UNIVERSITY OF GAZİANTEP
GRADUATE SCHOOL OF
NATURAL & APPLIED SCIENCES

A SEARCH ON HELIUM-LIKE ATOMS

M. Sc. THESIS
IN
ENGINEERING PHYSICS

BY
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JULY 2010

A SEARCH ON HELIUM-LIKE ATOMS

M.Sc. Thesis
in
Engineering Physics
University of Gaziantep

Supervisor
Prof. Dr. Bülent GÖNÜL

by
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JULY 2010

T.C.
UNIVERSITY OF GAZİANTEP
GRADUATE SCHOOL OF
NATURAL & APPLIED SCIENCES
Engineering Physics

Name of the thesis　　　: A Search on Helium-like Atoms
Name of the student　　: Mustafa ÇAPAK
Exam date　　　　　　: 27/07/2010

Approval of the Graduate School of Natural and Applied Sciences

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This is to certify that we have read this thesis and that in our opinion it is fully adequate, in scope and quality, as a thesis for the degree of Master of Science.

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ABSTRACT

A SEARCH ON HELIUM-LIKE ATOMS

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July 2010, 45 pages

In this thesis work, we scrutinize the relation between the correlation and screening effect of the electrons in He and He-like atoms. Within this context and using the basic ingredient of two-body problem, we propose accurate algebraic solutions in a closed form for the ground and excited states of such quantum systems. These simple but explicit expressions involve the exact screening parameters for each atom considered and provide an insight into their physical structure. The energy eigenvalues have been exactly calculated for atoms with nuclear charge Z in the range $1 \leq Z \leq 12$.

Keywords: He and He-like atoms; Screening in two-electron atoms

ÖZET

HELYUM BENZERİ ATOMLAR ÜZERİNE BİR ARAŞTIRMA

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Yüksek Lisans Tezi, Fizik Mühendisliği Bölümü
Tez Danışmanı: Prof. Dr. Bülent GÖNÜL
Temmuz 2010, 45 sayfa

Bu tez çalışmasında, Helyum ve Helyum benzeri atomlarda bulunan iki elektron arasında gerçekleşen etkileşim potansiyeli ile çekirdek ve elektronlar arasında etkileşim anında çekirdek yükünün yakın elektron tarafınca perdelenme olayı arasındaki ilişki dikkatlice incelenmiştir. Bu çerçevede ve iki-cisim etkileşim probleminin temel unsuru kullanılarak, söz konusu atomların temel ve uyarılmış kuantum seviyeleri için tam çözümler içeren analitik ifadeler tarafımızca önerilmektedir. Önerilen bu basit fakat açık fiziksel ifadeler, ele alınan her bir sistem için perdeleme parametresini tam olarak içermekte ve sistemlerin fiziksel yapısına ışık tutmaktadır. Teklif edilen teorik model ışığında, çekirdek yükü $1 \leq Z \leq 12$ aralığında olan tüm iki-elektronlu atomlar için enerji özdeğerleri kesin olarak hesaplanmıştır.

Anahtar Kelimeler: He ve Helyum benzeri atomlar, iki elektron arasında perdeleme olayı

ACKNOWLEDGEMENTS

First of all, I thank my wife, Serpil, for listening and supporting me during the prepration of my thesis work presented here.

I also deeply thank my advisor, Prof. Dr. Bülent GÖNÜL due to his valuable help, advice and supervision during my works. This thesis would indeed not have been possible without his support. His encouragement and suggestions caused to construct this thesis properly.

I dedicate this thesis to my father who died in 2008.

CONTENTS

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CHAPTER 1

INTRODUCTION

Since the early days of quantum mechanics, helium and helium-like atoms have been a subject of intensive study. Particularly, the ground state wave function and the corresponding energy of such atoms have been considered by many authors during the last decades. There are in fact many reasons for these kind of investigations. For instance, in the collision processes the initial state of target atom plays an important role where the state can be determined by a convenient form of the related ground state wavefunction. Generally, the search for simpler accurate wavefunction results in insight and a deeper understanding of such physical processes. The well known variational method is one of the important approachs in the investigation of similar topics, where the main problem is to define, in a closed and appropriate form, the correlated electron system in such atoms by the choice of a simple trial wave function.

For the ground state of a two-electron atom one chooses in general a product of the identical hydrogenic orbitals, one being a function of r_1 and the other of r_2, or which is a linear combination of antisymmetrized products of one-electron orbitals [1,2]. Alternatively, a Hylleraas (1929) type correlated function depending explicitly on the interelectronic separation can also be chosen [3]. These latter type of functions, as clearly demonsrated by the pioneering work of Hylleraas , generally yield a rapidly convergent result for the variational energy. In any case, the accuracy in the calculation is usually improved by introducing progressively a higher and higher number of variational parameters into the trial function. It is worth mentioning here that some of such significant calculations in the literature are the one performed by Chandrasekhar and Herzberg [4], by Hart and Herzberg [5], by Hylleraas and Midtdal [6,7], by Pekeris [8,9], by Roothan *et al* [2], by Weiss [1], by Schwartz [10], by Frankowski and Pekeris [11,12] and by Thakkar and Smith [13].In 1984

Freund *et al* [14] also dealt with the non-relativistic ground state energy of the helium isoelectronic sequence in their calculations within the range of $(1 \le Z \le 10)$ employing a 230 term trial function, and reported the energies accurate to within one part in 10^{13} based on the variatioanl procedure, which has far exceeded the limits of accuracy in any experimental measurement. Also noteworthy are the recent calculations due to Kleindienst and Emrich in 1990 [15] and de Saavedra and Buendia in 1994 [16].

