solutions and a fully correlated part have been suggested. For example, Myers *et al* [33] suggested the following trial wave function:

$$\Psi_{Myers}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_{12}) = e^{-Z(r_1+r_2)}\, e^{\frac{r_{12}}{2}} \tag{2.9a}$$

The correlation factor $e^{r_{12}/2}$ in equation $(2.9a)$ allows one to correctly describe the behavior of the wave function when the two electrons are close to each other. The mean energy was found analytically by applying the expression

$$E_{Myers}(Z) = \frac{(1-8Z+28Z^2-64Z^3)(2Z-1)}{4(1-10Z+32Z^2)} \tag{2.9b}$$

The mean energy for Helium atom, $E_{Myers}(Z) = -2.8555\,a.u.$, differ from the experimental value by $-0.0482\,a.u.$.

Patil [34, 35] considered a simple trial wave function

$$\Psi_{Patil}\left(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_{12}\right) = e^{-Z(r_1+r_2)}\left(1+\frac{r_{12}}{2}\right) \tag{2.10a}$$

to obtain the mean energy in the form

$$E_{Patil}(Z) = \frac{(35-16Z-100Z^2-64Z^3)Z}{4(24+35Z+16Z^2)} \tag{2.10b}$$

The mean energy for Helium atom, $E_{Patil}(Z) = -2.8766\,a.u.$, differ from the experimental value by $-0.0271\,a.u.$.

Ancarani *et al* [36] developed a simple parameter-free trial wave function

$$\Psi_{Anc}\left(\mathbf{r}_1,\mathbf{r}_2\right) = Ne^{Z(r_1+r_2)}\left(1+\frac{r_{12}}{2}\right)\left[1+c(r_1^2+r_2^2)\right] \tag{2.11a}$$

where c is a variation parameter and N the normalization constant. The mean energy was evaluated analytically in terms of c and Z from the expression is

$$\begin{aligned} E_{Anc}(Z) = -\frac{Z}{4A}[&Z^4(-35+16Z+100Z^2+64Z^3)+cZ^2(-567+864Z+1792Z^2+768Z^3) \\ &+\frac{3}{8}c^2(-10065+19968Z+27612Z^2+8704Z^3)] \end{aligned} \tag{2.11b}$$

where

$$A = 9c^2(460 + 3355Z/8 + 112Z^2) + 3cZ^2(168 + 189Z + 64Z^2)$$

$$+Z^4(24 + 35Z + 16Z^2) \qquad (2.11c)$$

Thus, for Helium atom it was found that $E_{Anc}(Z) = -2.8954\,a.u.$ which differs by $-0.0083\,a.u.$.

It can be seen from equations $(2.9a)$, $(2.10a)$ and $(2.11a)$ that the addition of the electron-electron interaction term r_{12} in the trial wave function is able to improve the accuracy of the mean energies obtained in equations $(2.9b)$, $(2.10b)$ and $(2.11b)$, respectively. Therefore, the variational calculations depend crucially on the form of the trial wave-function used.

In general analytical solution for the Schrödinger equation (1.2) for the two-electron atoms has not been found to date. However, it is widely believed that there is distinct advantage in viewing problems of physics within the framework of simple analytical models. This has led some authors like Auzinsh and Damdburg [37] and Sakho *et al* [38] to set up much simpler models for the ground state of two-electron atoms, permitting one to obtain fairly accurate results that can be used as first estimates or as starting point for more complex calculations.

Auzinsh and Damdburg [37] combined the one parameter variational approach with the Niels Bohr "old" quantum theory ideas about electron correlation in a two-electron atom, to obtain a very simple expression for the ground state energy

$$E_{Anz}(1, Z) = -\left(Z - \frac{1 + \frac{1}{4}\sqrt{1 - Z_0/Z}}{4}\right)^2, \qquad (2.12)$$

where $Z_0 \approx 0.85355$ is the smallest nuclear charge for which stable two electron negative ion will still exist. The ground state energies $E_{Anz}(1, Z)$ obtained using (2.12) for $Z = 1 - 6$ are given in Table 2.3.

Sakho *et al* [38], in combining the perturbation theory with the Ritz variation method, developed a technique for analytic calculation of the ground-state energy, the first ionization energy and the radial correlation expectation value for two-electron atoms. The analytical expression of ground-state energy was given by

$$E_{Sak} = -\frac{Z^2}{2}\left[1 + \left(1 - \frac{0.625}{Z}\right)^2\right] \tag{2.13}$$

The ground state energies E_{Sak} obtained using (2.13) for $Z = 1 - 6$ are given in Table 2.3.

Table 2.3. The ground state energy obtained by Auzinsh *et al* $E_{Anz}(1, Z)$ and Sakho *et al* E_{Sak} for $Z = 1 - 6$ compared with the exact energy $E^{(exa)}$

Atom	H^-	He	Li^+	Be^{2+}	B^{3+}	C^{4+}
Z	1	2	3	4	5	6
E_{Sak}	-0.5703	-2.9453	-7.3203	-13.6953	-22.0703	-32.4453
$E_{Anz}(1, Z)$	-0.5272	-2.8991	-7.2745	-13.6498	-22.0250	-32.4002
$E^{(exa)}$	-0.5275	-2.9035	-7.2798	-13.6556	-22.0310	-32.4062

It is noted that, the ground state energies $E_{Anz}(1, Z)$ and E_{Sak} obtained in Table 2.3 have almost the same accuracy as the exact energy $E^{(exa)}$. The analytical procedure adopted by Sakho *et al* [38] (i.e. the screening constant by unit charge) has been extended to the calculation of the total energies, total electron-electron interactions and the excitation energies for the doubly excited states of the Helium and Helium-like ions [39, 40] without having to appeal to a computer program and/or to large basis-set computations invoking a fair amount of mathematical complexity.

We observe that the variational method and the variational-perturbation method have been applied to calculate ground-state energies and other properties of atomic and molecular systems with a high degree of precision. The development of suitable many-parameter trial wave functions with good convergence properties required for calculations in variational and variational-perturbation methods have continued to date. However, a major weakness of the variation method and variational-perturbation method is its inability to account for the mechanisms which cause important physical phenomena such as nuclear charge screening, usually introduced as one of the parameters to be determined through optimization. The thesis is an effort to develop a simple analytic solution to the Schrödinger equation for the two-electron atoms based on a model that formulates the nuclear charge screening in terms of electron-electron repulsive interaction.

Chapter 3

3 Repulsive electron-electron interaction and nuclear charge screening

In this chapter, the main ideas of the model developed in [24] that specify the role of the direct role of repulsive electron-electron interaction in nuclear charge screening are summarized. Considering that the distance r_{12} (1.2) between the electrons is invariant under the interchange of the coordinates of the two electrons, i.e., $r_{12} = r_{21}$, we express the repulsive Coulomb interaction term $1/r_{12}$ (1.4) in the symmetrized form,

$$\begin{aligned} H' &= H'_{12} + H'_{21} \\ &= \frac{1}{2}\left(\frac{1}{r_{12}} + \frac{1}{r_{21}}\right) \end{aligned} \tag{3.1}$$

This provides for two equivalent interpretations of the repulsive Coulomb interaction term. In one interpretation

$$H'_{12} = \frac{1}{2r_{12}} \tag{3.2a}$$

represents the repulsive interaction term due to the motion of electron-1 in the Coulomb field of electron-2. Electron-2 thus shields the nucleus from electron-1, leading to the screening of the nuclear charge seen by electron-1. This describes an orbit configuration in which $r_1 \geq r_2$. In the alternative interpretation

$$H'_{21} = \frac{1}{2r_{21}} \tag{3.2b}$$

represents the repulsive interaction term due to the motion of electron-2 in the Coulomb field of electron-1. Electron-1 thus shields the nucleus from electron-2, leading to the screening of the nuclear charge seen by electron-2. This describes an orbit configuration in which $r_2 \geq r_1$.

By applying equation (3.1) in equation (1.1a), the Hamiltonian becomes

$$H = H_1 + H_2 \ , \tag{3.3a}$$

where,

$$H_1 = -\frac{1}{2}\nabla_1^2 - \frac{Z}{r_1} + \frac{1}{2r_{12}} \quad , \quad r_1 \geq r_2 \tag{3.3b}$$

and

$$H_2 = -\frac{1}{2}\nabla_2^2 - \frac{Z}{r_2} + \frac{1}{2r_{21}} \quad , \quad r_2 \geq r_1 \tag{3.3c}$$

are one-electron atom Hamiltonians each describes the motion of a single electron in the Coulomb field of the nucleus screened by the other electron. To determine how the nuclear charge screening arises, equations (3.3b) and (3.3c) are rewritten in the general form as

$$H_i = -\frac{1}{2}\nabla_i^2 - \frac{Z}{r_i} + \frac{1}{2r_{ij}}, \quad r_i \geq r_j, \quad i,j = 1,2 \tag{3.4}$$

where the distance r_{ij} between the electron pair (i,j) is expressed as

$$\begin{aligned} r_{ij} &= |\mathbf{r}_i - \mathbf{r}_j| \\ &= r_i \left(1 + \left(\frac{r_j}{r_i}\right)^2 - 2\left(\frac{r_j}{r_i}\right)\cos\vartheta\right)^{\frac{1}{2}} \\ &= \frac{r_i}{S_{ij}} \qquad r_i \geq r_j \end{aligned} \tag{3.5a}$$

with ϑ being the orientation angle between the position vectors $\mathbf{r}_i$ and $\mathbf{r}_j$ and the parameter S_{ij} is defined by

$$S_{ij} = \left(1 + \left(\frac{r_j}{r_i}\right)^2 - 2\left(\frac{r_j}{r_i}\right)\cos\vartheta\right)^{-\frac{1}{2}} \quad , \quad r_i \geq r_j \tag{3.5b}$$

thus, by applying equation (3.5a), equations (3.2a) and (3.2b) may be expressed, in general form as

$$\begin{aligned} H'_{ij} &= \frac{1}{2r_{ij}} \\ &= \frac{1}{2r_i} S_{ij}, \qquad r_i \geq r_j \end{aligned} \tag{3.6}$$

Further, the substitution of equation (3.6) into equation (3.4) yields

$$\begin{aligned} H_i &= -\frac{1}{2}\nabla_i^2 - \frac{1}{r_i}\left(Z - \frac{1}{2}S_{ij}\right) \\ &= -\frac{1}{2}\nabla_i^2 - \frac{Z_{ij}}{r_i}, \qquad r_i \geq r_j \end{aligned} \tag{3.7a}$$

which is the Hamiltonian of a one-electron atom with an effective screened nuclear charge

$$Z_{ij} = Z - \frac{1}{2}S_{ij}, \qquad r_i \geq r_j \tag{3.7b}$$

due to the repulsive Coulomb interaction. The one-electron atom Hamiltonians in equations (3.3b) and (3.3c) are now expressed in the form

$$H_1 = -\frac{1}{2}\nabla_1^2 - \frac{1}{r_1}\left(Z - \frac{1}{2}S_{12}\right), \qquad r_1 \geq r_2 \tag{3.8a}$$

and

$$H_2 = -\frac{1}{2}\nabla_2^2 - \frac{1}{r_2}\left(Z - \frac{1}{2}S_{21}\right), \qquad r_2 \geq r_1 \tag{3.8b}$$

respectively.

Therefore, the parameter S_{ij} as defined in equations (3.7a) and (3.7b), is recognized as the nuclear charge screening parameter that determines the shielding of the nucleus by electron-j; it leads to screening of the nuclear charge seen by electron-i. According to equation (3.6) the nuclear charge screening parameter arises entirely from the repulsive Coulomb interaction term.

3.1 Nuclear charge screening parameter, S_{ij}

The nuclear charge screening parameter S_{ij} as defined in equation (3.5*b*), is essentially a number which takes a set of values depending on the relative positions and orientations of the electrons in the pair (i, j) within an atom. To specify the form of S_{ij} and establish its role in determining the appropriate one-electron atom Hamiltonian, simplifying notation

$$x = \cos\vartheta \quad ; \quad h = \frac{r_j}{r_i} \quad , \quad r_i \geq r_j, \tag{3.9}$$

are introduced in equation (3.5*b*), to obtain

$$\begin{aligned} S_{ij} &= S(h, x) \\ &= \left(1 - 2hx + h^2\right)^{-\frac{1}{2}} \end{aligned} \tag{3.10}$$

The orbit condition $r_i \geq r_j$ means that h, as defined in equation (3.9), satisfies the condition,

$$h \leq 1 \tag{3.11}$$

Hence, to specify the form of $S_{ij} = S(h, x)$, the two conditions $h < 1$ and $h = 1$ are considered separately, since they form two distinct configurations of the dynamics of each electron within the atom.

3.2 Configuration $h < 1$ $(r_i > r_j)$

The configuration $h < 1$ $(r_i > r_j)$ characterizes electron dynamics in which one electron is nearer the nucleus than the other. Therefore, the nucleus is effectively shielded by electron r_j through the repulsive Coulomb interaction. In the configuration $h < 1$, equation (3.10) is recognized as the generating function for the Legendre polynomial satisfying a power series expansion in h [41]

$$S(h,x) = \left(1 - 2hx + h^2\right)^{-\frac{1}{2}}$$
$$= \sum_{l=0} P_l(x)h^l, \qquad h < 1 \tag{3.12a}$$

Hence, in the configuration $h < 1$, equations (3.10) and (3.6) are expressed in the form

$$S_{ij} = \sum_{l=0}^{\infty} \left(\frac{r_j}{r_i}\right)^l P_l(\cos\vartheta), \quad r_i > r_j \tag{3.12b}$$

and

$$H'_{ij} = \frac{1}{2r_i} \sum_{l=0}^{\infty} \left(\frac{r_j}{r_i}\right)^l P_l(\cos\vartheta), \quad r_i > r_j \tag{3.12c}$$

respectively.

Since $\mathbf{r}_i$ and $\mathbf{r}_j$ are two vectors having polar angles (θ_i, ϕ_i) and (θ_j, ϕ_j), respectively, and ϑ the angle between them, then the addition theorem for spherical harmonics gives [5]

$$P_l\left(\cos\vartheta\right) = \frac{4\pi}{2l+1} \sum_{m_l=-l}^{l} Y_{lm_l}(\theta_i, \phi_i) Y^*_{lm_l}(\theta_j, \phi_j) \tag{3.13a}$$

which when substituted into equations (3.12b) and (3.12c) leads to

$$S_{ij} = \sum_{l=0}^{\infty} \sum_{m_l=-l}^{l} \frac{4\pi}{2l+1} \left(\frac{r_j}{r_i}\right)^l Y_{lm_l}(\theta_i, \phi_i) Y^*_{lm_l}(\theta_j, \phi_j), \quad r_i > r_j \tag{3.13b}$$

and

$$H'_{ij} = \frac{1}{2r_i} \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} \frac{4\pi}{2l+1} \left(\frac{r_j}{r_i}\right)^l Y_{lm_l}(\theta_i, \phi_i) Y^*_{lm_l}(\theta_j, \phi_j), \quad r_i > r_j, \tag{3.13c}$$

respectively. According to equation (3.13b), nuclear charge screening due to the electron-electron repulsive interaction in the configuration $h < 1$ $(r_i > r_j)$ depends on the relative distances and the polar angles of the two electrons. Equation (3.13c) is generally applied in the evaluation of the expectation value of the repulsive Coulomb interaction energy treated as a perturbation in the standard quantum theory of two-electron atoms [2, 5].

To see how S_{ij} in the mode $r_i > r_j$ influences the dynamics of the system, a special case where one electron-j is very near while the other electron-i is very far away from the nucleus is considered. In this case

$$r_i >> r_j, \tag{3.14a}$$

$$h << 1 \tag{3.14b}$$

and

$$hx \approx 0 \tag{3.14c}$$

Substitution of equations (3.14b) and (3.14c) in equation (3.10) gives the maximum value of nuclear charge screening parameter

$$\begin{aligned} S(h << 1, x) &= S_{\max} \\ &= 1 \qquad r_i >> r_j \end{aligned} \tag{3.14d}$$

With one electron very close to the nucleus, the repulsive Coulomb interaction term is no longer symmetrical. Considering electron 1 to be closer to the nucleus, $r_2 >> r_1$, the Hamiltonian equations (3.3b) and (3.3c) are now written as

$$H_1 = -\frac{1}{2}\nabla_1^2 - \frac{Z}{r_1} \tag{3.14e}$$

and

$$\begin{aligned} H_2 &= -\frac{1}{2}\nabla_2^2 - \frac{Z - S_{\max}}{r_2} \\ &= -\frac{1}{2}\nabla_2^2 - \frac{Z-1}{r_2} \qquad r_2 >> r_1, \end{aligned} \tag{3.14f}$$

respectively. This represents the well known Heisenberg model of excited states [1, 5].

In the present work, equation (3.13b) completely determines the nuclear charge screening factor S_{ij} under the condition $r_i > r_j$, where electron-j is closer to the nucleus, thus shielding it from electron-i. It generalizes the Heisenberg model by including the intermediate values of the nuclear charge screening for any configuration $r_i > r_j$, i.e., $h < 1$.