Although one achieves the desired accuracy in energy eigenvalue by introducing a large number of variational parameters in the trial function, however one quickly loses the physical meaning of these parameters, and also is required to do a lot of cumbersome calculations in the theoretical study of the atomic properties using such functions. Hence, there is a need to obtain a simple, yet meaningful, wavefunction by choosing a smaller number of parameters. Several such attempts have already been reported in the literature. Some them are the calculations by Green *et al* [17], the one performed by Byron and Joachain in 1966 [18], Banyard and Seddon in 1973 [19], Srivastava and Bhaduri in 1977 [20], by Wu in 1982 [21], the one by Abbott and Maslen in 1986 [22], together with Siebbeles and Le Sech in 1994 [23], Le Sech in 1997 [24] and by Patil in 1984 [25] and in 2003 [26].

In a completely distinct framework, in 1995 Tripathy *et al* [27] suggested an alternative but simple two-parameter wavefunction for the ground state by introducing variational parameters in the Hamiltonian rather than in the trial wavefunction. The binding energies obtained in this work are in a reasonable agrrement with very accurate multiparameter results reported by earlier workers.

In the calculations regarding with helium-like atoms, the most important parameter is the one due to the screening of nucleus by the inner electron. Physically, the nuclear charge is screened and this effect produces a change in the wavefunctions corresponding to the interaction of the individual electrons with the nucleus. Because of this, one of the chapters of this thesis will focus on the physics behind this phenomenon and clarifies the interconnection between the screening and correlation within the frame of such atoms under consideration.

Overall, it should also be emphasised that a true, physically meaningful, wave function must satisfy a set of "cusp conditions" [28] and should agree with the Fock

expansion $[29]$. Eigenfunctions of Hamiltonians for atomic and moleculer systems exhibit singular behavior at those points in configuration space where two or more charged particles come together and the resulting potential becomes infinite. At two-particle coalescences, derivatives of the wavefunction with respect to cartesian coordinates have a discontinuity characterized by the famous Kato cusp condition. There are also singularities involving more than two particles, such as the triple-collision singularity in the helium atom, when two electron simultaneously approach the nucleus. A formal expansion in powers of the hyperradius r and its logarithm $\ln r$ about this singular point was proposed by Fock for helium atom S-state wave functions. These significant consraints will be discussed in detail by the second chapter of the this thesis work which summarizes theoretical background on the problem of interest.

Additinally, supersymmetric quantum mechanics (SUSY QM) $[30]$ has been found to give encouraging results towards understanding atomic systems in the literature recently. Therefore, the present work is also studied within the powerful framework of SUSYQM, which is presented in Chapter 3.

Furthermore, the applications of a novel treatment to the ground and excited states of the two-electron atoms is discussed in Chapter 3. We have analysed carefully the results obtained with the consideration of those calculated by numerical techniques. It is seen that the results obtained is remarkable. Finally, the concluding remarks and an outlook are given in Chapter 4.

CHAPTER 2

THEORETICAL BACKGROUND

2.1. The Variational Method

An exact solution of the Schrödinger equation is possible only for one electron system. In larger systems, approximate methods have to be used. The variational method is one of the main approximate methods used in quantum mechanics for solving atomical or molecular structures. The variational method is used in physics both for theory construction and for calculational purposes.

Using the method, we find an approximate wavefunction and corresponding energy eigenvalue for the system. The basic idea of the variational method is to guess a ``trial'' wavefunction for the problem, which consists of some adjustable parameters called "variational parameters." These parameters are adjusted until the energy of the trial wavefunction is minimized. The resulting trial wavefunction and its corresponding energy are variational method approximations to the exact wavefunction and energy.

Why would it make sense that the best approximate trial wavefunction is the one with the lowest energy? This results from the variational theorem, which states that the energy of any trial wavefunction E is always an upper bound to the exact ground state energy ε_0. This can be proven easily. Let the trial wavefunction be denoted Φ. Any trial function can formally be expanded as a linear combination of the exact eigenfunctions Ψ_i. Of course, in practice, we don't know the Ψ_i, since we're assuming that we're applying the variational method to a problem we can't solve analytically. Nevertheless, this doesn't prevent us from using the exact eigenfunctions in our proof since they certainly exist and form a complete set, even if we don't happen to know them. So, the trial wavefunction can be written as

$$\Phi = \sum C_i \Psi_i \quad , \qquad\qquad (2.1.1)$$

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and the approximate energy corresponding to this wavefunction is

$$E[\Phi] = \frac{\int \Phi^* \hat{H} \Phi}{\int \Phi^* \Phi} \quad .$$

(2.1.2)

Substituting the expansion over the exact wavefuntions, we obtain

$$E[\Phi] = \frac{\sum_{ij} C_i^* C_j \int \Psi_i^* \hat{H} \Psi_j}{\sum_{ij} C_i^* C_j \int \Psi_i^* \Psi_j}$$

(2.1.3)

Since the functions Ψ_I are the exact eigenfunctions of $\hat{H}$, we can use $\hat{H}\Psi_j = \varepsilon_j \Psi_j$ to obtain

$$E[\Phi] = \frac{\sum_{ij} C_i^* C_j \varepsilon_i \int \Psi_i^* \Psi_j}{\sum_{ij} C_i^* C_j \int \Psi_i^* \Psi_j}$$

(2.1.4)

Now using the fact that eigenfunctions of a Hermitian operator form an orthonormal set (or can be made to do so),

$$E[\Phi] = \frac{\sum_{ij} C_i^* C_j \varepsilon_i}{\sum_{ij} C_i^* C_j}$$

(2.1.5)

We now subtract the exact ground state energy ε_0 from both sides to obtain

$$E[\Phi] - \varepsilon_0 = \frac{\sum_{ij} C_i^* C_j (\varepsilon_i - \varepsilon_0)}{\sum_{ij} C_i^* C_j}$$

(2.1.6)

Since every term on the right-hand side is greater than or equal to zero, the left-hand side must also be greater than or equal to zero, or

$$E[\Phi] \geq \varepsilon_0$$

(2.1.7)

This explains the strategy of the variational method: The energy of any approximate wavefunction is always greater than or equal to the exact ground state energy ε_0. We may therefore select, perhaps by guessing, any approximate trial wave function that includes parameter that may be varied to minimize $E[\Phi]$. We leave these parameter in the trial wave function and evaluate $E[\Phi]$ in terms of them. We then minimize $E[\Phi]$ with respect to the parameter:

$$\frac{\partial E[\Phi]}{\partial \alpha} = 0 \quad . \tag{2.1.8}$$

Where α is variational parameter of the trial wave function. This is variational principle! According to this principle, the result will always be greater than the true energy. We see then that we may choose a complicated function, containing as many parameters as we please, and, if computer time is available, we can obtain an answer to any degree of precision. For our purposes, however, we use parameters that provide physical insight and for which the variational principle can be implemented analytically.

2.2. Some Local Properties of the Eigenfunctions

2.2.1. Asymptotic Behavior of the Wave Functions

The energy eigenfunctions of the two-electron atom and ions satisfy the Schrödinger equation

$$H\Psi(\hat{r}_1, \hat{r}_2) = E\Psi(\hat{r}_1, \hat{r}_2)$$

$$H = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - (Z/r_1) - (Z - r_2) + (1/r_{12}) \tag{2.2.1}$$

Z being the charge of the nucleus. The asymptotic behavior of the wave function when electron 1 is far away, is given [31,32,33] by

$$\Psi(\vec{r}_1, \vec{r}_2) \rightarrow \eta_1(r_1)\Phi_0(r_2) \quad \text{for} \quad r_1 \rightarrow \infty, \tag{2.2.2}$$

$$\eta_1(r_1) = C_0(r_1^{u_1} + b_1 r_1^{u_1 - 1})e^{a_1 r_1} Y_l^m(\theta_1, \phi_1),$$

$$a_1 = (2E_1)^{1/2}, \quad u_1 = (Z - 1)/a_1 - 1$$
$$b_1 = (l - u_1)(l + u_1 + 1)/(2a_1)$$

with E_1 being the ionization energy of the atom or ion, l is the angular momentum quantum number of electron 1 when it is far away, and $\Phi_0(r_2)$ is the lowest-energy eigenfunction of the remaining electron. One has $l = 0$ for $(1s)(ns)$ states, $l = 1$ for $(1s)(np)$ states, and

$$\Phi_0(r_2) = e^{Zr_2}, \quad E_1 = -E - Z^2/2 \tag{2.2.3}$$

for $(1s)(nl)$ states, E being the total energy.

2.2.2. Behavior of the Wave Functions for $r_i \to 0$

When electron 1 approaches the nucleus, the Schrödinger equation reduces to

$$-\frac{1}{2}\nabla_1^2\Psi - (Z/r_1)\Psi = O(\Psi), \quad r_1 \to 0, \tag{2.2.4}$$

where $O(\Psi)$ is of finite order for $r_1 \to 0$. Keeping other variables fixed, Ψ is expanded in terms of spherical harmonics to get

$$\Psi = \sum_{l,m} G_{l,m}(r_1)Y_l^m(\theta_1,\phi_1), \tag{2.2.5}$$

$$\frac{d^2}{dr_1^2}\left[r_1 G_{l,m}(r_1)\right] - \frac{l(l+1)}{r_1}G_{l,m}(r_1) + 2ZG_{l,m}(r_1) = O(r_1^{l+1}) \quad \text{for} \quad r_1 \to 0 \tag{2.2.6}$$

By substituting

$$G_{l,m}(r_1) = r_1^l(c_0 + c_1 r_1 + ...) \tag{2.2.7}$$

into Eq. (2.2.6), and equating the coefficients of the two leading power terms, it is obtained that

$$c_1 = -Zc_0/(l+1), \; c_1 = -Zc_0 \quad \text{for} \, l = 0 \tag{2.2.8}$$

This relation [28] may be described as the coalescence condition.

2.2.3. Behavior of the Wave Functions for $r_{12} \to 0$

When the electrons are close to each other, one goes to the center-of-mass frame of the two electrons whose reduced mass is 1/2, so that

$$-\nabla_{12}^2\Psi + (1/r_{12})\Psi = O(\Psi), \quad r_{12} \to 0 \tag{2.2.9}$$

Ψ is expanded in terms of spherical harmonics, following similar steps [33] to obtain

$$G_{l,m}(r_{12}) = r_{12}^l(d_0 + d_1 r_{12} + ...), \quad d_1 = d_0/[2(l+1)] \tag{2.2.10}$$

The two electrons have even l in the singlet state and odd l in the triplet state. Therefore the leading behavior for $r_{12} \to 0$ is

$$\Psi \to d_0(1 + r_{12}/2) \quad \text{(singlet)}$$

$$\Psi \to d_0 r_{12}(1 + r_{12}/4)Y_l^m(\theta_{12}, \phi_{12}) \quad \text{(triplet)} \tag{2.2.11}$$

which may be described as cusp condition.

2.3. Kato's Cusp Conditions and Fock's Expansion

2.3.1. Kato's Cusp Conditions

Two-particle cusps arise because the Coulomb interaction between charged particles diverges as they approach each other. In other words, the eigenfunctions of $\hat{H}$ contain singularities at the points of configuration space where two charged particles collide, which results in an infinite Coulomb potential. Because of this fact, it is necessary that a compensating divergence in the kinetic energy occurs in such a way that the total energy remains finite; this divergence is manifested as a cusp in the electronic wave function at zero interparticle separation.

The true wave function must satisfy a set of "cusp conditions" which prescribe the proper derivative discontinuity at the collision points. Kato[28] first rigorously derived these conditions as a general property of Coulombic systems, arriving at the conclusion that in the limit that two particles of masses m_i and m_j and charges q_i and q_j approach each other and all other interparticle distances remain larger than zero,

$$\left. \frac{\partial \hat{\Psi}}{r_{ij}} \right|_{r_{ij}=0} = \mu_{ij} q_i q_j \Psi \, (r_{ij} = 0) \,, \tag{2.3.1}$$

where $\mu_{ij} = m_i m_j/(m_i + m_j)$ is the reduced mass of the two-particle subsystem and $\hat{\Psi}$ is the average of Ψ over an infinitesimally small sphere centered at $r_{ij} = 0$. Pack and Byers-Brown $[34]$ generalized Kato's result by solving the multiparticle Scrödinger equation in the neighborhood of a two-particle coalescence.