3.3 Configuration $h = 1$ $(r_j = r_i)$

The configuration $h = 1$, where

$$r_j = r_i \quad , \quad j \neq i \ , \tag{3.15a}$$

constitutes a special case of the electron-electron interaction, in which the two electrons in the pair (i, j) are *equidistant* from the nucleus, but satisfy the condition $j \neq i$ to exclude the physically unacceptable possibility of both occupying exactly the same point in space.

The position vectors $\mathbf{r}_i$ and $\mathbf{r}_j$ of the two electrons now differ only in their orientations, with angle ϑ between them. We define the position vectors $\mathbf{r}_i$ and $\mathbf{r}_j$ through the unit vectors $\hat{\mathbf{r}}_i$ and $\hat{\mathbf{r}}_j$ in their respective directions in the form

$$\mathbf{r}_i = r_i\hat{\mathbf{r}}_i \quad ; \quad \mathbf{r}_j = r_j\hat{\mathbf{r}}_j = r_i\hat{\mathbf{r}}_j \quad ; \quad j \neq i \ , \tag{3.15b}$$

satisfying the orbit orientation condition,

$$\hat{\mathbf{r}}_i \cdot \hat{\mathbf{r}}_j = \cos\vartheta \tag{3.15c}$$

which implies that

$$\mathbf{r}_i \cdot \mathbf{r}_j = r_i^2 \cos\vartheta; \quad r_i\hat{\mathbf{r}}_j = r_j\hat{\mathbf{r}}_j \tag{3.15d}$$

A good example of electron trajectory satisfying the orbit condition given by equations (3.15a)-(3.15d), is the s-orbital, which is spherical in shape and provides circular orbits. Elliptic orbits would also be possible, depending on the orientation angle.

By substituting $h = 1$ into equation (3.10) it is found that

$$S_{ij} = S_\vartheta$$

$$= (2(1-\cos\vartheta))^{-\frac{1}{2}}, \tag{3.16a}$$

which on applying the trigonometric identity [41]

$$2\sin^2\frac{1}{2}\vartheta = 1 - \cos\vartheta, \tag{3.16b}$$

reduces to the form

$$S_\vartheta = \frac{1}{2\sin\frac{1}{2}\vartheta} \tag{3.16c}$$

Thus, the nuclear charge screening parameter in the mode $r_j = r_i$, $j \neq i$, depends only on the orientation angle ϑ. The values of the orientation angle ϑ would determine suitable orbitals for the repelling electron pair (i, j). In the case of two-electron atoms, the orbit condition $r_2 = r_1$, $j \neq i$ places both electrons in the s-orbital which specifies the normal or ground state configuration $1s^2$.

Further, by substituting equation (3.16c) into equations (3.7a) and (3.7b), the individual one-electron atom Hamiltonian and the screened nuclear charge are rewritten as

$$H_i = H_\vartheta$$

$$= -\frac{1}{2}\nabla^2 - \frac{1}{r}\left(Z - \frac{1}{4\sin\frac{1}{2}\vartheta}\right), \quad r_i = r_j = r \tag{3.17a}$$

and

$$
\begin{aligned}
Z_{ij} &= Z_{\vartheta} \\
&= Z - \frac{1}{4\sin\frac{1}{2}\vartheta},
\end{aligned}
\tag{3.17b}
$$

respectively. It is observed that the configuration $h = 1$ effectively decouples the two-electron atoms Hamiltonian into two equivalent one-electron atom Hamiltonians, $H_1 = H_2 = H_{\vartheta}$ (3.17a), each describing the motion of a single electron in a screened Coulomb field of the nucleus. The two electrons are equidistant from the nucleus and they experience equal nuclear charge screening depending only on their orbit orientation angle ϑ.

The total symmetrized Hamiltonian for the two-electron atom is defined according to equations (3.3a) and (3.17a) as

$$
H = 2H_{\vartheta} \tag{3.18}
$$

Thus a desired separation of the two-electron atom Hamiltonians has been achieved. In contrast to the independent electron model adopted in standard quantum mechanics textbooks [2, 5], the separation achieved here maintains the repulsive electron-electron interaction whose role in the dynamics is characterized by nuclear charge screening depending only on the the orbit orientation angle ϑ as an adjustable parameter. The dynamics generated by the symmetrized Hamiltonian defined above in the configuration $h = 1$ includes the para-states of the two-electron atoms.

3.3.1 Minimum nuclear charge screening parameter

According to equation (3.16c), the only adjustable parameter which governs the repulsive electron-electron interaction and, therefore, determines the nuclear charge screening parameter in the configuration $h = 1$ is the orbit orientation angle ϑ. Decreasing ϑ towards zero brings the electrons closer together leading to an increase in the repulsive interaction and a corresponding increase in the nuclear charge screening parameter, whereas increasing ϑ away from zero pushes the electrons farther apart leading to a decrease in the repulsive interaction and a corresponding decrease in the nuclear charge screening parameter.

We notice that according to equations (3.16c) and (3.17b), the nuclear charge screening parameter S_ϑ becomes infinitely large, while the screened nuclear charge Z_ϑ become ill-defined for values of ϑ given by

$$\vartheta = 2n\pi, \quad n = 0, 1, 2, 3, ... , \tag{3.19a}$$

which implies that

$$\sin \frac{1}{2}\vartheta = 0 \tag{3.19a}$$

leading to

$$S_{\vartheta=2n\pi} = \infty, \quad n = 0, 1, 2, 3, ... \tag{3.20}$$

In general, the orbital orientation angle $\vartheta = 2n\pi$ for $n = 0, 1, 2, 3, ...$, are to be discarded since they lead to large values of the electron-electron interaction energy, thus driving the atom towards a state of instability.

The optimal value of ϑ that gives minimum nuclear charge screening parameter is determined through,

$$\frac{\partial S_\vartheta}{\partial \vartheta} = 0 \tag{3.21}$$

which on substituting S_ϑ (3.16c), yields

$$\frac{\cos \frac{1}{2}\vartheta}{\sin^2 \frac{1}{2}\vartheta} = 0 \tag{3.22}$$

Since in equation (3.22), $\sin \frac{1}{2}\vartheta \neq 0$, then

$$\cos \frac{1}{2}\vartheta = 0 \tag{3.23a}$$

which is valid if and only if

$$\vartheta = (2n+1)\pi, \qquad n = 0, 1, 2, 3, \ldots. \tag{3.23b}$$

Therefore, the optimal values of $\vartheta = (2n+1)\pi$ that leads to

$$\cos\vartheta = \cos{(2n+1)\pi} = -1, \qquad n = 0, 1, 2, 3, \ldots, \tag{3.24}$$

constitute *anti-parallel* orbit orientation.

The two electrons in the repelling pair (i, j) then satisfy the *anti-parallel* orbit condition

$$\mathbf{r}_j = -\mathbf{r}_i, \qquad j \neq i\ , \tag{3.25}$$

leading to corresponding relative position vector

$$r_{ij} = |\mathbf{r}_i - \mathbf{r}_j| = 2r_i, \qquad r_i = r_j \tag{3.26}$$

This condition reproduces the Bohr "old" quantum theory ideas about electron correlation in a two-electron atom, where it was assumed that the electrons were permanently located exactly at the opposite sides of the nucleus, so that $\mathbf{r}_1 = -a\mathbf{r}_2$ (a being positive) [42, 43].

It can be seen from equation (3.25) that the two electrons have equal, but opposite linear momenta,

$$\mathbf{p}_j = -\mathbf{p}_i; \qquad \mathbf{p}_i = m\dot{\mathbf{r}}_i, \quad \mathbf{p}_j = m\dot{\mathbf{r}}_j \tag{3.27}$$

Further, equations (3.25) and (3.27) show that the two electrons have equal kinetic energy and orbital angular momenta expressed as

$$\frac{\mathbf{p}_j^2}{2m} = \frac{\mathbf{p}_i^2}{2m} \tag{3.28}$$

and

$$\mathbf{L} = \mathbf{r}_j \times \mathbf{p}_j = -\mathbf{r}_i \times -\mathbf{p}_i, \tag{3.29}$$

respectively.

Thus, substitution of ϑ (3.23b) into equations (3.16c), (3.17a) and (3.17b) yields the minimum nuclear charge screening parameter as

$$\begin{aligned} S_{\vartheta=(2n+1)\pi} &= S_{\min} \\ &= \frac{1}{2}, \end{aligned} \tag{3.30}$$

the effective one-electron Hamiltonian of the form

$$\begin{aligned} H_{\vartheta=(2n+1)\pi} &= \mathcal{H} \\ &= -\frac{1}{2}\nabla^2 - \frac{1}{r}\left(Z - \frac{1}{4}\right) \\ &= -\frac{1}{2}\nabla^2 - \frac{\zeta}{r} \end{aligned} \tag{3.31a}$$

and the effective nuclear charge as

$$\begin{aligned} Z_{\vartheta=(2n+1)\pi} &= \zeta \\ &= Z - \frac{1}{4}, \end{aligned} \tag{3.31b}$$

respectively.

Equation (3.31a) represents an optimal Hamiltonian describing the stable state of the two-electron atoms when the repulsive Coulomb interaction term H_{ij} (3.6) takes a minimum value given by,

$$H_{ij}^{(min)} = \frac{1}{2r} S_{\min}, \qquad r_i = r_j = r \tag{3.32a}$$

which becomes

$$\begin{aligned} H_{ij}^{(min)} &= \mathcal{H}^{(min)} \\ &= \frac{1}{4r} \end{aligned} \tag{3.32b}$$

after substituting for S_{min} (3.30).

Equation (3.32b) may be expressed as

$$\begin{aligned}\mathcal{H} &= -\frac{1}{2}\nabla^2 - \frac{Z}{r} + \frac{1}{4r} \\ &= H^{(ind)} + \mathcal{H}^{(min)}, \end{aligned} \tag{3.32c}$$

where

$$H^{(ind)} = -\frac{1}{2}\nabla^2 - \frac{Z}{r} \tag{3.32d}$$

represents the Hamiltonian of an entirely independent electron in the Coulomb field of nucleus of charge Z and $\mathcal{H}^{(min)}$ is the minimum repulsive Coulomb interaction term (3.32b). Therefore, under the *anti-parallel* orbit orientation, the two electrons are on opposite sides of the nucleus, experiencing equal minimal shielding from the nucleus due to their minimal repulsive Coulomb interaction (3.32b).

The total Hamiltonian H (3.18) of the two-electron atoms under the *anti-parallel* orbit orientation, takes the form

$$H = 2\mathcal{H}; \qquad \mathcal{H}_1 = \mathcal{H}_2 = \mathcal{H} \tag{3.33}$$

which represents the sum of independent one-electron atom modes in a central field in which the two electrons maintain minimal repulsive Coulomb interaction. The two electrons then behave independently but maintain a finite distance ($< \infty$) between them due to the minimal repulsive interaction energy captured through the minimum screened nuclear charge ζ occurring in the definition of $\mathcal{H}$ (3.31a). The minimum values of the repulsive interaction energy and the Hamiltonian, under the *anti-parallel* orbit orientation are consistent with the "stretched helium" configuration applied in studies of chaotic behavior in helium, where the lowest energy state is achieved when the two electrons are on opposite sides of the nucleus [44, 45]. The ground state configuration $1S^2$ occurs in this mode ($h = 1$) with both electrons occupying opposite points on the K-shell which is a circular orbital with radius r.

3.3.2 The Ground state energy

Using the effective one-electron Hamiltonian (3.31a), the Schrödinger equation describing the motion of a single electron in the Coulomb field of the nucleus screened by the other electron takes the form

$$\left(-\frac{\nabla^2}{2} - \frac{\varsigma}{r}\right)\Psi(\mathbf{r}) = \mathcal{E}\Psi(\mathbf{r}) \tag{3.34}$$

after introducing the one-electron atom eigenfunction $\Psi(\mathbf{r}_1) = \Psi(\mathbf{r}_2) = \Psi(\mathbf{r})$ and energy eigenvalue $\mathcal{E}_1 = \mathcal{E}_2 = \mathcal{E}$, related to the two-electron-atoms eigenfunction $\Psi(\mathbf{r}_1, \mathbf{r}_2)$ and total energy E by

$$\begin{aligned} \Psi(\mathbf{r}_1, \mathbf{r}_2) &= \Psi(\mathbf{r}_1)\Psi(\mathbf{r}_2) \\ &= \Psi^2(\mathbf{r}) \end{aligned} \tag{3.35}$$

and

$$\begin{aligned} E^{(0)}_{cal} &= \mathcal{E}_1 + \mathcal{E}_2 \\ &= 2\mathcal{E}, \end{aligned} \tag{3.36}$$

respectively.

The hydrogen-like atom Schrödinger equation (3.34) is easily solved to obtain the eigenfunction and energy eigenvalue [3, 4, 6]

$$\Psi^{(0)}(\mathbf{r}) = \sqrt{\frac{\varsigma^3}{\pi}}\exp(-\varsigma r) \tag{3.37}$$

and

$$\mathcal{E} = \frac{-\varsigma^2}{2}, \tag{3.38}$$

respectively.

To test the consistency and accuracy of the optimal stable state theory developed here, the optimal ground state (i.e., $1s^2$ configuration) eigenfunction and energy of the two-electron atoms under the *anti-parallel* orbit orientation in the mode $h = 1$ are calculated. Then, on applying equation (3.37) to equation (3.35), the eigenfunction

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{\zeta^3}{\pi} \exp(-2r\zeta) \tag{3.39}$$

is obtained. Similarly, application of equation (3.38) to equation (3.36) yields the ground state energy of the two-electron atoms in the model as

$$\begin{aligned} E^{(0)}_{cal} &= -\zeta^2 \\ &= -\left(Z - \frac{1}{4}\right)^2 \end{aligned} \tag{3.40}$$

after substituting for ζ (3.31*b*). Exactly the same results were obtained in the Bohr 1913 model for the ground state energy of Helium-like ions in which the two electrons revolve in a single circular orbit on the opposite ends of the diameter [42, 43].

The theoretical results of the ground state energy under the *anti-parallel* orbit orientation $E^{(0)}_{cal}$ (3.40) for $Z = 1 - 10$ are given in Table 3.1 and compared with $E^{(0)}$ (1.6) obtained using the standard independent electron approximation [5] and the exact energy $E^{(exa)}$ [26]. It is noted in Table 3.1 that the theoretical results for the ground state energy $E^{(0)}_{cal}$ under the *anti-parallel* orbit orientation are closer to the exact energy $E^{(exa)}$ compared to the ground state energy $E^{(0)}$ obtained using the independent particle approximation found in textbooks of quantum mechanics. In particular, the present model gives the ground state energy of helium atom as $E^{(0)}_{cal} = -3.0625\,a.u$ which is about

5.47% lower than the exact energy, while the standard independent electron model gives the ground state energy of helium atom $E^{(0)} = -4.0\,a.u.$ which is about 37.76% lower than the exact energy.

Table 3.1. The ground state energy under the *anti-parallel* orbit orientation $E^{(0)}_{cal}$ for $Z = 1 - 6$ compared with $E^{(0)}$ and the exact energy $E^{(exa)}$

Z	Atom	$E^{(0)}$	$E^{(0)}_{cal}$	$E^{(exa)}$
1	H^-	-1.0000	-0.5625	-0.5278
2	He	-4.0000	-3.0625	-2.9037
3	Li^+	-9.0000	-7.5625	-7.2799
4	Be^{2+}	-16.0000	-14.0625	-13.6556
5	B^{3+}	-25.0000	-22.5625	-22.0310
6	C^{4+}	-36.0000	-33.0625	-32.4062
7	N^{5+}	-49.0000	-45.5625	-44.7814
8	O^{6+}	-64.0000	-60.0625	-59.1444
9	F^{7+}	-81.0000	-76.5625	-75.5317
10	Ne^{8+}	-100.0000	-95.0625	-93.9068

The remarkable improvement is due to the minimal repulsive interaction energy maintained in the present model as can be seen in equation (3.32*c*), whereas in the standard independent electron model, the electrons are treated as entirely independent as shown by equation (1.4), i.e., have zero repulsive interaction energy. However, it does not seem possible that in an atom of finite size, the two electrons can be separated from each other by an infinite distance (within an atom of finite size) to justify zero repulsive interaction energy, i.e., each electron moves in a fully unscreened field of the nucleus. These confirm our interpretation that the *anti-parallel* orbit orientation which incorporates nuclear charge screening provides a stable or normal state of the two-electron atoms.

It is also noted in Table 3.1 that the calculated ground state energy $E_{cal}^{(0)}$ of the two-electron atoms are lower than the exact energy $E^{(exa)}$. Improvement on the results will be done by considering a general dynamics of the two-electron atoms that combines the configurations $h = 1$ and $h < 1$.

3.4 General dynamics: perturbation theory

To study the dynamics of the two-electron atoms over the broad range of locations and orientations of the electrons, the Hamiltonian as presented in equation (3.7a) which applies under configurations $h = 1$ and $h < 1$ is considered. The analysis so far shows that the configuration $h = 1$ characterizes optimal stable state dynamics, while the configuration $h < 1$ characterizes a general repulsive interaction of the electrons which under certain orientations may drive the system to states of excitation or instability.