Finally, we arrive at a set of cusp conditions for a singlet S state of a two-electron atom, which are valid without the need for spherically averaging. One condition describes the collision of one electron and the nucleus, and the other, the collision of two (opposite-spin) electrons.

$$\left.\frac{\partial \hat{\Psi}}{\partial r_i}\right|_{r_i=0} = -Z\Psi(r_i = 0), \quad \text{electron and nucleus} \qquad (2.3.2)$$

$$\left.\frac{\partial \hat{\Psi}}{\partial r_{ij}}\right|_{r_{ij}=0} = -\frac{1}{2}\Psi(r_{ij} = 0), \text{ electron}(\uparrow) \text{ and electron}(\downarrow) \qquad (2.3.3)$$

2.3.2. Fock's Expansion

Fock [29] showed that a formal solution for the helium wave function could be obtained in terms of hyperspherical coordinates and that this would take the form of a power series in $R = (r_1^2 + r_2^2)^{1/2}$ and $\ln R$, multiplied by functions of the hyperspherical angles, α and θ_{12}. The lowest-order terms of Fock's expansion for the ground state wave function are,

$$\Psi = 1 - Z(r_1 + r_2) + \frac{1}{2}r_{12} - Z\frac{\pi - 2}{3\pi}r_1 r_2 \cos\theta_{12} \ln R \qquad (2.3.4)$$

The second and third terms handle two-body collisions while the fourth term is related to the three-body collision. The term second-order in R in the Fock expansion is also known, and Myers, *et al.*[35] have verified that this term eliminates the discontinuity in the local energy at the origin. The article also contains an analysis of the behavior of the wave function in the vicinity of these singular points.

2.4. Earlier Studies

2.4.1. Accurate Analytic Wavefunctions for Two-electron Atoms

(C. Le Sech, J. Phys. B.: At. Mol. Opt. Phys. (1997) L47-L50)

If one wants to show an example involving the variational method, the works carried out by Le Sech are appropriate for this purpose. In one of his papers, Le Sech proposed a simple analytic two variational parameters wavefunctions for the ground state of $H^-, He, Li^+, Be^{2+}, B^{3+}$ atom (ions). These functions fulfil the cusp conditions at the singularities of the Coulombic field, and include the correct behaviour for large interparticle separations. The accuracy of the calculated energies is found to be about 10^{-3} au.

The Schrödinger equation for a two-electron atomic system with nuclear charge, Z, is written in atomic units, within the nonrelativistic approximation and with obvious notations as:

$$\left(-\frac{1}{2}\vec{\nabla}_6^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} \right)\Psi = E\Psi \tag{2.4.1}$$

where $\vec{\nabla}_6^2 = \vec{\nabla}_1^2 + \vec{\nabla}_2^2$; the indices 1,2 and 6 stand for the three coordinates of electrons 1 and 2 and all the (six) coordinates of the Laplacian, respectively. The wavefunction, Ψ , will be written as a product of two functions: $\Psi = \Phi\Omega$. The basic idea is to include in the Φ function the orbital motion of the free electrons in the field of the nucleus, and to include the inter-electronic correlation depending explicitly upon the inter-electronic distance r_{12} into Ω. In this respect the present approach has some similarity with the so-called correlated quantum Monte Carlo theory, see for example the work of Schmidt and Moscowitz $[36]$, and we think that the functional $E[\Psi]$ given below, which is general and very convenient, could also be useful in this field. Siebbeles *et al* $[23]$ have shown that for any function, $\Psi = \Phi\Omega$, written as a product, the calculation of the energy, E, reduces to the computation of a single multidimensional quadrature, i.e.

$$E[\Psi] = E_0 + \int \Phi^2 \left[\frac{\vec{\nabla}_6\Omega \bullet \vec{\nabla}_6\Omega}{2} + \frac{\Omega^2}{r_{12}} \right] d\tau_6 \tag{2.4.2}$$

where $\vec{\nabla}_6^2 = \vec{\nabla}_1^2 + \vec{\nabla}_2^2$ is the gradient and $\vec{\nabla}_6\Omega \bullet \vec{\nabla}_6\Omega$ is the dot product. To derive this expression of the energy, we assume that the function, $\Phi(r_1, r_2)$ is the solution of the independent particle problem:

$$\left(-\frac{1}{2}\vec{\nabla}_6^2 - \frac{Z}{r_1} - \frac{Z}{r_2}\right)\Phi(r_1, r_2) = E_0\Phi(r_1, r_2) \tag{2.4.3}$$

For S states, the quadrature Eq.(2.4.2) reduces to a three-dimensional one, easily performed on any small desk computer. Full computation takes less than 1s. For the ground state Φ is taken as (with the usual notation for the spin functions $\alpha(i), \beta(j), Z$ is the true nuclear charge and N is the normalization constant):

$$\Phi(r_1, r_2) = Ne^{-Zr_1}e^{-Zr_2}[\alpha(1)\beta(2) - \alpha(2)\beta(1)] \tag{2.4.4}$$

Now we determine the function $\Omega(r_1, r_2, r_{12})$, which describes the correlation of the electrons due to their Coulomb repulsion. It is presently chosen as:

$$\Omega(r_1, r_2, r_{12}) = [\cosh(\lambda r_1) + \cosh(\lambda r_2)][1 + 0.5r_{12}e^{(-ar_{12})}] \tag{2.4.5}$$

where λ and a are variational parameters. The reason for using the cosh function is to fulfil the cusp conditions at the nucleus and the right behaviour at large electron–nucleus distances. It is easy to see that λ can be interpreted as a screening constant when r_1 or $r_2 \gg 1$ au i.e.:

$$\lim r_1 \gg 1: \quad \Psi \to e^{-Zr_1}e^{-Zr_2}e^{\lambda r_1} = e^{-(Z-\lambda)r_1}e^{-Zr_2}$$

and when

$$\lim r_1 \text{ and } r_2 \ll 1: \quad \Psi \to 1 - Zr_1 - Zr_2 + 0.5r_{12} + O(r_1^2, r_2^2, r_{12}^2)$$

The last expression is in agreement with the first terms in the Fock expansion. Let us point out here that the common way to take into account the screening by exponential functions in the usual open-shell approximation, is not suitable for the electron–nucleus cusp conditions. The exponential function depends linearly upon $r_1; r_2$ when $r_1, r_2 \ll 1$, and it is not able to correctly reproduce the cusp condition at the nucleus

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$$\lim r_1 \to 0 \qquad \left\langle \frac{\partial \Psi}{\partial r_1} \right\rangle = -Z \qquad \text{and} \qquad \lim r_2 \to 0 \qquad \left\langle \frac{\partial \Psi}{\partial r_2} \right\rangle = -Z$$

This is the reason we have chosen the *cosh* function. The r_{12} part of the function was already suggested by Hirschfelder in 1963 [37], and we found this choice is quite efficient in many problems. This function ensures the right description of the electron-electron cusps conditions (Kato's theorem) [28].

In the Table 2.1 the results for the different atomic sysrems are presented. The wavefunction is writen explicitly below, omitting the obvious spin factor:

$$\Psi = N e^{-Zr_1} e^{-Zr_2} \left[\cosh(\lambda r_1) + \cosh(\lambda r_2) \right] \left[1 + 0.5 r_{12} e^{(-ar_{12})} \right] \qquad (2.4.6)$$

Table 2.1. Ground state energies of $H^-, He, Li^+, Be^{2+}, B^{3+}$ calculated using the wavefunction given in equation (2.4.6) and corresponding optimized values of the parameters λ and a

Atom ^1S	λ values	a values	Energy for this method (au)	Accurate energy (au)	Two-parameters results(Tripathy et al 1995) [27]
H^-	0.52	0.00	-0.5252	-0.5277	-0.5052
He	0.7	0.17	-2.9020	-2.9037	-2.8840
Li^+	0.84	0.36	-7.2781	-7.2799	-7.2599
Be^{2+}	0.9	0.45	-13.6535	-13.6555	-13.6352
B^{3+}	1.1	0.65	-22.0286	-22.0309	-22.0104

Columns two and three of Table 2.1 report optimized values of the variational parameters, λ and a, of the systems $H^-, He, Li^+, Be^{2+}, B^{3+}$ and the corresponding calculated energies. In all cases the agreement between experimental and accurate values is better than 2×10^{-3} au. In the last column of Table 2.1, the values calculated with a two-parameter wavefunction by Tripathy et al in 1995 [27] is reported, in order to illustrate the improvement in this work. In spite of the simplicity of the present wavefunction using only two parameters, the accuracy is outstanding.

A further improvement can be obtained easily if the term $b(r_1 - r_2)^2$ with b as a third parameter is added to cosh part of the function. It could be added in the r_{12} factor, leading to the same accuracy. The expression of $\vec{\nabla}_6 \Omega \bullet \vec{\nabla}_6 \Omega$ is a little bit simpler if we choose the cosh part. Then the function now becomes:

$$\Psi = Ne^{-Zr_1}e^{-Zr_2}\left[\cosh(\lambda r_1) + \cosh(\lambda r_2) + b(r_1 - r_2)\right]\left[1 + 0.5r_{12}e^{(-ar_{12})}\right] \quad (2.4.7)$$

Table 2.2. Ground state energies of $H^-, He, Li^+, Be^{2+}, B^{3+}$ calculated using the wavefunction given in equation (2.4.7) and corresponding optimized values of the parameters λ, a and b

Atom ^1S	λ values	a values	b values	Energy for this method (au)	Accurate energy (au)	Three-parameters results(Wu 1982)[21]
H^-	0.54	0.04	0.04	-0.5266	-0.5277	-0.5213
He	0.68	0.17	0.06	-2.9026	-2.9037	-2.8994
Li^+	0.82	0.34	0.08	-7.2788	-7.2799	-7.2757
Be^{2+}	0.9	0.45	0.09	-13.6541	-13.655	-13.6513
B^{3+}	1.0	0.6	0.15	-22.0290	-22.0309	

In Table 2.2 the optimized values of the parameters λ, a and b is given. In all cases the energy values are lower. The agreement between the calculated energy values and accurate value is about 10^{-3} au. The improvement in the case of the H^- ion is particularly significant giving a very good accuracy for the energy of this ion. In the last column of Table 2.2, the best values calculated with a three-parameter wavefunction [21] are recalled, in order to show the improvement achieved by the present wavefunctions.

It has been there shown that accurate values for the energies within 2×10^{-3} au can be obtained using a quite simple two-parameter wavefunction. If necessary, a significant improvement can be obtained adding a third term as shown above. It is known that the description of inelastic processes involving two electrons necessitates the accurate description of the correlation in the initial state of the target.

2.4.2. Two-parameter Wavefunction For The Ground State Of Helium-like Atoms (D N Tripathy, B Padhy and D K Rai, J. Physc. B: At. Mol. Opt. Phys. 28(1995) L41-L46)

Tripathy et al. derived an interesting approach to compute the ground state energies of the helium isoelectronic squence. Their method consists of introducing variational parameters in the Hamiltonian rather than in the trial wavefunction.

Physically, the parameters used, on the one hand, screen the nuclear charge and, on the other hand, produce a change in the centrifugal potential term that appears in the radial part of the one-electron Schrödinger equation. The interelectronic interaction is repulsive. Therefore, mechanistically, one may think of this repulsion resulting in some kind of positional displacement for the electronic wavefunction such that the correlated atomic state might not be associated only with pure s orbitals. This justifies the claim that correlation can also be accounted for by introducing variational parameters in the Hamiltonian.