If a nuclear charge screening parameter is defined as

$$\sigma_{ij} = \frac{1}{2} S_{ij} \qquad r_i \geq r_j, \qquad h \leq 1\,, \tag{3.41}$$

then, in accordance with equations (3.14d) and (3.30), the minimum and maximum screening constants,

$$\begin{aligned} \sigma_{\max} &= \frac{1}{2} S_{\max} \\ &= \frac{1}{2} \quad ; \quad h << 1 \end{aligned} \tag{3.42}$$

and

$$\begin{aligned} \sigma_{\min} &= \frac{1}{2} S_{\min} \\ &= \frac{1}{4} \quad ; \quad h = 1 \end{aligned} \tag{3.43}$$

are obtained, respectively. These results agree exactly with the conclusions drawn under similar conditions in [45, 46], where the calculation of the nuclear charge screening parameter, i.e., $\sigma_{ij} \equiv \sigma$ is based on the interaction between an electron and the average charge distribution of the other electron(s).

From the above observations, it is necessary to decompose the Hamiltonian presented in equation (3.7a) into two components. One component, $H_i^{(0)}$, composed of an effective one-electron atom Hamiltonian describing stable state dynamics in the configuration $h = 1$, and the other component, H_i', composed of interaction energy terms which may be treated as perturbations arising from the configuration $h < 1$. Recalling that the stable state occurs under the *anti-parallel* orientation, equation (3.7a) can be rewritten in the alternative form as

$$\begin{aligned} H_i &= -\frac{1}{2}\nabla_i^2 - \frac{1}{r_i}\left(Z - \frac{1}{4}\right) + \frac{1}{2r_i}\left(S_{ij} - \frac{1}{2}\right) \\ &= H_i^{(0)} + H_i', \qquad r_i \geq r_j \end{aligned} \tag{3.44a}$$

where we have introduced the minimum repulsive interaction term $H_{ij}^{(min)}$ (3.32b) under the central field approximation to obtain an effective separation from the configurations $h = 1$ and $h < 1$.

The first component in equation (3.44a)

$$\begin{aligned} H_i^{(0)} &= -\frac{1}{2}\nabla_i^2 - \frac{1}{r_i}\left(Z - \frac{1}{4}\right) \\ &= -\frac{1}{2}\nabla_i^2 - \frac{\zeta}{r_i} \end{aligned} \tag{3.44b}$$

represents the unperturbed Hamiltonian which is just the effective one-electron Hamiltonian $\mathcal{H}$ (3.31a) in the configuration $h = 1$, whereas the second component in equation (3.44a)

$$H_i' = \frac{1}{2r_i}\left(S_{ij} - \frac{1}{2}\right) \tag{3.44c}$$

represents the interaction energy treated as a perturbing Hamiltonian in the configuration $h < 1$. By applying equation (3.44a) the Hamiltonian of the two-electron atoms (3.3a) under the perturbation theory, may be expressed in the form

$$\begin{aligned} H &= -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{\zeta}{r_1} - \frac{\zeta}{r_2} + \frac{1}{2r_1}\left(S_{12} - \frac{1}{2}\right) + \frac{1}{2r_2}\left(S_{21} - \frac{1}{2}\right) \\ &= H^{(0)} + H' \end{aligned} \qquad (3.45a)$$

The unperturbed Hamiltonian in equation (3.45a)

$$H^{(0)} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{\zeta}{r_1} - \frac{\zeta}{r_2} \qquad (3.45b)$$

is interpreted as the effective Hamiltonian for the two-electron atoms and represents the sum of independent one-electron atom modes in a central field in which the two electrons maintain minimal repulsive Coulomb interaction energy under the *anti-parallel* orientation. It differs from the generally used Hamiltonian in the standard independent electron approximation through the inclusion of the minimum repulsive Coulomb interaction term (3.32b). The perturbing Hamiltonian in equation (3.45a)

$$\begin{aligned} H' &= \frac{1}{2r_1}\left(S_{12} - \frac{1}{2}\right) + \frac{1}{2r_2}\left(S_{21} - \frac{1}{2}\right) \\ &= -\frac{1}{4}\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{1}{2}\left(\frac{S_{12}}{r_1} + \frac{S_{21}}{r_2}\right) \\ &= H'_{mag} + H'_{rep} \end{aligned} \qquad (3.45c)$$

is, generally, understood to be the binding energy associated with the magnetic shielding term [11, 13]

$$H'_{mag} = -\frac{1}{4}\left(\frac{1}{r_1} + \frac{1}{r_2}\right) \qquad (3.46a)$$

and the repulsive Coulomb interaction term

$$
\begin{aligned}
H'_{rep} &= \frac{1}{2}\left(\frac{S_{12}}{r_1} + \frac{S_{21}}{r_2}\right) \\
&= \frac{1}{r_{12}} \qquad (3.46b)
\end{aligned}
$$

Hence, application of equation (3.46*b*) in equation (3.45*a*) leads to the Hamiltonian of the form

$$
\begin{aligned}
H &= -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{\zeta}{r_1} - \frac{\zeta}{r_2} - \frac{1}{4}\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{1}{r_{12}} \\
&= H^{(0)} + H' \qquad (3.47)
\end{aligned}
$$

Thus, equation (3.47) completely specifies the Hamiltonian to be used for perturbation calculations in the present model.

Chapter 4

4 Methodology

The Schrödinger equation for atoms is exactly solvable only for single-electron atoms. However, the majority of the problems in quantum mechanics lead to equations which are too complex to be solved exactly. In such cases approximation methods, such as perturbation theory, variational approach and variational-perturbation approach are used. In the thesis, the perturbation theory shall be applied.

Perturbation theory is an approximation method applied to those cases in which the real system can be described by a small change in an easily solvable, idealized system [1, 5]. The Hamiltonian H of the system is expressed in the form,

$$H = H^{(0)} + \lambda H', \tag{4.1}$$

where $H^{(0)}$, the unperturbed Hamiltonian, is the Hamiltonian of the system for which the Schrödinger can be solved exactly, H' is the small change treated as a perturbation and λ is a real parameter which allow the expansion of the wave function and energy into a power series in λ.

In this form,a great number of problems encountered in atomic physics, in which the nucleus provides the strong central potential for the electrons can described. Furthermore, interaction of less strength, such as magnetic interaction (spin-orbit coupling), the electrostatic repulsion of electrons and the influence of the external field can be described by perturbation theory [1, 5].

Perturbation theories are of two kinds, that is, the time-independent perturbation theory where the Hamiltonian does not depend on time and the time-dependent perturbation theory where the Hamiltonian depends explicitly on time. In this chapter only the approximate determination of the energy eigenvalues and corresponding eigenfunctions for the stationary states of a time-independent Hamiltonian are discussed.

4.1 Time-independent perturbation theory

The discrete set of all the eigenvalues $E^{(0)}$ and the orthonormal set of eigenfunctions $\Psi^{(0)}$ of the 'unperturbed' Hamiltonian $H^{(0)}$ of a system satisfy an eigenvalue equation [1, 2, 5, 14]

$$H^{(0)}\Psi^{(0)} = E^{(0)}\Psi^{(0)} \tag{4.2}$$

If a small perturbation is added to the system so that the Hamiltonian changes to $H = H^{(0)} + \lambda H'$ (4.1), then the energy levels and the stationary states of the system are described by

$$H\Psi = E\Psi \tag{4.3}$$

Usually this equation is not exactly solvable for the two-electron atoms. The perturbation theory provides a systematic method of successive approximation of the eigenfunction Ψ and eigenvalues E in terms of the unperturbed eigenfunctions $\Psi^{(0)}$ and eigenvalues $E^{(0)}$.

The eigenfunctions Ψ and eigenvalues E of H are expanded in terms of the perturbation parameter λ, i.e.,

$$\Psi = \sum_{n=0}^{\infty} \lambda^{(n)}\Psi^{(n)} = \Psi^{(0)} + \lambda\Psi^{(1)} + \lambda^2\Psi^{(2)} + \ldots\ldots\ldots \tag{4.4a}$$

$$E = \sum_{n=0}^{\infty} \lambda^{(n)}E^{(n)} = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \ldots\ldots\ldots, \tag{4.4b}$$

where the index n refers to the order of the perturbation [1, 2, 5].

Hence, substitution of equations (4.1), (4.4a) and (4.4b) into equation (4.3) and group the terms of the same order of λ together, yields

$$\lambda^0 \left\{\left(H^{(0)} - E^{(0)}\right) \Psi^{(0)}\right\} + \lambda^1 \left\{\left(H^{(0)} - E^{(0)}\right) \Psi^{(1)} + \left(H' - E^{(1)}\right) \Psi^{(0)}\right\}$$

$$+\lambda^2 \left\{\left(H^{(0)} - E^{(0)}\right) \Psi^{(2)} + \left(H' - E^{(1)}\right) \Psi^{(1)} - E^{(2)}\Psi^{(0)}\right\} + \ldots\ldots\ldots = 0 \tag{4.5}$$

Since $\lambda \neq 0$, then each individual term in the curly bracket is equal to zero, leading to a family of perturbation equations

$$\left(H^{(0)} - E^{(0)}\right) \Psi^{(0)} = 0 \tag{4.6a}$$

$$\left(H^{(0)} - E^{(0)}\right) \Psi^{(1)} + \left(H' - E^{(1)}\right) \Psi^{(0)} = 0 \tag{4.6b}$$

$$\left(H^{(0)} - E^{(0)}\right) \Psi^{(2)} + \left(H' - E^{(1)}\right) \Psi^{(1)} - E^{(2)}\Psi^{(0)} = 0 \tag{4.6c}$$

$$\vdots$$

$$\left(H^{(0)} - E^{(0)}\right) \Psi^{(n)} + \left(H' - E^{(1)}\right) \Psi^{(n-1)} - \Sigma_{k=2}^{n} E^{(k)}\Psi^{(k-n)} = 0$$

Equations (4.6a), (4.6b) and (4.6c) are identified as the zero-order, first-order and second-order perturbation equations respectively. The remainder are higher-order perturbation equations.

The zero-order perturbation equation (4.6a) has a whole spectrum of solutions. One *particular* solution of equation (4.6a) is considered, where $\Psi^{(0)}$ and $E^{(0)}$ are known completely with $\Psi^{(0)}$ normalized. By multiplying equation (4.6a) by $\Psi^{(0)\star}$ and then integrate over the volume element $d\tau$, the zero-order energy is obtained as

$$\begin{aligned} E^{(0)} &= \int \Psi^{(0)\star} H^{(0)} \Psi^{(0)} d\tau \\ &= \langle \Psi^{(0)} |\, H^{(0)} \,| \Psi^{(0)} \rangle \end{aligned} \tag{4.7}$$

Similarly, multiplication of equation (4.6b) by $\Psi^{(0)\star}$ and then integrate over the volume element $d\tau$, noting that $H^{(0)}$ is Hermitian, the first-order perturbation energy is obtained as

$$\begin{aligned} E^{(1)} &= \int \Psi^{(0)\star} H' \Psi^{(0)} d\tau \\ &= \langle \Psi^{(0)} | \, H' \, | \Psi^{(0)} \rangle \end{aligned} \tag{4.8}$$

Thus, a knowledge of the zero-order wave function $\Psi^{(0)}$, for one particular state alone yields both $E^{(0)}$ (4.7) and $E^{(1)}$ (4.8) for this state.

In equation (4.6b), for the particular state considered, the constants $E^{(0)}$ (4.7) and $E^{(1)}$ (4.8) and the eigenfunction $\Psi^{(0)}$ are known. Therefore, equation (4.6b) is an inhomogeneous differential equation for the first-order perturbed wave function $\Psi^{(1)}$ which does not contain any unknown eigenvalues. Since $\Psi^{(1)}$ must satisfy some definite boundary conditions, then equation (4.6b) determines the function $\Psi^{(1)}$ for the particular state uniquely. However, in the case where the electron-electron repulsive interaction term is treated as a perturbation, i.e., $H' = 1/r_{12}$, analytical solutions of equation (4.6b) for $\Psi^{(1)}$ have not been found to date. This is one of the objectives of the thesis, as we shall discuss a practical method for direct calculation of equation (4.6b) in the next chapter.

Once $\Psi^{(1)}$ has been found, then the second-order energy $E^{(2)}$ can be evaluated as follows. By multiplying equation (4.6c) by $\Psi^{(0)\star}$ and then integrating over the volume element $d\tau$, the second-order perturbation energy is obtained as

$$\begin{aligned} E^{(2)} &= \int \Psi^{(0)\star} \left(H' - E^{(1)} \right) \Psi^{(1)} d\tau \\ &= \langle \Psi^{(0)} | \, H' - E^{(1)} \, | \Psi^{(1)} \rangle \end{aligned} \tag{4.9}$$

The first-order perturbed wave function $\Psi^{(1)}$ can also be applied to determine the third-order perturbation energy expressed in the form

$$
\begin{aligned}
E^{(3)} &= \int \Psi^{(1)\star}\left(H' - E^{(1)}\right)\Psi^{(1)}d\tau - E^{(2)}\int \Psi^{(0)\star}\Psi^{(1)}d\tau \\
&= \langle\Psi^{(1)}|\left(H' - E^{(1)}\right)|\Psi^{(1)}\rangle - E^{(2)}\langle\Psi^{(1)}|\Psi^{(0)}\rangle
\end{aligned}
\tag{4.10}
$$

After $E^{(2)}$ and $\Psi^{(1)}$ have been found, equation (4.6*c*) determines the function $\Psi^{(2)}$ (in principle), and so on. Once $\Psi^{(2)}$ has been found, two additional eigenvalues, $E^{(4)}$ and $E^{(5)}$, can be evaluated. In general, the knowledge of the nth-order wave function is sufficient to determine the perturbation energy to order $(2n+1)$ [1, 14].

The total energy, in terms of the perturbation energies, is

$$E = E^{(0)} + E^{(1)} + E^{(2)} + E^{(3)} + \ldots\ldots\ldots \tag{4.11}$$

In this thesis the ground state energy up to second-order perturbation is calculated, i.e.,

$$E = E^{(0)} + E^{(1)} + E^{(2)} \tag{4.12}$$

4.2 Reduction of the many-electron equation

In this subsection, the method for reduction of the many-electron atom problem discussed in section 4.1 to one-electron atom problem in the simplest case is outlined. This is possible when the total Hamiltonian H is the sum of one-electron atom Hamiltonians H_i, that is

$$H = \sum_i H_i \tag{4.13a}$$

and

$$H_i = h^{(0)}(i) + \lambda v(i), \tag{4.13b}$$

where $h^{(0)}(i)$ and $v(i)$ are the unperturbed and perturbed Hamiltonians, respectively [14]. The Schrödinger equation for one-electron atom becomes

$$H_i\phi_i = \epsilon_i\phi_i, \tag{4.14}$$

where the eigenfunctions ϕ_i and the eigenvalues ϵ_i of H_i are expanded in terms of the perturbation parameter λ as

$$\begin{aligned}\phi_i &= \sum_{n=0}^{\infty} \lambda^{(n)} \phi_i^{(n)} \\ &= \phi_i^{(0)} + \lambda \phi_i^{(1)} + \lambda^2 \phi_i^{(2)} + \ldots\ldots\ldots \qquad (4.15a)\\ \epsilon_i &= \sum_{n=0}^{\infty} \lambda^{(n)} \epsilon_i^{(n)} \\ &= \epsilon_i^{(0)} + \lambda \epsilon_i^{(1)} + \lambda^2 \epsilon_i^{(2)} + \ldots\ldots\ldots \qquad (4.15b)\end{aligned}$$

Following steps in equations (4.5)-(4.6c), a family of one-electron atom perturbation equations are obtained as

$$\left(h^{(0)}(i) - \epsilon_i^{(0)}\right) \phi_i^{(0)} = 0 \qquad (4.16a)$$

$$\left(h^{(0)}(i) - \epsilon_i^{(0)}\right) \phi_i^{(1)} + \left(v(i) - \epsilon_i^{(1)}\right) \phi_i^{(0)} = 0 \qquad (4.16b)$$

$$\left(h^{(0)}(i) - \epsilon_i^{(0)}\right) \phi_i^{(2)} + \left(v(i) - \epsilon_i^{(1)}\right) \phi_i^{(1)} - \epsilon_i^{(2)} \phi_i^{(0)} = 0 \qquad (4.16c)$$

$$\vdots$$

$$\left(h^{(0)}(i) - \epsilon_i^{(0)}\right) \phi_i^{(n)} + \left(v(i) - \epsilon_i^{(1)}\right) \phi_i^{(n-1)} - \Sigma_{k=2}^{n} \epsilon_i^{(k)} \phi_i^{(k-n)} = 0$$

Equations (4.16a), (4.16b) and (4.16c) are identified as the one-electron atom zero-order, first-order and second-order perturbation equations, respectively. The remainder are one-electron atom higher-order perturbation equations.