The motivation for adopting the alternative approach stems from the consideration of the one-parameter wavefunction for the two-electron atom amounting to screening of the nucleus. It is observed that the effective value of Z becomes $Z - \beta$, where $\beta = \dfrac{5}{16}$, irrespective of the value Z, and has been interpreted as the screening parameter. Alternatively, the idea of screening the nucleus can be reflected in the Hamiltonian of the system by writing it (in atomic units) as

$$H = H_0 + H_1 \tag{2.4.8}$$

where

$$H_0 = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - (Z - \beta)\left(\frac{1}{r_1} + \frac{1}{r_2}\right) \tag{2.4.9}$$

and

$$H_1 = \frac{1}{r_{12}} - \beta\left(\frac{1}{r_1} + \frac{1}{r_2}\right) \tag{2.4.10}$$

The unperturbed Hamiltonian H_0 is separable and hence the corresponding Schrödinger equation is solved analytically. The avarage value of H with respect to this unperturbed wavefunction can be obtained as a function , $\in(\beta)$, of β. Minimizing $\in(\beta)$ with respect to β, it is observed that β comes out to be exactly $\dfrac{5}{16}$ for the ground state irrespective of the value of Z.

With the above conclusion in mind, they assume in the next step that an electron, due to presence of another electron, will see not only a screened nuclear charge , but also a change in the centrifugal potential term that appears in the radial equation part of the Schrödinger equation for the one-electron atoms. Consequently, the Hamiltonian for a two-electron atom is recast as

$$H = H_0 + H_1 \tag{2.4.11}$$

where

$$H_0 = \sum_{i=1}^{2} \left[-\frac{1}{2}\nabla_i^2 - (Z-\beta)\frac{1}{r_i} + \frac{\gamma}{r_i^2} \right] \tag{2.4.12}$$

and

$$H_1 = \frac{1}{r_{12}} - \beta\left(\frac{1}{r_1} + \frac{1}{r_2}\right) - \gamma\left(\frac{1}{r_1^2} + \frac{1}{r_2^2}\right) \tag{2.4.13}$$

Here β and γ are the two variational parameters: β accounts for screening, and γ, for the change in the centrifugal potantial term.

The Schrödinger equation corresponding to the unperturbed Hamiltonian , H_0 can be solved analytically. They obtain, as solutions, the following orthonormal and complete set of one-electron wavefunctions U_{nlm} :

$$U_{nlm}(r_i) = R_{nl}(r_i)Y_{lm}(\hat{r}_i) \qquad i = 1,2 \tag{2.4.14}$$

where $Y_{lm}(\hat{r})$ are the spherical harmonics [38] and $R_{nl}(r)$ are the normalized radial functions given by

$$R_{nl}(r) = N_{nl}\rho^{sl}e^{-\rho/2}L_{n-l-1}^{2sl+1}(\rho) \tag{2.4.15}$$

with

$$N_{nl} = \left[\frac{(n-l-1)!(2\sqrt{-2\in_{nl}})^3}{2(n-l+s_l)\Gamma(n-l+2s_l+1)} \right]^{1/2} \tag{2.4.16}$$

$$\rho = (2\sqrt{-2\in_{nl}})r \tag{2.4.17}$$

$$\in_{nl} = -\frac{(Z-\beta)^2}{2(n-l+s_l)^2} \tag{2.4.18}$$

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$$s_l = \frac{1}{2}\left[-1 + \sqrt{(2l+1)^2 + 8\gamma}\right] \tag{2.4.19}$$

$$L_n^\alpha(x) = \frac{\Gamma(n+\alpha+1)}{n!\Gamma(\alpha+1)} F(-n; \alpha+1; x) \qquad \alpha > -1 \tag{2.4.20}$$

and

$$F(a;b;x) = 1 + \frac{a}{b}x + \frac{a(a+1)}{b(b+1)}\frac{x^2}{2!} + \dots \tag{2.4.21}$$

Here , N_{nl} are the normalization constants corresponding to the radial functions R_{nl}, $\in_{nl}$ are the one-electron energy eigenvalues, s_l is the modified value of l due to the parameter γ, L_n^α are the associated Lagueree polynomials which are related to the confluent hypergeometric functions $F(a;b;x)$, the symbol Γ stands for the gamma function, $n = 1,2,3,...$ is the principal quantum number, $\iota = 0,1,2,....,n-1$ is the orbital quantum number and $m = -l, -l+1, ..., l$ is the magnetic quantum number.

It is clearly observed that s_l may assume fractional values. Also $\in_{nl}$ has come out to be a function of both n and l, thus removing the orbital degeneracy. It is further observed that if $\gamma \to 0$, $s_l \to l$, then $U_{nlm}(r)$ simply reduces to the solution for one-electron atomic system with a screened nuclear charge $Z - \frac{5}{16}$ thereby again introducing the orbital degeneracy.

The unperturbed wavefunction for any state of a two-electron atom can be constructed out of the above one-electron functions. Averaging H with respect to this unperturbed wavefunction, an expression for the energy, $E(\beta, \gamma)$, can be obtained, which is then minimized with respect to the parameters β and γ. Thus the minimum of energy and the corresponding optimum values of the parameters β and γ are ascertained.