This procedure leads to simple sums over the electrons for all the perturbation energies; for example, the zero-order energy (4.7), first-order energy (4.8) and second-order energy (4.9), become

$$\begin{aligned}E^{(0)} &= \Sigma_i \epsilon_i^{(0)} \\ &= \Sigma_i \langle \phi_i^{(0)}, h^{(0)}(i) \phi_i^{(0)} \rangle, \qquad (4.17a)\end{aligned}$$

$$\begin{aligned} E^{(1)} &= \Sigma_i \epsilon_i^{(1)} \\ &= \Sigma_i \langle \phi_i^{(0)}, v(i) \phi_i^{(0)} \rangle \end{aligned} \tag{4.17b}$$

and

$$\begin{aligned} E^{(2)} &= \Sigma_i \epsilon_i^{(2)} \\ &= \Sigma_i \langle \phi_i^{(1)}, (v(i) - \epsilon_i^{(1)}) \phi_i^{(0)} \rangle, \end{aligned} \tag{4.17c}$$

respectively.

4.3 Rayleigh-Schrödinger $1/Z$ perturbation expansion

The Rayleigh-Schrödinger $1/Z$ perturbation expansion provides a powerful means of studying the atomic characteristic of atoms and ions [1, 14]. Hylleraas [17], observed that the scaling transformation of the space co-ordinates $r \to r/Z$ applied to the non-relativistic Hamiltonian (1.1a) of a two-electron atomic ions of nuclear charge Z yielded a scaled Hamiltonian

$$H = Z^2 \left(-\frac{\nabla_1^2}{2} - \frac{\nabla_1^2}{2} - \frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{Z} \frac{1}{r_{12}} \right) \tag{4.18a}$$

The Rayleigh-Schrödinger perturbation theory can be applied to the Hamiltonian by letting the unperturbed Hamiltonian be

$$H^{(0)} = -\frac{\nabla_1^2}{2} - \frac{\nabla_1^2}{2} - \frac{1}{r_1} - \frac{1}{r_2}, \tag{4.18b}$$

the perturbing Hamiltonian $H' = 1/r_{12}$ (1.1a) and the perturbation parameter

$$\lambda = \frac{1}{Z} \tag{4.18c}$$

Then the eigenvalue $E(\lambda)$ and eigenvector $\Psi(\lambda)$ of $H(\lambda) = H^{(0)} + (\lambda)H'$ can be expanded as power series in λ (4.18c), in the form

$$E(\lambda) = \Sigma_{n=0}^{\infty} E^{(n)} \frac{1}{Z^n} \tag{4.19a}$$

and

$$\Psi(\lambda) = \Sigma_{n=0}^{\infty} \Psi^{(n)} \frac{1}{Z^n}, \tag{4.19b}$$

respectively. For ground state energy of the two-electron atoms, the first two coefficients of equation (4.19a), expressed earlier as equations (1.6) and (1.7), become $E^{(0)} = -1\, a.u.$ and $E^{(1)} = 5/8\, a.u.$, respectively.

In the thesis, the Rayleigh-Schrödinger $1/Z$ perturbation expansion shall be applied when developing appropriate equations for solving equation (4.6b) for the first-order perturbed wave function $\Psi^{(1)}$.

4.4 Expectation values

The expectation value of an operator L in the kth state of the system may be expanded into different orders [11, 12, 14]

$$\begin{aligned} \langle L \rangle_k &= \frac{\langle \Psi_k | L | \Psi_k \rangle}{\langle \Psi_k | \Psi_k \rangle} \\ &= L_k^{(0)} + L_k^{(1)} + \ldots\ldots, \end{aligned} \tag{4.20}$$

where $L_k^{(0)}$ is the zero-order approximation to the diagonal matrix element of any dynamical variable given by

$$L_k^{(0)} = \langle \Psi_k^{(0)} | L | \Psi_k^{(0)} \rangle \tag{4.21}$$

and $L_k^{(1)}$ the first-order correction given by

$$L_k^{(1)} = 2 \langle \Psi_k^{(1)} | \left(L - L_k^{(0)} \right) | \Psi_k^{(0)} \rangle \tag{4.22}$$

To first-order approximation, the expectation value of an operator L is given by

$$\begin{aligned} \langle L \rangle &= L_k^{(0)} + L_k^{(1)} \\ &= \langle \Psi_k^{(0)} | L | \Psi_k^{(0)} \rangle + 2 \langle \Psi_k^{(1)} | \left(L - L_k^{(0)} \right) | \Psi_k^{(0)} \rangle \end{aligned} \tag{4.23}$$

which may be written in alternative form [12] as

$$\begin{aligned}\langle L\rangle &= L_k^{(0)} + L_k^{(1)} \\ &= \langle\Psi^{(0)}|L|\Psi^{(0)}\rangle + 2\left(\langle\chi_k^{(1)}|H'|\Psi_k^{(0)}\rangle - E^{(1)}\langle\chi_k^{(1)}|\Psi_k^{(0)}\rangle\right) \qquad (4.24)\end{aligned}$$

after taking $L = H'$, $L_k^{(0)} = E^{(1)}$ and $\Psi_k^{(1)} = \chi_k^{(1)}$. The first-order wave function $\chi_k^{(1)}$ then satisfy the first-order perturbation equation of the type

$$\left(H^{(0)} - E^{(0)}\right)\chi_k^{(1)} + \left(L - \langle\Psi_k^{(0)}|L|\Psi_k^{(0)}\rangle\right)\Psi_k^{(0)} = 0 \qquad (4.25)$$

The integral in equation (4.25) is usually tractable if L is a one-electron operator. The mathematical problem is therefore to solve one-electron first-order wave equations (4.25) for $\chi_k^{(1)}$. Once $\chi_k^{(1)}$ has been found, the first-order correction can be evaluated as

$$L_k^{(1)} = 2\langle\chi_k^{(1)}|\left(L - L_k^{(0)}\right)|\Psi_k^{(0)}\rangle \qquad (4.26)$$

Chapter 5

5 Ground state energy to second-order perturbation

In this chapter the time independent perturbation theory is applied to calculate the ground state energy to second-order perturbation by using the Hamiltonian (3.47) which represents the general dynamics of the two-electron atoms. The Schrödinger equation becomes

$$\left(-\frac{\nabla_1^2}{2}-\frac{\nabla_2^2}{2}-\frac{\zeta}{r_1}-\frac{\zeta}{r_2}-\frac{1}{4}\left(\frac{1}{r_1}+\frac{1}{r_2}\right)+\frac{1}{r_{12}}\right)\Psi\left(\mathbf{r}_1,\mathbf{r}_2\right)=E\Psi\left(\mathbf{r}_1,\mathbf{r}_2\right) \tag{5.1}$$

The main difficulty in finding an exact solution to equation (5.1) has to do with the fact that the Hamiltonian is not separable due to the presence of the repulsive Coulomb interaction term H'_{rep} (3.46*b*) in the perturbation term (3.45*c*). If we ignore the perturbation term (3.45*c*) in equation (3.47), the Hamiltonian becomes separable and is given by the unperturbed Hamiltonian $H^{(0)}$ (3.45*b*) for the stable state dynamics of the two-electron atoms. Hence, the Schrödinger equation for the unperturbed Hamiltonian $H^{(0)}$ (3.45*b*) takes the form

$$\left(-\frac{\nabla_1^2}{2}-\frac{\nabla_2^2}{2}-\frac{\zeta}{r_1}-\frac{\zeta}{r_2}\right)\Psi^{(0)}\left(\mathbf{r}_1,\mathbf{r}_2\right)=E^{(0)}\Psi^{(0)}\left(\mathbf{r}_1,\mathbf{r}_2\right) \tag{5.2a}$$

Equation (5.2*a*) may be separated by writing the zero-order wave function $\Psi^{(0)}\left(\mathbf{r}_1,\mathbf{r}_2\right)$ and energy $E^{(0)}$ as

$$\Psi^{(0)}(\mathbf{r}_1,\mathbf{r}_2)=\Psi^{(0)}(\mathbf{r}_1)\Psi^{(0)}(\mathbf{r}_2) \tag{5.2b}$$

and

$$E^{(0)}=E_1^{(0)}+E_2^{(0)}, \tag{5.2c}$$

respectively. Substituting equations (5.2*b*) and (5.2*c*) into equation (5.2*a*) leads to two independent Schrödinger equations

$$\left(-\frac{1}{2}\nabla_1^2 - \frac{\zeta}{r_1}\right)\Psi^{(0)}(\mathbf{r}_1) = E_1^{(0)}\,\Psi^{(0)}(\mathbf{r}_1) \tag{5.3a}$$

and

$$\left(-\frac{1}{2}\nabla_2^2 - \frac{\zeta}{r_2}\right)\Psi^{(0)}(\mathbf{r}_2) = E_2^{(0)}\,\Psi^{(0)}(\mathbf{r}_2), \tag{5.3b}$$

one for each hydrogen-like atom describing the motion of a single electron in the Coulomb field of the nucleus screened by the other electron. The hydrogen-like atom Schrödinger equations (5.3*a*) and (5.3*b*) are easily solved to obtain the zero-order wave functions and energy

$$\Psi^{(0)}(\mathbf{r}_1) = \sqrt{\frac{\zeta^3}{\pi}}\exp(-\zeta r_1), \tag{5.3c}$$

$$\Psi^{(0)}(\mathbf{r}_2) = \sqrt{\frac{\zeta^3}{\pi}}\exp(-\zeta r_2) \tag{5.3d}$$

and

$$E_1^{(0)} = E_2^{(0)} = \frac{-\zeta^2}{2}, \tag{5.3e}$$

respectively.

The application of equations (5.3*c*) and (5.3*d*) in equation (5.2*b*), yields

$$\begin{aligned}\Psi^{(0)}(\mathbf{r}_1, \mathbf{r}_2) &= \Psi^{(0)} \\ &= \frac{\zeta^3}{\pi}\exp(-\zeta(r_1 + r_2))\end{aligned} \tag{5.4a}$$

Similarly, the application of equation(5.3*e*) in equation (5.2*c*), leads to

$$\begin{aligned}E^{(0)} &= E_1^{(0)} + E_2^{(0)} \\ &= -\zeta^2\end{aligned} \tag{5.4b}$$

It is noted that the zero-order energy (5.4*b*) has the same form as the ground state energy $E_{cal}^{(0)}$ (3.40) under the *antiparallel* orbit orientation. The theoretical results of the zero-order energy $E_{cal}^{(0)} = E^{(0)}$ (5.4*b*) for values $Z = 1 - 10$ are given in Table 3.1. Further, Table 3.1 shows that the zero-order energy are lower than the exact energy $E^{(exa)}$ because the perturbation term has been neglected. The effect of the neglected perturbation term (3.45*c*) on the ground state energy is usually estimated by perturbation theory.

5.1 First-order perturbation energy

When the perturbation term H' (3.45*c*) is substituted into equation (4.8), the first-order perturbation energy is obtained as

$$E^{(1)} = E_{mag}^{(1)} + E_{rep}^{(1)}, \tag{5.5}$$

where

$$\begin{aligned} E_{mag}^{(1)} &= \langle \Psi^{(0)} | H'_{mag} | \Psi^{(0)} \rangle \\ &= -\frac{1}{4} \langle \Psi^{(0)} | \left(\frac{1}{r_1} + \frac{1}{r_2} \right) | \Psi^{(0)} \rangle \end{aligned} \tag{5.6a}$$

and

$$\begin{aligned} E_{rep}^{(1)} &= \langle \Psi^{(0)} | H'_{rep} | \Psi^{(0)} \rangle \\ &= \langle \Psi^{(0)} | \frac{1}{r_{12}} | \Psi^{(0)} \rangle \end{aligned} \tag{5.6b}$$

are components of $E^{(1)}$ due to the magnetic shielding term H'_{mag} (3.46*a*) and repulsive Coulomb interaction term H'_{rep} (3.46*b*), respectively. The expectations values in equations (5.6*a*) and (5.6*b*) are expressed in alternative form as

$$E_{mag}^{(1)} = -\frac{1}{4} \int \int \Psi^{(0)\star} \left(\frac{1}{r_1} + \frac{1}{r_2} \right) \Psi^{(0)} d\tau_1 d\tau_2 \tag{5.7a}$$

and

$$E_{rep}^{(1)} = \int \int \Psi^{(0)\star} \frac{1}{r_{12}} \Psi^{(0)} d\tau_1 d\tau_2, \tag{5.7b}$$

respectively. The volume elements $d\tau_1$ and $d\tau_2$, in spherical polar coordinates (r_1, θ_1, ϕ_1) and (r_2, θ_2, ϕ_2), are defined as

$$d\tau_1 = r_1^2 d\,r_1 sin\,\theta_1 d\,\theta_1 d\,\phi_1 \tag{5.8a}$$

and

$$d\tau_2 = r_2^2 d\,r_2 sin\,\theta_2 d\,\theta_2 d\,\phi_2, \tag{5.8b}$$

respectively. The polar angles (θ_1, ϕ_1) and (θ_2, ϕ_2) of the two-electrons with position vectors $\mathbf{r}_1$ and $\mathbf{r}_2$ respectively are shown in figure 2.

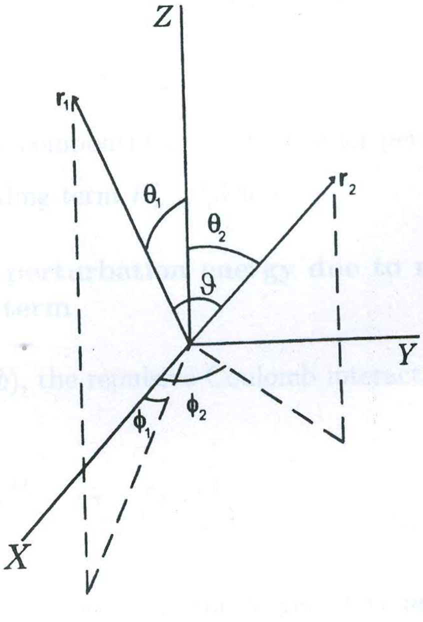

Figure 2: Polar angles of two-electron atoms.

5.1.1 First-order perturbation energy due to magnetic shielding term

By substituting equations (5.4a), (5.8a) and (5.8b) into (5.7a) and integrate over the polar angles (θ_1, ϕ_1) and (θ_2, ϕ_2), it is found that

$$
\begin{aligned}
E^{(1)}_{mag} &= -4\zeta^6 \int_0^\infty r_1\, e^{-2\zeta r_1} dr_1 \int_0^\infty r_2^2\, e^{-2\zeta r_2} dr_2 \\
&\quad -4\zeta^6 \int_0^\infty r_1^2\, e^{-2\zeta r_1} dr_1 \int_0^\infty r_2\, e^{-2\zeta r_2} dr_2
\end{aligned}
\tag{5.9}
$$

Hence, on application of the standard integral [47]

$$
\int_0^\infty r^n e^{-\mu r} dr = \frac{n!}{\mu^{n+1}} \tag{5.10}
$$

in equation (5.9) yields

$$
\begin{aligned}
E^{(1)}_{mag} &= -4\zeta^6 \left(\frac{1}{16\zeta^5} + \frac{1}{16\zeta^5} \right) \\
&= -\frac{\zeta}{2}
\end{aligned}
\tag{5.11}
$$

Equation (5.11) is the component of the first-order perturbation energy due to the magnetic shielding term H'_{mag} (3.46*a*).