For the ground state, in particular, the unperturbed wavefunction has been chosen as

$$\Psi_0(r_1, r_2) = U_{100}(r_1)U_{100}(r_2) \tag{2.4.22}$$

Averaging H with respect to $\Psi_0(r_1, r_2)$, it is succeeded in obtaining the following closed-form expression for $E(\beta, \gamma)$:

$$E(\beta, \gamma) = \sum_{i=1}^{4} T_i \tag{2.4.23}$$

where

$$T_1 = -\left(\frac{Z-\beta}{1+s_0}\right)^2 \quad , \quad T_2 = \frac{-2\beta(Z-\beta)}{(1+s_0)^2} \quad , \quad T_3 = -\frac{2s_0}{1+2s_0}\left(\frac{Z-\beta}{1+s_0}\right)^2$$

$$T_4 = \frac{9}{8}\frac{(Z-\beta)(3+s_0)}{(1+s_0)^3(1+2s_0)^2}\frac{1}{(1-s_0)(1-2s_0)}\frac{\sin(2\pi s_0)}{2\pi s_0}\left[\prod_{k=3}^{\infty}\left(1+\frac{4s_0}{2k-1}\right)\left(1-\frac{2s_0}{k}\right)\right]^{-1}-\left[\frac{(Z-\beta)(11-8s_0)}{(1+s_0)(4+8s_0)}\right]$$

with γ related to s_0 through the equation $\gamma = s_0(s_0+1)/2$. Here T_1 is the expression for $\langle H_0 \rangle$ while T_4 is that for $\left\langle \dfrac{1}{r_{12}} \right\rangle$. T_2 and T_3, respectively, are the expectation values of the second and third terms of H_1 in Eq. (2.4.13). It is worth mentioning here that some circuitous manipulations were needed while evaluating $\langle 1/r_{12} \rangle$. The difficulty arose only because of the possibility that s_0 might assume a fractional value. Further, it is observed that in the limit $\gamma \to 0$, the right-hand side of Eq.(2.4.23) reduces to an expression that is identical with the one obtained for the energy $\in (\beta)$ involving only the screening parameter. This observation indicates that the deduction leading to the terms in the right-hand side in Eq. (2.4.23) is correct.

An expression for $(\partial E/\partial \beta)$ was obtained analytically, which, when equated to zero, yielded β as an explicit function of γ. If $\gamma \to 0$, this function gives $\beta = 5/16$, irrespective of the value Z, as expected. Replacing β by the latter function, $E(\beta, \gamma)$ is reduced to a function of γ alone, and then minimized with respect to γ. The binding energy (BE) and the corresponding optimum values of γ and β for the ground state of the helium isoelectronic sequence for the nuclear

charge $1 \le Z \le 12$ are the computed in a single calculation. These results are displayed in Table 2.3 along with the binding energies reported by some earliers workers for comparison.

It is further observed from Table 2.3 that γ comes out to be negative, and both β and γ depend on the value of the nuclear charge; β increases with Z while the absolute value of γ decreases with Z. It appears that the values of the both β and γ will stabilize for large values of Z. The dependence of β on nuclear charge Z is in quite striking contrast with the one-parameter (only screening) trial functions where $\beta = 5/16$ irrespective of Z. It is concluded that the calculation simple, and yields binding energies comparable with that of the multiparameter cumbersome calculations reported by several workers. Secondly, it has been demonsrated that physically meaningful parameters can be included in the Hamiltonian rather than in the trial function. Further, since the same β and the same γ values have been chosen for both the electrons, this method can be easily extended to doubly–excited configurations in which both the electrons occupy the same orbital.

Table 2.3. Results for the binding energies (in Hatrees), β and γ for the ground state of H^-, He and $He-like$ ions

	H^-	He	Li^+	Be^{2+}	B^{3+}	C^{4+}	N^{5+}	O^{6+}	F^{7+}	Ne^{8+}	Na^{9+}	Mg^{10+}
BE^a	0.52775	2.90372	7.27991	13.65556	22.03097	32.40624	44.78144	59.15659	75.53171	93.90680	114.28188t	136.65694t
BE^b	0.47266	2.84766	7.22266	13.59766	21.97266	32.34766	44.72266	59.09766	75.47266	93.84766	114.22266	136.59766
BE^c	0.506	2.873	7.246	13.621								
BE^d	0.508	2.890	7.267	13.65	22.02	32.39	44.76					
BE^e	0.5226	2.895	7.269	13.643								
BE^f	0.5213	2.8994	7.2757	13.6513								
BE^g	0.50552	2.88403	7.25990	13.63527	22.01048	32.38562	44.76071	59.13578	75.51083	93.88587	114.26090	136.63593
β	0.54378	0.62630	0.65349	0.66681	0.67469	0.67989	0.68358	0.68633	0.68846	0.69015	0.69154	0.69269
$-\gamma \times 10^2$	7.62875	4.41755	3.06644	2.34224	1.89324	1.58816	1.36754	1.20064	1.06998	0.96495	0.87867	0.80654

[a] Exact value reported by Freund et al in 1984 [14]; t these particular values have been taken from the work of Thakkar and Smith in 1977 [13]

[b] One-parameter results introducing only screening parameter $(\beta = 5/16)$

[c] Two-parameter results of Srivastava and Bhaduri in 1977 [20]

[d] Two-parameter results of Abbott and Maslen in 1986 [22]

[e] One-parameter results of Patil in 1984 [25]

[f] Three-parameter results of Wu in 1982 [21]

[g] Two-parameter results in the present calculation.

2.4.3. Simple Wavefunctions For $(1s)(ns)^{1,3}S$ and $(1s)(np)^{1,3}P$ States of He and isoelectronic ions (S. H. Patil, 2003 Physical Review A 68, 044501)

To provide an insight into physical structure of excited states of He and He-like atoms, the work of Patil can be demonsrated as a good example. Patil have developed model wave functions for the excited $(1s)(ns)^{1,3}S$ and $(1s)(np)^{1,3}P$ states of He and isoelectronic ions, incorporating the asymptotic behavior when one of the electrons is far away, coalescence property when it is close to the nucleus, and cusp property when the two electrons are close to each other. They lead to accurate values for the energies and other properties.

The eigenfunctions of the two-electron atom and ions satisfy the Schrödinger equation

$$H\Psi(\hat{r}_1,\hat{r}_2) = E\Psi(\hat{r}_1,\hat{r}_2)$$

$$H = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - (Z/r_1) - (Z - r_2) + (1/r_{12}) \qquad (2.4.24)$$

Z being the charge of the nucleus.