5.1.2 First-order perturbation energy due to repulsive Coulomb interaction term

Using equation (3.13*b*), the repulsive Coulomb interaction term (3.46*b*) may be expressed as

$$
H'_{rep} = \frac{1}{r_>} \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} \frac{4\pi}{2l+1} \left(\frac{r_<}{r_>} \right)^l Y^{\star}_{l_1 m_1}(\theta_1, \phi_1)\, Y_{l_2 m_2}(\theta_2, \phi_2) \tag{5.12}
$$

where $r_<$ is the smaller and $r_>$ is the larger of r_1 and r_2. By substituting equations (5.4*a*), (5.8*a*), (5.8*b*) and (5.12) into equation (5.7*b*) and then integrating over the polar angles (θ_1, ϕ_1) and (θ_2, ϕ_2) yields

$$
\begin{aligned}
E^{(1)}_{rep} &= 16\zeta^6 \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} \frac{(4\pi)}{2l+1} \int_0^\infty dr_1\, r_1^2 \int_0^\infty dr_2\, r_2^2\, e^{-2\zeta(r_1+r_1)} \\
&\qquad \times \frac{(r_<)^l}{(r_>)^{l+1}}\, \delta_{l,0}\, \delta_{m_l,0}
\end{aligned}
\tag{5.13}
$$

after applying the orthogonality relation of spherical harmonics

$$\int Y^{\star}_{l'm'_l}(\theta,\phi)\,Y_{lm_l}(\theta,\phi)\,d\Omega = \delta_{ll'}\,\delta_{m_l m'_l}; \qquad (d\Omega = \sin\theta d\theta d\phi) \tag{5.14}$$

[7, 8]. The sums in the double sum in equation (5.13) vanish, except the first one for which $l = m_l = 0$, resulting in

$$\begin{aligned} E^{(1)}_{rep} &= 16\zeta^6 \int_0^\infty r_1^2 dr_1\, e^{-2\zeta r_1} \\ &\qquad \times \left[\int_0^{r_1} \frac{r_2^2 dr_2}{r_1} e^{-2\zeta r_2} + \int_{r_1}^\infty \frac{r_2^2 dr_2}{r_2} e^{-2\zeta r_2}\right] \end{aligned} \tag{5.15}$$

where the first integral in the square bracket arises when $r_1 > r_2$ and the second when $r_2 > r_1$ with appropriate integration limits. Thus, using the standard integrals [47]

$$\int_0^{r'} r^n e^{-\mu r} dr = \frac{n!}{\mu^{n+1}} - e^{-\mu r'} \sum_{s=0}^{n} \frac{n!}{s!} \frac{r'^s}{\mu^{(n+1)-s}} \tag{5.16a}$$

and

$$\int_{r'}^\infty r^n e^{-\mu r} dr = e^{-\mu r'} \sum_{s=0}^{n} \frac{1}{s!} \frac{r'^s}{\mu^{(n+1)-s}} \tag{5.16b}$$

in equation (5.15) leads to

$$\begin{aligned} E^{(1)}_{rep} &= 16\zeta^6 \int_0^\infty r_1 e^{-2\zeta r_1}\, dr_1 \left(\frac{2!}{(2\zeta)^3} - e^{-2\zeta r_1} \sum_{s=0}^{2} \frac{2!}{s!} \frac{r_1^s}{(2\zeta)^{3-s}}\right) \\ &\qquad + 16\zeta^6 \int_0^\infty r_1^2 e^{-4\zeta r_1}\, dr_1 \sum_{s=0}^{1} \frac{1}{s!} \frac{r_1^s}{(2\zeta)^{2-s}} \end{aligned} \tag{5.17a}$$

which becomes

$$\begin{aligned} E^{(1)}_{rep} &= 16\zeta^6 \left\{ \frac{2}{(2\zeta)^5} - \sum_{s=0}^{2} \frac{2}{s!} \frac{(s+1)!}{(2\zeta)^{3-s}(4\zeta)^{s+2}} + \sum_{s=0}^{1} \frac{1}{s!} \frac{(s+2)!}{(2\zeta)^{2-s}(4\zeta)^{s+3}} \right\} \\ &= \frac{5\zeta}{8} \end{aligned} \tag{5.17b}$$

after applying standard integral (5.10). Equation (5.17b) is the component of the first-order perturbation energy due to the repulsive Coulomb interaction term H'_{rep} (3.46b).

By substitution of equations (5.11) and (5.17b) into equation (5.5), the first-order perturbation energy in the model is obtained as

$$E^{(1)} = \frac{\zeta}{8} \tag{5.18}$$

Using equations (5.4b) and (5.18) the ground state energy to first order perturbation is found to be

$$\begin{aligned} E_{cal} &= E^{(0)} + E^{(1)} \\ &= -\left(\zeta^2 - \frac{\zeta}{8}\right) \end{aligned} \tag{5.19a}$$

which becomes

$$E_{cal} = -Z^2 + \frac{5Z}{8} - 0.09375 \tag{5.19b}$$

after substituting for ζ (3.31b). By comparing the results in equation (5.19b) with the ground state energy to first-order perturbation (2.5) obtained within the standard independent electron approximation, then the value -0.09375 would be interpreted as a contribution to the second-order perturbation energy.

The calculated values of the ground state energy to first order perturbation (5.19b) compared with the ones obtained using the standard independent electron approximation (1.8), simple one parameter variational method (2.3) and the many parameter variational method [26], respectively, are presented in Tables 5.1. In Table 5.1, it is noted that the ground state energy to first-order perturbation, E_{cal}, obtained using the model under consideration, gives better results than the energy, E, given by equation (2.5) obtained by applying the standard independent electron approximation. However application of the simple one-parameter variation method leads to the energy, $(E(Z_e)$, given by equation (2.8), which are nearly the same results, although it does not either account for the mechanism which causes the nuclear charge screening or provide for improvement of results through higher order expansions like in the present theory. The close agrement of E_{cal} to the exact energy $E^{(exa)}$ is also remarkable; it is attributed to the minimal repulsive interaction energy maintained between the electrons under the *anti-parallel* orbit orientations.

Table 5.1 The ground state energy to first-order perturbation E_{cal} for $Z = 1 - 10$, are compared with energies E (2.5), $E(Z_e)$ (2.8) and $E^{(exa)}$, respectively.

Z	Atom	E_{cal}	E	$E(Z_e)$	$E^{(exa)}$
1	H^-	-0.4688	-0.3750	-0.4727	-0.5278
2	He	-2.8438	-2.7500	-2.8477	-2.9037
3	Li^+	-7.21875	-7.1250	-7.2227	-7.2799
4	Be^{2+}	-13.5938	-13.5000	-13.5977	-13.6556
5	B^{3+}	-21.9688	-21.8750	-21.9727	-22.0310
6	C^{4+}	-32.3438	-32.2500	-32.3477	-32.4062
7	N^{5+}	-44.7188	-44.6250	-44.7227	-44.7814
8	O^{6+}	-59.0938	-59.0000	-59.0977	-59.1444
9	F^{7+}	-75.4688	-75.3750	-75.4727	-75.5317
10	Ne^{8+}	-93.8438	-93.7500	-93.8477	-93.9068

The next problem is to determine the first-order perturbed wave function, this is considered in section 5.2. The result obtained will be used to calculate the second-order perturbation energy as explained earlier.

5.2 First-order perturbed wave functions

The analytical calculation of the first-order perturbed wave function $\Psi^{(1)}$ using equation (4.6*b*) with $H^{(0)}$, H', $\Psi^{(0)}$, $E^{(0)}$ and $E^{(1)}$ given by equations (3.45*b*), (3.45*c*), (5.4*a*), (5.4*b*) and (5.18), respectively, is complicated due to the repulsive Coulomb interaction term $H'_{rep} = 1/r_{12}$. Consequently, the Rayleigh-Schrödinger $1/Z$ perturbation expansion (section 4.3) will be first applied and latter case where the two-electron atoms first-order perturbation equation (4.6*b*) can be separated into one-electron equation (4.16*b*) is considered.

By applying a scaling transformation of the co-ordinate $r \longrightarrow r/\zeta$ [17] to the Hamiltonian H (3.47), a scaled Hamiltonian

$$\begin{aligned} H_{sc} &= \frac{H}{\zeta^2} \\ &= -\frac{\nabla_1^2}{2} - \frac{\nabla_2^2}{2} - \frac{1}{r_1} - \frac{1}{r_2} - \frac{1}{\zeta}\left(\frac{1}{4}\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{1}{r_{12}}\right) \\ &= H_{sc}^{(0)} + \frac{H'}{\zeta} \end{aligned} \tag{5.20a}$$

is obtained, where

$$H_{sc}^{(0)} = -\frac{\nabla_1^2}{2} - \frac{1}{r_1} - \frac{\nabla_2^2}{2} - \frac{1}{r_2} \tag{5.20b}$$

is the scaled unperturbed Hamiltonian (expressed earlier as (3.45*b*)) and H' is the perturbing Hamiltonian (3.45*c*).

The ground state energy (4.12) to second-order perturbation is now expressed as a series in powers of the perturbation parameter $1/\zeta$

$$E = \zeta^2 E_{sc}^{(0)} + \zeta E_{sc}^{(1)} + E_{sc}^{(2)} \tag{5.21}$$

The hydrogen-like wave functions and energy in equations (5.3*c*) and (5.3*d*) and (5.3e) becomes

$$\Psi_{sc}^{(0)}(\mathbf{r}_1) = \sqrt{\frac{1}{\pi}}\exp(-r_1) \tag{5.22a}$$

$$\Psi_{sc}^{(0)}(\mathbf{r}_2) = \sqrt{\frac{1}{\pi}}\exp(-r_2) \tag{5.22b}$$

and

$$E_{1_{sc}}^{(0)} = E_{2_{sc}}^{(0)} = -\frac{1}{2}, \tag{5.23}$$

respectively. Consequently, the zeroth-order perturbation equation (4.2), is now expressed as

$$H_{sc}^{(0)}\Psi_{sc}^{(0)} = E_{sc}^{(0)}\Psi_{sc}^{(0)}, \tag{5.24}$$

where

$$\begin{aligned}\Psi_{sc}^{(0)} &= \Psi_{sc}^{(0)}(\mathbf{r}_1)\Psi_{sc}^{(0)}(\mathbf{r}_2)\\ &= \frac{1}{\pi}\exp(-(r_1+r_2))\end{aligned} \tag{5.25a}$$

is the scaled zero-order eigenfunction (expressed earlier as (5.4a))and

$$\begin{aligned}E_{sc}^{(0)} &= E_{1_{sc}}^{(0)} + E_{2_{sc}}^{(0)}\\ &= -1\end{aligned} \tag{5.25b}$$

the corresponding scaled zero-order eigenvalue(expressed earlier as (5.4b)).

Similarly, the first-order perturbation energy (5.18) become

$$\begin{aligned}E_{sc}^{(1)} &= E_{mag_{sc}}^{(1)} + E_{rep_{sc}}^{(1)}\\ &= \frac{1}{8},\end{aligned} \tag{5.26}$$

where

$$E_{mag_{sc}}^{(1)} = -\frac{1}{2} \tag{5.27a}$$

and

$$E_{rep_{sc}}^{(1)} = \frac{5}{8} \tag{5.27b}$$

which were expressed earlier by equations (5.11) and (5.17b), respectively.

Thus the first-order perturbation equation (4.6b) in scaled form is expressed as

$$\left(H_{sc}^{(0)} - E_{sc}^{(0)}\right) \Psi_{sc}^{(1)} + \left(H' - E_{sc}^{(1)}\right) \Psi_{sc}^{(0)} = 0 \tag{5.28}$$

Noting that $H' = H'_{mag} + H'_{rep}$ (3.45c) and $E_{sc}^{(1)} = E_{mag_{sc}}^{(1)} + E_{rep_{sc}}^{(1)}$ (5.26), then the scaled first-order perturbed wave function $\Psi_{sc}^{(1)}$ can be expressed in equivalent form as

$$\Psi_{sc}^{(1)} = \Psi_{mag_{sc}}^{(1)} + \Psi_{rep_{sc}}^{(1)} \tag{5.29}$$

By substituting equations (3.45c), (5.26) and (5.29) into equation (5.28) and then rearrange, a pair of first-order perturbation equations

$$\left(H_{sc}^{(0)} - E_{sc}^{(0)}\right) \Psi_{mag_{sc}}^{(1)} + \left(H'_{mag} - E_{mag_{sc}}^{(1)}\right) \Psi_{sc}^{(0)} = 0 \tag{5.30a}$$

$$\left(H_{sc}^{(0)} - E_{sc}^{(0)}\right) \Psi_{rep_{sc}}^{(1)} + \left(H'_{rep} - E_{rep_{sc}}^{(1)}\right) \Psi_{sc}^{(0)} = 0 \tag{5.30b}$$

for $\Psi_{mag_{sc}}^{(1)}$ and $\Psi_{rep_{sc}}^{(1)}$, respectively, are obtained; similar equations were obtained by Dalgarno and Stewart in 1960 [13].

5.2.1 The first-order perturbed wave function due to magnetic shielding term

The first order perturbation equation (5.30a) can be solved directly for the first-order perturbed wave function due to magnetic shielding term $\Psi_{mag}^{(1)}$ as follows. Substitution of equations (5.20b), (5.25b), (3.46a) and (5.27a) into equation (5.30a) yields

$$\left(-\frac{\nabla_1^2}{2} - \frac{1}{r_1} - \frac{\nabla_2^2}{2} - \frac{1}{r_2}\right) \Psi_{mag_{sc}}^{(1)} + \left(-\frac{1}{4}\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{1}{2}\right) \Psi_{sc}^{(0)} = 0 \tag{5.31a}$$

which can be expressed in alternative form as

$$\begin{aligned}\left(-\frac{\nabla_1^2}{2}-\frac{1}{r_1}\right)\Psi^{(1)}_{mag_{sc}}+\left(-\frac{1}{4r_1}+\frac{1}{4}\right)\Psi^{(0)}_{sc}&\\ +\left(-\frac{\nabla_2^2}{2}-\frac{1}{r_2}\right)\Psi^{(1)}_{mag_{sc}}+\left(-\frac{1}{4r_2}+\frac{1}{4}\right)\Psi^{(0)}_{sc}&=0\end{aligned}\tag{5.31b}$$

In equation (5.31b), the two-electron atoms first order perturbation equation (5.31a) is expressed as a sum of individual one-electron equations. Thus, in general equation (5.31b) may be rewritten as

$$\left(-\frac{\nabla_i^2}{2}-\frac{1}{r_i}\right)\Psi^{(1)}_{mag_{sc}}+\left(-\frac{1}{4r_i}+\frac{1}{4}\right)\Psi^{(0)}_{sc}=0,\qquad i=1,2\tag{5.32a}$$

which becomes

$$\left(-\frac{1}{2}\frac{d^2}{dr_i^2}-\frac{1}{r_i}\frac{d}{dr_i}-\frac{1}{r_i}+\frac{1}{2}\right)\Psi^{(1)}_{mag_{sc}}+\left(-\frac{1}{4r_i}+\frac{1}{4}\right)\Psi^{(0)}_{sc}=0,\qquad i=1,2\tag{5.32b}$$

after applying equation (1.1b). The solution to the ordinary differential equation (5.32b) is of the form [48]

$$\Psi^{(1)}_{mag_{sc}}=g(r_i)\Psi^{(0)}_{sc},\qquad i=1,2,\tag{5.32c}$$

where $g(r_i)$ is an arbitrary first-order radial function dependent only on the electron distance r_i. Hence, substitution of equations (5.25a) and (5.32c) into equation (5.32b), for $i=1$, leads to

$$-\frac{1}{2}\frac{d^2g(r_1)}{dr_1^2}+\frac{dg(r_1)}{dr_1}-\frac{1}{r_1}\frac{dg(r_1)}{dr_1}-\frac{1}{4r_1}+\frac{1}{4}=0\tag{5.33a}$$

which has a simple solution

$$g(r_1)=-\frac{r_1}{4}\tag{5.33b}$$

Similarly, for $i=2$, substitution of equations (5.25a) and (5.32c) into (5.32b) yields

$$g(r_2)=-\frac{r_2}{4}\tag{5.34}$$

is an effective scaled one-electron Hamiltonian and the zero-order perturbation equations for Hamiltonians $H_{1_{sc}}^{(0)}$ and $H_{2_{sc}}^{(0)}$ are

$$H_{1_{sc}}^{(0)}\Psi_{sc}^{(0)}(\mathbf{r}_1) = E_{1_{sc}}^{(0)}\Psi_{sc}^{(0)}(\mathbf{r}_1) \tag{5.39a}$$

and

$$H_{2_{sc}}^{(0)}\Psi_{sc}^{(0)}(\mathbf{r}_2) = E_{2_{sc}}^{(0)}\Psi_{sc}^{(0)}(\mathbf{r}_2), \tag{5.39b}$$

respectively. Hence, substitution of equations (5.25b) and (5.38a) into terms on the left hand side of equation (5.37) and then rearranged, it is found that

$$\int \Psi_{sc}^{(0)}(\mathbf{r}_1)\left(E_{sc}^{(0)} - H_{sc}^{(0)}\right)\Psi_{rep_{sc}}^{(1)} d\tau_1 = \int \Psi_{sc}^{(0)}(\mathbf{r}_1)\left(E_{1sc}^{(0)} - H_{1sc}^{(0)}\right)\Psi_{rep_{sc}}^{(1)} d\tau_1$$
$$+ \int \Psi_{sc}^{(0)}(\mathbf{r}_1)\left(E_{2sc}^{(0)} - H_{2sc}^{(0)}\right)\Psi_{rep_{sc}}^{(1)} d\tau_1 \tag{5.40a}$$

Then, the application of equation (5.39a) to the left hand side of equation (5.40a) and noting that the Hamiltonian $H_{1sc}^{(0)}$ is Hermitian yields

$$\int \Psi_{sc}^{(0)}(\mathbf{r}_1)\left(E_{sc}^{(0)} - H_{sc}^{(0)}\right)\Psi_{rep_{sc}}^{(1)} d\tau_1 = \left(E_{2sc}^{(0)} - H_{2sc}^{(0)}\right)\int \Psi_{sc}^{(0)}(\mathbf{r}_1)\Psi_{rep_{sc}}^{(1)} d\tau_1 \tag{5.40b}$$

Further, the substitution of equations (5.23) and (5.38b) into the left hand side of equation (5.40b) and then applying equation (1.1b) leads to the result

$$\int \Psi_{sc}^{(0)}(\mathbf{r}_1)\left(E^{(0)} - H_{sc}^{(0)}\right)\Psi_{rep_{sc}}^{(1)} d\tau_1$$
$$= \left(\frac{1}{2}\frac{d^2}{dr_2^2} + \frac{1}{r_2}\frac{d}{dr_2} + \frac{1}{r_2} - \frac{1}{2}\right)\int \Psi_{sc}^{(0)}(\mathbf{r}_1)\Psi_{rep_{sc}}^{(1)} d\tau_1 \tag{5.40c}$$

The right hand side of equation (5.37) may be rewritten as

$$\int \Psi_{sc}^{(0)}(\mathbf{r}_1)\left(H'_{rep} - E_{rep_{sc}}^{(1)}\right)\Psi_{sc}^{(0)} d\tau_1$$
$$= \int \Psi_{sc}^{(0)}(\mathbf{r}_1)H'_{rep}\Psi_{sc}^{(0)} d\tau_1 - E_{rep_{sc}}^{(1)}\int \Psi_{sc}^{(0)}(\mathbf{r}_1)\Psi_{sc}^{(0)} d\tau_1 \tag{5.41a}$$

The first term on the left-hand side of equation (5.41a) is evaluated by substituting equations (5.12), (5.22a) and (5.25a) and then integrate over the polar angles (θ_1, ϕ_1) and (θ_2, ϕ_2) taking $l = m = 0$, to get

$$\int \Psi_{sc}^{(0)}(\mathbf{r}_1) H'_{rep} \Psi_{sc}^{(0)} d\tau_1 = 4 \left(\frac{1}{r_2} \int_0^{r_2} r_1^2 \, e^{-2r_1} dr_1 + \int_{r_2}^{\infty} r_1 \, e^{-2r_1} dr_1 \right) \Psi_{sc}^{(0)}(\mathbf{r}_2) \tag{5.41b}$$

which reduces to

$$\int \Psi_{sc}^{(0)}(\mathbf{r}_1) H'_{rep} \Psi_{sc}^{(0)} d\tau_1 = \frac{1}{r_2} \left(1 - (1 + r_2) \, e^{-2r_2}\right) \Psi_{sc}^{(0)}(\mathbf{r}_2) \tag{5.41c}$$

after the application of standard integrals (5.16a) and (5.16b), respectively. The second term on the left-hand side of equation (5.41a) is evaluated by substituting equations (5.25a) and (5.27b) and then integrating over the volume element (5.8a), to obtain

$$-E_{rep_{sc}}^{(1)} \int \Psi_{sc}^{(0)}(\mathbf{r}_1) \Psi_{sc}^{(0)} d\tau_1 = -\frac{5}{8} \Psi_{sc}^{(0)}(\mathbf{r}_2) \tag{5.41d}$$

after the applying of normalization condition

$$\int_0^{\infty} \Psi_{sc}^{(0)}(\mathbf{r}_1) \Psi_{sc}^{(0)}(\mathbf{r}_1) d\tau_1 = 1 \tag{5.41e}$$

Hence, by applying equations (5.41c) and (5.41d), equation (5.41a) reduces to

$$\int \Psi_{sc}^{(0)}(\mathbf{r}_1) \left(H'_{rep} - E_{rep_{sc}}^{(1)}\right) \Psi_{sc}^{(0)} d\tau_1 = \left(\frac{1}{r_2} \left(1 - (1 + r_2) \, e^{-2r_2}\right) - \frac{5}{8} \right) \Psi_{sc}^{(0)}(\mathbf{r}_2) \tag{5.42}$$

which is dependent only on the dynamics of electron 2.

Further, the application of the results in equation (5.40c) and (5.42) to equation (5.37) yields

$$\left(\frac{1}{2}\frac{d^2}{dr_2^2}+\frac{1}{r_2}\frac{d}{dr_2}+\frac{1}{r_2}-\frac{1}{2}\right)\int \Psi_{sc}^{(0)}(\mathbf{r}_1)\Psi_{rep_{sc}}^{(1)}d\tau_1$$

$$=\left(\frac{1}{r_2}\left(1-(1+r_2)\,e^{-2r_2}\right)-\frac{5}{8}\right)\Psi_{sc}^{(0)}(\mathbf{r}_2) \qquad (5.43a)$$

which may be rewritten as

$$\left(\frac{1}{2}\frac{d^2}{dr_2^2}+\frac{1}{r_2}\frac{d}{dr_2}+\frac{1}{r_2}-\frac{1}{2}\right)\Phi_{rep_{sc}}^{(0)}(\mathbf{r}_2)$$

$$=\left(\frac{1}{r_2}\left(1-(1+r_2)\,e^{-2r_2}\right)-\frac{5}{8}\right)\Psi_{sc}^{(0)}(\mathbf{r}_2) \qquad (5.43b)$$

Since the variables of electron 1 have been integrating out in equation (5.43b), then

$$\Phi_{rep_{sc}}^{(0)}(\mathbf{r}_2)=\int \Psi_{sc}^{(0)}(\mathbf{r}_1)\Psi_{rep_{sc}}^{(1)}d\tau_1 \qquad (5.43c)$$

is the contribution of electron 2 to the first order wave function $\Psi_{rep_{sc}}^{(1)}$. It is noted that equation (5.43b) is dependent only on the radial variables of electron 2 and can be solved independently for $\Phi_{rep_{sc}}^{(0)}(\mathbf{r}_2)$. Hence, the solution for $\Phi_{rep_{sc}}^{(0)}(\mathbf{r}_2)$ of the form [48]

$$\Phi_{rep_{sc}}^{(0)}(\mathbf{r}_2)=f(r_2)\Psi_{sc}^{(0)}(\mathbf{r}_2) \qquad (5.44)$$

where $f(r_2)$ is an arbitrary function dependent only on the electron distance r_2, will be considered.

Further, the substitution of equations (5.22b) and (5.44) into equation (5.43b) leads to a second order differential equation

$$\frac{1}{2}\frac{d^2f(r_2)}{dr_2^2}+\left(\frac{1}{r_2}-1\right)\frac{df(r_2)}{dr_2}=\frac{1}{r_2}\left(1-(1+r_2)\,e^{-2r_2}\right)-\frac{5}{8} \qquad (5.45)$$

which may be solved using the following command in Mathematica

$$Dsolve[\frac{1}{2}f''[r_2] + (\frac{1}{r_2} - 1)f'[r_2] == \frac{1}{r_2}(1 - (1 + r_2)Exp[-2r_2]) - \frac{5}{8},$$
$$f[0] == 0,\ f'[0] == 0,\ f\ , r] \tag{5.46}$$

to obtain

$$f(r_2) = -\frac{3.07944}{8} - \frac{1}{4}\exp(-2r_2) - \frac{3}{8}\log(r_2) - \frac{3}{8}\,EulerGamma$$
$$+\frac{3}{16r_2}(1 - \exp(-2r_2)) + \frac{5}{8}r_2 + \frac{3}{8}\,expIntegralE_i(-2r_2) \tag{5.47}$$

The boundary conditions $f[0] = 0$ and $f'[0] = 0$ satisfied by equation (5.46) ensures that the wave function $\Phi^{(0)}_{rep_{sc}}(\mathbf{r}_2)$ and its derivative $d\Phi^{(0)}_{rep_{sc}}(\mathbf{r}_2)/dr_2$ are finite and continuous at $r = 0$ [2]. Our results for $f(r_2)$ (5.47) takes similar form as the first-order Hartree factor $f_{HF}(r)$ for helium sequence [49, 50] and the function $ZF(r)$ obtained by Hall *et al* [51] in a similar calculation to determine the ground-state electron density function for helium.

Similarly, by multiplying equation (5.36) from the left by $\Psi^{(0)}_{sc}(\mathbf{r}_2)$ and integrate over the volume element (5.8b) for electron 2 (i.e., integrating out the variables of electron 2), then following steps in equations (5.40a)-(5.46), it is found that

$$\Phi^{(0)}_{rep_{sc}}(\mathbf{r}_1) = f(r_1)\Psi^{(0)}_{sc}(\mathbf{r}_1), \tag{5.48}$$

where

$$f(r_1) = -\frac{3.07944}{8} - \frac{1}{4}\exp(-2r_1) - \frac{3}{8}\log(r_1) - \frac{3}{8}\,EulerGamma$$
$$+\frac{3}{16r_1}(1 - \exp(-2r_1)) + \frac{5}{8}r_1 + \frac{3}{8}\,expIntegralE_i(-2r_1) \tag{5.49}$$

is an arbitrary function dependent only on the electron distance r_1.

The two functions $\Phi^{(0)}_{rep_{sc}}(\mathbf{r}_2)$ and $\Phi^{(0)}_{rep_{sc}}(\mathbf{r}_1)$ obtained in equations (5.44) and (5.48), respectively, represent the contribution of the two electrons to the first-order wave function $\Psi^{(1)}_{rep_{sc}}$, then by linear combination of atomic orbital method [9, 10], $\Psi^{(1)}_{rep_{sc}}$ is expressed in the form

$$\begin{aligned}\Psi^{(1)}_{rep_{sc}} &= \Phi^{(0)}_{rep_{sc}}(\mathbf{r}_1)\Psi^{(0)}(\mathbf{r}_2) + \Phi^{(0)}_{rep_{sc}}(\mathbf{r}_2)\Psi^{(0)}(\mathbf{r}_1) \\ &= \left(f(r_1) + f(r_2)\right)\Psi^{(0)}_{sc} \qquad (5.50)\end{aligned}$$

Using the results in equations (5.35) and (5.50) in equation (5.29), the first-order perturbed wave function in the form become

$$\begin{aligned}\Psi^{(1)}_{sc} &= \Psi^{(1)}_{mag_{sc}} + \Psi^{(1)}_{rep_{sc}} \\ &= \left(-\frac{1}{4}(r_1 + r_2) + f(r_1) + f(r_2\right)\Psi^{(0)}_{sc} \qquad (5.51)\end{aligned}$$

In has already been shown that equation (5.51) is the analytically determined first-order perturbed wave function [25].

5.3 Second-order perturbation energy

The second-order perturbation energy (4.9) may be rewritten in scaled form as

$$E^{(2)}_{sc} = \langle\Psi^{(0)}_{sc}|H' - E^{(1)}_{sc}|\Psi^{(1)}_{sc}\rangle \qquad (5.52)$$

By substituting equations (3.45*c*) and (5.26) into equation (5.52) and then rearranged, it is found that

$$E^{(2)}_{sc} = E^{(2)}_{mag_{sc}} + E^{(2)}_{rep_{sc}} \qquad (5.53a)$$

where

$$E^{(2)}_{mag_{sc}} = \langle\Psi^{(0)}_{sc}|\left(H'_{mag} - E^{(1)}_{mag_{sc}}\right)|\Psi^{(1)}_{sc}\rangle \qquad (5.53b)$$

and

$$E^{(2)}_{rep_{sc}} = \langle\Psi^{(0)}_{sc}|\left(H'_{rep} - E^{(1)}_{rep_{sc}}\right)|\Psi^{(1)}_{sc}\rangle \qquad (5.53c)$$

are components of the second-order perturbation energy due to the magnetic shielding term and the Coulomb interaction term, respectively.

5.3.1 Second-order perturbation energy due to magnetic shielding term

Substitution of equation (5.51) into equation (5.53*b*) yields

$$E^{(2)}_{mag_{sc}} = \langle\Psi^{(0)}_{sc}|\left(H'_{mag} - E^{(1)}_{mag_{sc}}\right)|\Psi^{(1)}_{mag_{sc}} + \Psi^{(1)}_{rep_{sc}}\rangle \tag{5.54a}$$

which, on expansion, become

$$E^{(2)}_{mag_{sc}} = \epsilon^{(2)}_1 + \epsilon^{(2)}_2 \tag{5.54b}$$

where

$$\epsilon^{(2)}_1 = \langle\Psi^{(0)}_{sc}|H'_{mag} - E^{(1)}_{mag_{sc}}|\Psi^{(1)}_{mag_{sc}}\rangle \tag{5.55a}$$

and

$$\epsilon^{(2)}_2 = \langle\Psi^{(0)}_{sc}|H'_{mag} - E^{(1)}_{mag_{sc}}|\Psi^{(1)}_{rep_{sc}}\rangle \tag{5.55b}$$

are second-order perturbation energy components that will be solved individually.

5.3.1.1 The second-order perturbation energy component $\epsilon^{(2)}_1$

By substitution of equations (3.46*a*), (5.27*a*) and (5.35) into equation (5.55*a*), it is found that

$$\epsilon^{(2)}_1 = -\frac{1}{4}\int\int \Psi^{(0)}_{sc}\left(-\frac{1}{4}\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{1}{2}\right)(r_1 + r_2)\,\Psi^{(0)}_{sc}d\tau_1 d\tau_2 \tag{5.56a}$$

Further, substitution of equations (5.8*a*), (5.8*b*) and (5.25*a*) into equation (5.56*a*) and integrating over the polar angles (θ_1, ϕ_1) and (θ_2, ϕ_2), yields

$$\begin{aligned}\epsilon^{(2)}_1 = {} & 2\int_0^\infty r_1^2 e^{-2r_1}dr_1 \int_0^\infty r_2^2 e^{-2r_2}dr_2 + \int_0^\infty r_1 e^{-2r_1}dr_1 \int_0^\infty r_2^3 e^{-2r_2}dr_2 \\ & + \int_0^\infty r_1^3 e^{-2r_1}dr_1 \int_0^\infty r_2 e^{-2r_2}dr_2 - 2\int_0^\infty r_1^3 e^{-2r_1}dr_1 \int_0^\infty r_2^2 e^{-2r_2}dr_2 \\ & -2\int_0^\infty r_1^2 e^{-2r_1}dr_1 \int_o^\infty r_2^3 e^{-2r_2}dr_2\end{aligned} \tag{5.56b}$$

which reduces to

$$\epsilon_1^{(2)} = -0.0625\, a.u. \tag{5.57}$$

after the application of standard integral (5.10).

5.3.1.2 The second-order perturbation energy component $\epsilon_2^{(2)}$

By substituting equations (3.46*a*), (5.27*a*) and (5.50) into equation (5.55*b*) yields

$$\epsilon_2^{(2)} = -\frac{1}{4}\int\int \Psi_{sc}^{(0)} \left(\frac{1}{r_1}+\frac{1}{r_2}\right)(f(r_1)+f(r_2))\,\Psi_{sc}^{(0)} d\tau_1 d\tau_2$$
$$+\frac{1}{2}\int\int \Psi_{sc}^{(0)}\,(f(r_1)+f(r_2))\,\Psi_{sc}^{(0)} d\tau_1 d\tau_2 \tag{5.58a}$$

Further, the substitution of equations (5.8*a*), (5.8*b*) and (5.25*a*) into equation (5.58*a*) and integrating over the polar angles (θ_1, ϕ_1) and (θ_2, ϕ_2) leads to

$$\epsilon_2^{(2)} = -4\int_0^\infty r_1^2 dr_1 \int_0^\infty r_2^2 dr_2 \left(\frac{1}{r_1}+\frac{1}{r_2})\,(f(r_1)+f(r_2))\right) e^{-2(r_1+r_2)}$$
$$+8\int_o^\infty r_1^2 dr_1 \int_o^\infty r_2^2 dr_2\,(f(r_1)+f(r_2))\, e^{-2(r_1+r_2)} \tag{5.58b}$$

which reduces to

$$\epsilon_2^{(2)} = 0.078125\, a.u. \tag{5.59}$$

after the application of equations (5.47) and (5.49) and solving of the resulting integral equations using NIntegrate command in mathematica.

5.3.2 Second-order perturbation energy due to Coulomb interaction term

Substitution of equations (5.51) into equation (5.53*c*) leads to

$$E_{rep_{sc}}^{(2)} = \langle \Psi_{sc}^{(0)}|\left(H'_{rep} - E_{rep_{sc}}^{(1)}\right)|\Psi_{mag_{sc}}^{(1)} + \Psi_{rep_{sc}}^{(1)}\rangle \tag{5.60a}$$

which, on expansion, becomes

$$E^{(2)}_{rep_{sc}} = \epsilon^{(2)}_3 + \epsilon^{(2)}_4 \tag{5.60b}$$

where

$$\epsilon^{(2)}_3 = \langle \Psi^{(0)}_{sc} | H'_{rep} - E^{(1)}_{rep_{sc}}) | \Psi^{(1)}_{mag_{sc}} \rangle \tag{5.61a}$$

and

$$\epsilon^{(2)}_4 = \langle \Psi^{(0)}_{sc} | H'_{rep} - E^{(1)}_{rep_{sc}}) | \Psi^{(1)}_{rep_{sc}} \rangle \tag{5.61b}$$

are second-order perturbation energy components that will be solved individually.

5.3.2.1 The second-order perturbation energy component $\epsilon^{(2)}_3$

By substituting of equations (3.46*b*), (5.27*b*) and (5.35) in equation (5.61*a*), yields

$$\epsilon^{(2)}_3 = -\frac{1}{4}\int\int \Psi^{(0)}_{sc}\left(\frac{1}{r_{12}} - \frac{5}{8}\right)(r_1 + r_2)\Psi^{(0)}_{sc} d\tau_1 d\tau_2 \tag{5.62a}$$

Further, the substitution of equations (5.8*a*), (5.8*b*), (5.12) and (5.25*a*) into (5.62*a*) and then follow steps in equations (5.13)-(5.15) leads to

$$\begin{aligned}
\epsilon^{(2)}_3 = & -4\int_0^\infty r_1^3 dr_1 \left[\int_0^{r_1} \frac{r_2^2 dr_2}{r_1} + \int_{r_1}^\infty r_2 dr_2\right] e^{-2(r_1+r_2)} \\
& -4\int_0^\infty r_1^2 dr_1 \left[\int_0^{r_1} \frac{r_2^3 dr_2}{r_1} + \int_{r_1}^\infty r_2^2 dr_2\right] e^{-2(r_1+r_2)} \\
& +\frac{5}{2}\int_0^\infty r_1^3 e^{-2r_1} dr_1 \int_0^\infty r_2^2 e^{-2r_2} dr_2 \\
& +\frac{5}{2}\int_0^\infty r_1^2 e^{-2r_1} dr_1 \int_0^\infty r_2^3 e^{-2r_2} dr_2
\end{aligned} \tag{5.62b}$$

which becomes

$$\epsilon^{(2)}_3 = 0.078125\, a.u. \tag{5.63}$$

after application of the standard integrals (5.10), (5.16*a*) and (5.16*b*).

5.3.2.2 The second-order perturbation energy component $\epsilon_4^{(2)}$

By substituting equations (3.46b), (5.27b) and (5.50) into (5.61b), yields

$$\epsilon_4^{(2)} = \int\int \Psi_{sc}^{(0)} \frac{1}{r_{12}} \left(f(r_1) + f(r_2)\right) \Psi_{sc}^{(0)} d\tau_1 d\tau_2$$

$$-\frac{5}{8}\int\int \Psi_{sc}^{(0)} \left(f(r_1) + f(r_2)\right) \Psi_{sc}^{(0)} d\tau_1 d\tau_2 \qquad (5.64a)$$

Further, the substitution of equations (5.8a), (5.8b), (5.12) and (5.25a) in equation (5.64a) and then steps in equations (5.13)-(5.15) are followed to evaluate the resulting equation, to obtain

$$\epsilon_4^{(2)} = 16\int_0^\infty r_1^2 dr_1 \left(\frac{1}{r_1}\int_0^{r_1} r_2^2 dr_2 + \int_{r_1}^\infty r_2 dr_2\right) \left(f(r_1) + f(r_2)\right) e^{-2(r_1+r_2)}$$

$$-10\int_o^\infty r_1^2 dr_1 \int_o^\infty r_2^2 dr_2 \left(f(r_1) + f(r_2)\right) e^{-2(r_1+r_2)} \qquad (5.64b)$$

Thus, by substituting equations (5.47) and (5.49) into equation (5.64b) and the resulting integral equations solved using NIntegrate command in mathematica, it is found that

$$\epsilon_4^{(2)} = -0.111003\, a.u. \qquad (5.65)$$

The second-order perturbation energy component (5.65) is equivalent to the second-order perturbation energy obtained under the Hartree-Fock approximation [49, 52, 53], i.e.

$$E_{H.F.}^{(2)} = -\frac{1}{16}\left(9\log\frac{3}{4} - \frac{26}{27}\right)$$

$$= -0.111003 \quad a.u. \qquad (5.66)$$

Substitution of equations (5.54b) and (5.60b) in equation (5.53a) and then apply the results in equations (5.57), (5.59), (5.63) and (5.65), the second-*order perturbation energy* within our model is obtained to be

$$E_{sc}^{(2)} = \epsilon_1^{(2)} + \epsilon_2^{(2)} + \epsilon_3^{(2)} + \epsilon_4^{(2)}$$

$$= -0.017253 \ \ a.u. \tag{5.67}$$

By using results for zero-order energy (5.25*b*), first-order perturbation energy (5.26) and second-order perturbation energy (5.67) in equation (5.21), the ground state energy to second-order perturbation within our model is found to be

$$E = E_{cal}$$

$$= -\zeta^2 + \frac{1}{8}\zeta - 0.017253 \tag{5.68a}$$

which reduces to

$$E_{cal} = -Z^2 + \frac{5Z}{8} - 0.111003 \tag{5.68b}$$

after substituting for ζ (3.31*b*). This results agree exactly with the expression for ground state energy to second-order perturbation obtained in a perturbation scheme based explicitly on the the Hartree-Fock approximation [52, 53]. The terms in equation (5.68*b*) are identified as the zero-order energy ($-Z^2$), first-order perturbation energy ($5Z/8$) and second-order perturbation energy $E^{(2)} = -0.111003\, a.u.$ in the hydrogenic approximation [1, 5, 49, 52]. Therefore, the ground state energy to second-order perturbation of two-electron atom is independent of the nuclear charge screening constant in the unperturbed Hamiltonian with a central coulomb potential. A similar result was obtained in [54] using variational-perturbation method.

The calculated values of the ground state energy to first order perturbation (5.68*b*) compared with the ones obtained in a perturbation scheme based explicitly on the the Hartree-Fock approximation [52, 53] and the many parameter variational method [26], respectively, are presented in Tables 5.2.

Table 5.2. The ground state energies to second-order perturbation E_{cal} for $Z = 1 - 10$, are compared E_{HF} and exact energy $E^{(exa)}$. $\Delta_{corr} = E^{exa} - E_{(cal)}$.

Atom	Z	E_{cal}	E_{HF}	$E^{(exa)}$	Δ_{corr}
H^-	1	-0.4860	-0.4879	-0.5278	-0.0418
He	2	-2.8610	-2.8617	-2.9037	-0.0427
Li^+	3	-7.2360	-7.2364	-7.2799	-0.0439
Be^{2+}	4	-13.6110	-13.6113	-13.6556	-0.0446
B^{3+}	5	-21.9860	-21.9862	-22.0310	-0.0450
C^{4+}	6	-32.3610	-32.3612	-32.4062	-0.0452
N^{5+}	7	-44.7360	-44.7362	-44.7814	-0.0454
O^{6+}	8	-59.1110	-59.1111	-59.1444	-0.0334
F^{7+}	9	-75.4860	-75.4861	-75.5317	-0.0457
Ne^{8+}	10	-93.8610	-93.8611	-93.9068	-0.0458

It is noted that the calculated ground state energies E_{cal} have close agrement to those obtained in the Hartree-Fock model E_{HF}. However, the calculation for the ground state energy E_{cal} differ slightly with the exact energy $E^{(exa)}$, due to the absence of the contributions of the correlation energy Δ_{corr} (sum of radial and angular correlation energy) which has an average value $\Delta_{corr} =$ 0.0431 $a.u.$.

5.4 The expectation values of other physical quantities and their first-order approximations

The first-order approximation to the expectation values of radial quantities associated with the magnetic shielding constant, diamagnetic susceptibility and radial correlation are evaluated. The expectation values provide a means of testing the validity of the method adopted in calculating the first-order perturbed wave function and second-order perturbation energy in sections 5.2 and 5.3, respectively.

5.4.1 The magnetic shielding constant

The magnetic shielding constant is defined by the operator

$$L = \frac{1}{r_1} + \frac{1}{r_2} \tag{5.69}$$

By substituting equation (5.69) into equation (4.21), the zero-order expectation values is obtained as

$$L^{(0)} = \int\int \Psi^{(0)} \left(\frac{1}{r_1} + \frac{1}{r_2} \right) \Psi^{(0)} d\tau_1 d\tau_2 \tag{5.70a}$$

Substitution of equations (5.4*a*), (5.8*a*) and (5.8*b*) in equation (5.70*a*) and integrating over the polar angles (θ_1, ϕ_1) and (θ_2, ϕ_2) leads to

$$\begin{aligned} L^{(0)} &= 16\zeta^6 \int_0^\infty r_1 dr_1 \int_0^\infty r_2^2 dr_2 e^{-2\zeta(r_1+r_2)} \\ &\quad + 16\zeta^6 \int_0^\infty r_1^2 dr_1 \int_0^\infty r_2 dr_2 e^{-2\zeta(r_1+r_2)} \end{aligned} \tag{5.70b}$$

which reduces to

$$\begin{aligned} L^{(0)} &= 2\zeta \\ &= 2(Z - 1/4) \end{aligned} \tag{5.71}$$

after applying the standard integral (5.10). For helium $Z = 2$, equation (5.71) yields a value of $3.5000\,a.u.$, which differs by $-0.123\,a.u.$ from the exact expectation value $3.377\,a.u.$ obtained by Pekeris using Hylleraas-type trial wave function [26].

Hence, the problem is to evaluate the first-order approximation (4.24) to the expectation value of operator (5.69). When equations (3.45*b*), (5.4*b*), (5.69) and (5.71) are substituted into equation (4.25) and the resulting expression evaluated using steps similar to those in equations (5.31a)-(5.35), the first-order perturbed wave function associated with the operator L (5.69), may be expressed in the form

$$\chi^{(1)} = (r_1 + r_2)\Psi^{(0)} \tag{5.72}$$

Hence, by substituting equations (3.45c), (5.4a), (5.18), (5.71) and (5.72) into equation (4.26) and the resulting expression evaluated using steps similar to those in equations (5.56a)-(5.57), the first-order corrections is obtained as

$$L^{(1)} = -\frac{1}{8} \tag{5.73}$$

Using results in equations (5.71) and (5.73), the first-order approximation to the expectation value of magnetic shielding operator (5.69) becomes

$$\begin{aligned}\langle L\rangle &= L^{(0)} + L^{(1)}\\ &= 2\zeta - \frac{1}{8}\\ &= 2\left(Z - \frac{5}{16}\right)\end{aligned} \tag{5.74}$$

after substituting for ζ (3.31b). Our final results in equation (5.74) is identical to that of Dalgarno and Stewart obtained by analytical solution of equation (4.26) using arbitrary first-order trial wave function [13]. The expectation value of the magnetic shielding operator (5.74) to first order approximation for nuclear charge $Z = 1 - 3$ are compared with the exact expectation values [26] in Table 5.3. In Table 5.3, it is noted that the expectation values to first order approximation of the magnetic shielding operator are in close agreement with the exact expectation values. This agreement is certainly due to the fact that the quantity $1/r_i$ is quite sensitive to the behavior of the wave function close to the nucleus, the correct behavior of $\Psi^{(0)}$ and $\chi^{(1)}$ represented by equations (5.4a) and (5.72), respectively, in these region is reflected in the satisfactory values found in Table 5.3.

Table 5.3 The expectation value of the magnetic shielding operator of the two-electron atoms for nuclear charge $Z = 1 - 3$

Atom	Z	$\left\langle \frac{1}{r_1} + \frac{1}{r_2} \right\rangle$	Exact
H^-	1	1.3750	1.3766
He	2	3.3750	3.3766
Li^+	3	5.3750	5.3758

5.4.2 The diamagnetic susceptibility

The diamagnetic susceptibility is proportional to the expectation value of [11, 13]

$$L = r_1^2 + r_2^2 \tag{5.75}$$

By substituting equation (5.75) into equation (4.21), the zero-order expectation values become

$$L^{(0)} = \int\int \Psi^{(0)} \left(r_1^2 + r_2^2\right) \Psi^{(0)} d\tau_1 d\tau_2 \tag{5.76a}$$

Further, the substitution of equations (5.4a), (5.8a) and (5.8b) into equation (5.76a) and integrating the resulting equation over the polar angles (θ_1, ϕ_1) and (θ_2, ϕ_2), it is found that

$$\begin{aligned} L^{(0)} = {} & 16\zeta^6 \int_0^\infty r_1^4 dr_1 \int_0^\infty r_2^2 dr_2 e^{-2\zeta(r_1+r_2)} \\ & +16\zeta^6 \int_0^\infty r_1^2 dr_1 \int_0^\infty r_2^4 dr_2 e^{-2\zeta(r_1+r_2)} \end{aligned} \tag{5.76b}$$

Thus, application of the standard integral (5.10) in equation (5.76b) leads to

$$
\begin{aligned}
L^{(0)} &= \frac{6}{\zeta^2} \\
&= \frac{6}{(Z-1/4)^2}
\end{aligned}
\tag{5.77}
$$

For helium $Z = 2$, equation (5.77) yields a value of $1.9592\,a.u.$ which differs by $0.4308\,a.u.$ from the exact expectation value $2.3900\,a.u.$ obtained using Hylleraas-type trial wave function [26].

The first-order approximation (4.24) to the expectation value of operator (5.75) is evaluated, by first, substituting equations (3.45*b*), (5.4*b*), (5.75) and (5.77) into equation (4.25) and evaluating the resulting expression using steps similar to those equations (5.31*a*)-(5.35), to obtain the first-order perturbed wave function, expressed in the form

$$
\chi^{(1)} = -\left(\frac{3r_1^2 + \zeta r_1^3}{3\zeta^3} + \frac{3r_2^2 + \zeta r_2^3}{3\zeta^3}\right)\Psi^{(0)}
\tag{5.78}
$$

Then, the substitution of equations (3.45*c*), (5.4*a*), (5.18), (5.77) and (5.78) in equation (4.26) and evaluating the resulting expression using steps similar to those in equations (5.56*a*)-(5.57), the first-order corrections is obtained as

$$
L^{(1)} = \frac{57}{32\zeta^3}
\tag{5.79}
$$

Using results in equations (5.77) and (5.79), the first-order approximation to the expectation value associated to the diamagnetic susceptibility operator (5.75) becomes

$$
\begin{aligned}
\langle L \rangle &= L^{(0)} + L^{(1)} \\
&= \frac{6}{\zeta^2} + \frac{57}{32\zeta^3} \\
&= \frac{6(3+64Z)}{(-1+4Z)^3}
\end{aligned}
\tag{5.80}
$$

after substituting for ζ (3.31b). The final results in equation (5.80) is identical to those obtained in [13] by analytical solution of equation (4.25) using arbitrary first-order trial wave functions. The expectation value of the diamagnetic susceptibility operator to first-order approximation (5.80) for nuclear charge $Z = 1 - 3$ are compared with the exact expectation values obtained by Pekeris [26] in Table 5.4.

Table 5.4 The expectation value of the diamagnetic susceptibility operator of the two-electron atoms for nuclear charge $Z = 1 - 3$.

Atom	Z	$\langle r_1^2 + r_2^2 \rangle$	Exact
H^-	1	14.8889	23.8274
He	2	2.2915	2.3850
Li^+	3	0.8790	0.89256

In the view of the simplicity of the wave functions $\Psi^{(0)}$ (5.4a) and $\chi^{(1)}$ (5.78) used, the first-order approximation to the expectation value of the diamagnetic susceptibility operator in Table 5.4 are in close agreement with the 'exact' expectation value, except possibly for H^-. This is because the quantity r_i^2 is quite sensitive to the behavior of the wave function at large distances away from the nucleus; thus, $\Psi^{(0)}$ (5.4a) and $\chi^{(1)}$ (5.78) does not have the correct asymptotic behavior in this region for H^-.

5.4.3 The electron correlation

The electron correlation effects is defined by the operator

$$L = \frac{1}{r_{12}}, \tag{5.81}$$

i.e., the repulsive coulomb interaction term (3.46b). The zero-order expectation value is given in equation (5.17c) as

$$\begin{aligned} L^{(0)} &= \frac{5\zeta}{8} \\ &= \frac{5}{8}\left(Z - \frac{1}{4}\right) \end{aligned} \tag{5.82}$$

For helium $Z = 2$, equation (5.82) yields a value of $1.09375\,a.u.$ which differs by $0.14795\,a.u.$ from the exact expectation value $0.9458\,a.u.$ obtained by Pekeris using Hylleraas-type trial wave function [26].

Therefore, the problem is to evaluate the first-order approximation (4.24) to the expectation value of operator (5.81). It is noted that the first-order perturbation equation (4.25) and the first-order correction equation (4.25*b*) corresponding of the operator (5.81) are similar to equations (5.30*b*) and (5.53*c*) which were evaluated in sections 5.2.2 and 5.3.2, respectively. Hence, the first-order perturbed wave function corresponding to the operator (5.81) is given by equation (5.50) while the first-order correction is [25]

$$\begin{aligned} L^{(1)} &= 2E_{rep_{sc}} \\ &= 2(\epsilon_3^{(2)} + \epsilon_4^{(2)}) \\ &= -0.065756\,a.u. \end{aligned} \tag{5.83}$$

after substituting for $\epsilon_3^{(2)}$ and $\epsilon_4^{(2)}$ given in equations (5.63) and (5.65), respectively. Using results in equations (5.82) and (5.83), the first-order approximation to the expectation value associated to the electron correlation operator (5.81) becomes

$$\begin{aligned} \langle L \rangle &= L^{(0)} + L^{(1)} \\ &= \frac{5\zeta}{8} - 0.065756 \end{aligned} \tag{5.84a}$$

which reduces to

$$\langle L \rangle = \frac{5Z}{8} - 0.222006 \tag{5.84b}$$

after substituting for ζ (3.31b). The terms in equation (5.84b) are identified as the first-order perturbation energy ($5Z/8$) and two times the second-order perturbation energy ($2E^{(2)} = -0.222006\,a.u.$) in the hydrogenic approximation [1, 5, 49, 52]. The expectation value of the electron correction operator to first-order approximation (5.84b) for nuclear charge $Z = 1 - 3$ are compared with the exact expectation values [26] in Table 5.5.

Table 5.5 The expectation value of the electron correlation operator of the two-electron atoms for nuclear charge $Z = 1 - 3$.

Atom	Z	$\langle 1/r_{12} \rangle$	Exact
H^-	1	0.40299	0.31102
He	2	1.02799	0.94582
Li^+	3	1.65299	1.56772

It is noted in Table 5.5 that, given the simplicity of the wave functions $\Psi^{(0)}$ (5.4a) and $\chi^{(1)}$ (5.81) used, the calculated expectation value $\langle 1/r_{12} \rangle$ are quite satisfactory. The disparity between the calculated value and the exact expectation value arises because in the calculation for $\langle 1/r_{12} \rangle$ (5.84b), only the term $l = 0$ is considered in the expansion of Coulomb interaction term (5.12c). However, for each term in the expansion (5.12c) the expectation value $\langle 1/r_{12} \rangle$ (5.84b) must also have the angular structure given by $P_l(\cos\vartheta)$ for the terms $l = 1, 2, \ldots$ [9, 11].

Chapter 6

6 Conclusion and recommendations for future work

6.1 Conclusion

In this thesis, an alternative model of the quantum theory of the two-electron atoms that formulated the direct role of the repulsive Coulomb interaction in nuclear charge screening has been developed. The Hamiltonian (3.47) governing the general dynamics of the system is composed of a component describing the stable state of the system under the *anti-parallel* orbit orientation (3.45b) and the other describing the binding energies treated as perturbation (3.45c). The Hamiltonian (3.45b) for the two-electron atoms under the *anti-parallel* orbit orientation is the sum of independent one-electron atom modes in a central field in which the two electrons maintain minimal repulsive Coulomb interaction energy. The two electrons then behave independently but maintain a finite distance between them due to the minimal repulsive interaction energy captured through the minimum screened nuclear charge $\zeta = Z - 1/4$ (3.31b) in contrast with the independent electron model where each electron moves in the fully unscreened field of the nucleus. The ground state configuration occurs in this mode, i.e., $h = 1$, with both electrons occupying opposite points on the K-shell which is a circular orbital with radius r. In the general mode $h < 1$, the nuclear charge screening depends on the relative distances r_1, r_2 and the orientation angle ϑ. This mode of the repulsive interaction is treated as perturbations. The perturbing Hamiltonian H' (3.45c) is the sum of the binding energy associated with the repulsive coulomb interaction H'_{rep} (3.46a) and the magnetic shielding energy H'_{mag} (3.46b). The ground state energy under the *anti-parallel* orbit orientation and to first-order perturbation presented in Table 3.1 and Table 5.1 respectively, are far much better than those obtained in the standard independent particle approximation. The remarkable improvement in the theoretical values of ground state is attributed to the minimal repulsive interaction energy maintained between the electrons under the *anti-parallel* orbit orientations.

In this thesis, a simple model for the direct calculation of the first-order perturbed wave function and second-order perturbation energy for the two-electron atoms has also been developed. The scaling transformation of the co-ordinate $r \longrightarrow r/\zeta$ on the Hamiltonian (3.47) is applied to obtained the scaled Hamiltonian (5.20a) and then the Rayleigh-Schrödinger $1/\zeta$ perturbation expansion is followed. The resulting first-order perturbed wave function (5.51) is the sum of the components due to the magnetic shielding energy $\Psi^{(1)}_{mag_{sc}}$ (5.35) and Coulomb interaction energy $\Psi^{(1)}_{rep_{sc}}$ (5.50); this analytically determined first-order perturbed wave function (5.51) is appearing in the literature for the first time. The first-order perturbed wave function (5.51) is applied to determine analytically the second-order perturbation energy (5.67). The ground state energy to second-order perturbation E_{cal} (5.68b) for two-electron atoms given in Table 5.2 were found to have close agreement with those from the Hartree-fock model E_{HF} using arbitrary first-order wave functions. However, the ground state energy E_{cal} differ slightly with the exact energy $E^{(exa)}$ due to the absence of the correlation energy Δ_{corr}. It has also been noted that the total energy to second-order perturbation in the model is independent of the nuclear charge screening parameter.

The model applied in the calculation of first-order perturbed wave function and second-order perturbation energy was extended to calculate the first-order approximation of the expectation values of radial quantities associated with magnetic shielding constant, diamagnetic susceptibility and electron correlation. It was noted in Table 5.3, Table 5.4 and Table 5.5 that given the simplicity of the wave functions used, the calculated expectation values were quite satisfactory, except possibly for Hydrogen ion H^- in Table 5.4.

6.2 Recommendations for future work

In Table 5.2, it was noted that the disparity between E_{cal} and the exact energy was due to the absence of the correlation energy Δ_{corr}. In research literature, for example [26, 33, 34, 35, 36], the correlation energy is incorporated by choice of a two-electron atom wave function which depends explicitly on the electronic radial distances r_1 and r_2 and the interelectronic separation r_{12}. One can also study the correlation effect by working with a two-electron atoms wave function expressed in terms of the interaction between different configurations, i.e., configuration interaction method [10, 31, 32]. Admittedly, these wave functions predict accurate results for energy eigenvalues. But most of them do not lead to analytic expression for Hamiltonian and other related quantities.

In the thesis, the wave functions $\Psi^{(0)}$ $(5.4a)$ does not depend on the interelectronic separation r_{12}, hence, it does not include the correlation effects. Therefore, I recommend that further work should be addressed toward formulating simple analytic model of the quantum theory of the two-electron atoms that incorporates the correlation effects in the unperturbed Hamiltonian. For example, in some work under investigation, the energy transfer equations has been applied to define, in S.I units, the total energy function governing the dynamics of the two-electron atoms by

$$H = \mathcal{H}^{(0)} + \int_{t_0}^{t} (\mathbf{F}_1 \cdot \dot{\mathbf{r}}_2 + \mathbf{F}_2 \cdot \dot{\mathbf{r}}_1) dt', \tag{6.1}$$

where $\mathbf{F}_1$ and $\mathbf{F}_2$ denote the attractive Coulomb forces exerted by the nucleus on electron-1 and electron-2, respectively, and $\mathcal{H}^{(0)}$ the unperturbed Hamiltonian expressed in component form as

$$\mathcal{H}^{(0)} = \mathcal{H}_1^{(0)} + \mathcal{H}_1^{(0)} + \mathcal{H}_{12}^{(0)} \tag{6.2}$$

The components $\mathcal{H}_1^{(0)}$ and $\mathcal{H}_2^{(0)}$ are individual one-electron unperturbed Hamiltonians expressed as

$$\mathcal{H}_i^{(0)} = \frac{\mathbf{p}_i^2}{2m} - \frac{2Ze^2}{4\pi\epsilon_0 r_i}, \qquad i = 1, 2 \tag{6.3}$$

and the component $H_{12}^{(0)}$ the two-electron unperturbed Hamiltonian expressed as

$$\mathcal{H}_{12}^{(0)} = \frac{\mathbf{p}_{12}}{2m} + \frac{3Ze^2}{4\pi\epsilon_0 r_{12}} \tag{6.4}$$

where

$$\mathbf{p}_{12} = \frac{\mathbf{p}_1 - \mathbf{p}_2}{2m} \tag{6.5}$$

is the kinetic energy due to the relative motion of the two electrons.

The task under investigation is to solve analytically the Schrödinger equation

$$\mathcal{H}^{(0)} \Psi^{(0)}(r_1, r_2, r_{12}) = E^{(0)} \Psi^{(0)}(r_1, r_2, r_{12}) \tag{6.6}$$

for the unperturbed Hamiltonian $\mathcal{H}^{(0)}$ (6.2). It is suggested that the correlated wave function $\Psi^{(0)}(r_1, r_2, r_{12})$ be expressed in the form

$$\Psi^{(0)}(r_1, r_2, r_{12}) = \Psi^{(0)}(r_1)\Psi^{(0)}(r_2)\Psi^{(0)}(r_{12}) \tag{6.7}$$

where $\Psi^{(0)}(r_{12})$ incorporates the correlation effects into the wave function.

References

[1] Beth, H. A. and Salpeter E. E., *Quantum Mechanics of One and Two-Electron Atoms, Second ed.*, Dover Publications Inc., New York, Pg. 118-154, (2008)

[2] Saxena, A. K., *Textbook of Quantum Mechanics, First ed.*, CBS Publishers and distributors, New Delhi, Bangalore (India), Pg. 533-670, (2007)

[3] Ghoshal, S. N., *Atomic Physics, Seventh ed.*, S. Chand and company ltd., Ram Nagar, New Delhi (India), Pg. 334-420, (2006)

[4] Levine, I. N., *Quantum Chemistry , Fifth ed.*, Pearson Education Limited, England, Pg. 208-277, (2006)

[5] Brannsden, B. H. and Joahain C. J., *Physics of Atoms and Molecules, Second ed.*, Pearson Education Limited, England, Pg. 307-421, (2003)

[6] Atkins, P. W., *Molecular Quantum Mechanics, Second ed.*, Oxford university press, Oxford, Pg. 171-241, (1994)

[7] Harun ar Rashid A. M., *Quantum Mechanics, Second ed.* University of Dhaka, City Press, Dhaka, Pg. 528-562, (1988)

[8] Eyring, H., Walter, J. and Kimball, G. E., *Quantum Chemistry, First ed.*, John Wiley and Sons, New York, Pg. 92-107, (1944)

[9] Drake, W. F. (Ed.), *Springer Handbook of Atomic, Molecular and Optical Physics, First ed.*, Springer Science and Business Media Inc., New York, Pg. 199-219, 313-316, (1944)

[10] Friedrich, H.,, *Theoretical Atomic Physics, Third ed.*, Springer-Verlag, Berlin Heidelberg, Pg. 54-57, (2006)

[11] Stewart, A. L., *The properties of the helium atom and two-electron systems*, Advances in Physics, **12:47**, 299-353, (1963)

[12] Dalgarno, A. and Stewart, A. L., *A perturbation calculation of properties of helium iso-electronic sequence*, Proc. Roy. Soc.(London), Series A: Math. and Phy. Sc., Vol. **247**, No. **1249**, 245, (1958)

[13] Dalgarno, A. and Stewart, A. L., *The screening approximation for the helium sequence*, Proc. Roy. Soc.(London), Series A: Math. and Phy. Sc., Vol. **257**, No. **1291**, 534, (1960)

[14] Hirschfelder, J. O., Brown, B. W. and Epstein S. T., *Recent developments in Perturbation Theory*, Advances in Quantum Chemistry, Academic press, New York, 255-368, (1965)

[15] Ramaker, D. E., Hagnauer, G. L., Carlson, R. E., Gaetano, R. F., Grain, H. and Schrader, D. M., *Helium States II. Perturbation Treatment of the Ground State Using the Coordinates* $r_<$ *and* $r_>$, Int. J. Quant. Chem., **II**, 509, (1968)

[16] Hylleraas, E. A., *A new calculation of the energy of Helium in the Ground state as well as the lowest term in the ortho Helium*, Z. Physik., **54**, 347, (1929)

[17] Hylleraas, E. A., *On the Ground state term of two-electron problem for* H^-, He, Li^+, Be^{++}, *ETC*, Z. Physik., **65**, 209, (1930)

[18] Dalgarno, A. and Stewart, A. L., *A perturbation-variation calculation of Eigevalues*, Proc. Roy. Soc.(London), Series A: Math. and Phy. Sc., Vol. **257**, No. **1291**, 467, (1960)

[19] Hylleraas, E. A. and Midtal J., *Ground-State Energy of Two-Electron Atoms*, Phys. Rev., **103**, 829, (1958)

[20] Schwartz, C., *Ground state of the Helium atom*, Phys. Rev., **128**, 1146, (1962)

[21] Knight, R. E. and Scherr, C. W., *Two-Electron Atoms. I. Perturbation Study of the Ground State*, Phys. Rev., **128**, 2675, (1962)

[22] Knight, R. E. and Scherr, C. W., *Two-Electron Atoms. III. A Sixth-Order Perturbation Study of* $1\grave{s}$ *of the Ground State*, Phys. Rev., **35**, 436, (1963)

[23] Midtdal, John., *Perturbation-theory expansion through 21st order of nonrelativistic energies of two-electron systems* $(2p)^{2,3}P$ *and* $(1s)^{2,1}S^{\star}$, Phys. Rev., A**138**, 1010, (1965)

[24] Omollo, J. A. and Ndinya, B. O., *Repulsive Coulomb interaction and nuclear charge screening in helium and helium-like ions*, Indian. J. Theor. phys., Vol. **58**, No. **2**, 81, (2010)

[25] Ndinya, B. O. and Omollo, J. A., *A direct calculation of first-order wave function of Helium*, Commun. Theor. Phys. (Beijing, China), Vol. **54**, No. **4**, 647, (2010)

[26] Pekeris, C. L., *Ground State of Two-Electron Atoms*, Phys. Rev., **111**, 1649, (1958)

[27] Wang Zhi-Wen and Guan Xiao-Xu, *Variational Calculations of the Energy for Helium-like Ground State from Z* = 2 *to 5*, J. Chin.Chem. Soc., **48** , 515, (2001)

[28] Drake, G. W. F., Cessar, M. M. and Nistor, R. A., *Ground-state energies for Helium, H^-, and Ps^-*, Phys. Rev., A **65** , 054501, (2002)

[29] Korobov, I. V., *Nonrelativistic ionization energy for the helium ground state*, Phys. Rev., A**66**, 024501, (2002)

[30] Cowan, R. D., *The theory of atomic structure and spectra*, University of California Press, Ltd., England, Pg. 358-390, (1981)

[31] Joachain, C. J. and Vanderpoorten, R., *Configuration interaction wave functions for two-electron systems*, Physica., **46**, 333, (1970)

[32] Somerville, W. B. and Stewart, A. L., *The correlation energies of the Helium sequence*, Proc. Phys. Soc.(London), Vol. **80**, 97, (1962)

[33] Myers, C. R., Umrigar, C. J., Sethna, J. P. and Morgan III, J. D., *Fock's expansion, Kato's cusp conditions, and exponential ansatz*, Phys. Rev., A**44**, 5537, (1991)

[34] Patil, S. H., *Wave functions for two- and three-electron atoms and isoelectronic ions*, Eur. Phys. J., D**6**, 171, (1999)

[35] Patil, S. H., *Electron correlation in He and isoelectronic ions*, Eur. J. Phys, **25**, 91, (2004)

[36] Ancarani, L. U., Rodriguez, K. V. and Gasaneo, G., *A simple parameter-free wavefunction for the ground state of two-electron atoms*, J. Phys. B: Atom. Molec. Phys.,**40**, 2695, (2007)

[37] Auzinnsh, M. and Damburg, R., *A simple formula for ground state energy of a two-electron atom*, arXiv:quant-ph/990501**v1**, (1999)

[38] Sakho, I., Ndao, A. S., Biaye, M. and Wague, A., *Calculation of the ground-state energy, the first ionization energy and the radial correlatio expectation value for He-like atoms*, Phys. Scr., **74**, 180, (2006)

[39] Sakho, I., Ndao, A. S., Biaye, M. and Wague, A., *Screening constant by unit nuclear charge calculations for* $(ns^2)^1S^e$*,* $(np^2)^1D^e$ *and* $(Nsnp)^1P^0$ *excited states of He-like systems*, Eur. Phys. J. D, **47**, 37, (2008)

[40] Sakho, I., Konte, A., Ndao, A. S., Biaye, M. and Wague, A., *Investigation of* $2snp^{\pm 1,3}P^o$ *resonances of two-electron systems using the screening constant by unit nuclear charge method*, Phys. Scr., **77**, 055303, (2008)

[41] Arfken, G. B. and Weber, H. J., *Mathematical methods for physicits, Fifth ed.*, Academic Press, San Diego, Pg. 739-742, (2001)

[42] Harcourt, R. D.,*Bohr orbit theory revisited: I. Ground-state energies for helium isoelectronic sequence*, J. Phys. B: Atom. Molec. Phys.,**16**, 2647, (1983)

[43] Bagchi, B. and Holody, P., *An interesting application of Bohr theory*, Am. J. Phys., **56**, 746, (1988)

[44] Blumel, R. and Reinhardt, W. P., *Chaos in Atomic Physics* (Cambridge University Press, 1997) ; in *Quantum Chaos*, eds. G. Casati and B.V. Chirikov (Cambridge University Press, 1995)

[45] Slater, J. R., *The structure of helium atom. I*, Phys. Rev., **13**, 423, (1927)

[46] Read, H. F., *A modified Rydberg formula*, J. Phys. B: Atom. Molec. Phys., Vol.**10**, 449, (1977)