Wave functions for excited (1s)(ns) states:

Model wave functions for the excited $(1s)(ns)^{1,3}S$ and $(1s)(np)^{1,3}P$ states are

$$\Psi(\vec{r}_1,\vec{r}_2) = A\left[\Phi(r_1)e^{-Zr_2} \pm e^{-Zr_1}\Phi(r_2)\right]f_\pm(r_{12}) \qquad (2.4.25)$$

$$\Phi(r) = (r + c_0)^{u_1+1-n} F(1-n,2,2a_1(r + c_0))e^{-a_1 r}g_o(r)$$

where A is the normalization constant, + and − signs are for the singlet and triplet states, respectively, and $f_\pm$ are the corresponding correlation functions. In the expression for $\Phi(r)$, F is the confluent hypergeometric function, and a_1 and u_1 are related to the ionization energy E_1 as in Eq. (2.2.2). This choice of $\Phi(r)$ may be regarded as a hydrogenic wave function for the outer electron with scale factor a_1 and shifted by c_0 . For the correlation functions $f_\pm$ it is taken that

$$f_+(r_{12}) = 1 - \left[e^{-\lambda_+ r_{12}} /(1 + 2\lambda_+) \right] \quad \text{(singlet)}$$

$$f_-(r_{12}) = 1 - \left[e^{-\lambda_- r_{12}} /(1 + 4\lambda_-) \right] \quad \text{(triplet)} \tag{2.4.26}$$

which satisfy the cusp condition for the leading $l_{12} = 0$ and $l_{12} = 1$ terms for the singlet and triplet states, respectively, for $r_{12} \to 0$. For $g_0(r)$, which is described as the coalescence function,

$$g_0(r) = 1 + B_0 e^{-br} \tag{2.4.27}$$

with B_0 and b as parameters. Since the excited (*ns*) states have nodes and extend over large distances, incorporating asymptotic terms in Eq. (2.2.2). For large r, one has

$$F(1 - n, 2, 2a_1(r + c_0))$$

$$= \left[(-1)^{n-1}/n! \right] 2a_1(r + c_0)^{n-1} \times (1 - \{ [n(n-1)]/[2a_1(r + c_0)] \}) \quad \text{for } r \to \infty \tag{2.4.28}$$

Using this in Eq. (2.4.25), carrying out an expansion in powers of $1/r$, and comparing with the required asymptotic behavior in Eq. (2.2.2) leads to

$$c_0 = (1/2a_1 u_1) \left[n(n-1) - u_1(u_1 - 1) \right] \tag{2.4.29}$$

so that c_0 is determined in terms of the ionization energy. To incorporate the coalescence condition in Eq. (2.2.8), it is noted that $e^{-Zr} \to 1 - Zr$ for $r \to 0$ has the correct coalescence behavior. For imposing this behavior in $\Phi(r)$, it is carried out an expansion in powers of r. Writing

$$F(1 - n, 2, 2a_1(r + c_0)) = \sum_{i=0}^{n-1} s_i (r + c_0)^i \tag{2.4.30}$$

and expanding the $\Phi(r)$ in Eq. (2.4.25) in powers of r, the coalescence condition in Eq. (2.2.8) leads to

$$B_0 = \frac{Z - a_1 - t_1}{b + a_1 + t_1 - Z} \tag{2.4.31}$$

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$$t_1 = \frac{1}{c_0}\left[n-1-u_1-\sum_{i=0}^{n-1}is_ic_0^i \middle/ \sum_{i=0}^{n-1}s_ic_0^i\right]$$

Thus, the only remaining free parameter in $\Phi(r)$ is the exponent b in Eq. (2.4.27).

Wave functions for (1s)(np) state:

For the *(1s)(np)* states, since the penetration of the outer electron into the inner region is small and its wave function is close to the hydrogenic wave function, it is considered a wave function

$$\Psi(\vec{r}_1,\vec{r}_2) = A\left[\Phi(r_1)e^{-Zr_2} \pm e^{-Zr_1}\Phi(r_2)\right]f_\pm(r_{12}) \tag{2.4.32}$$

$$\Phi(r) = rF(1-n,4,2a_1r)e^{-a_1r}P_1(\cos\theta)g_1(r)$$

where A is the normalization constant, $+$ and $-$ signs are for the singlet and triplet states, respectively, and $f_\pm$ are the corresponding correlation functions. In the expression for $\Phi(r)$, a_1 is related to the ionization energy E_1 as in Eq. (2.2.2), which ensures that the wave function has the correct exponential part in the asymptotic region. For the correlation functions $f_\pm$, it is taken the functions in Eq. (2.4.26) which satisfy the cusp condition in Eq. (2.2.11) for the leading $l_{12}=0$ and $l_{12}=1$ terms for the singlet and triplet terms, respectively, for $r_{12}\to 0$. For $g_1(r)$ which it is described as the coalescence function

$$g_1(r) = 1 + B_1e^{-br} \tag{2.4.33}$$

with B_1 and b as parameters. To incorporate the coalescence property in Eq. (2.2.8) , it is noted that $e^{-Zr}\to 1-Zr$ for $r\to 0$ has the correct coalescence behavior in Eq. (2.2.8) for the leading $l=0$ term. The function $\Phi(r)$ in Eq. (2.4.32) corresponds to a state with $l=1$. $\Phi(r)$ is expanded in powers of r and impose the coalescence condition in Eq. (2.2.8) for $l=1$, which then leads to

$$B_1 = (Z-na_1)/(2b+na_1-Z) \tag{2.4.34}$$

Thus, the only remaining free parameter in $\Phi(r)$ is the exponent b in Eq. (2.4.33)
Correlation functions $f_\pm(r_{12})$:

An estimation is deduced for the parameter $\lambda_\pm$ in Eq. (2.4.26) for $f_\pm(r_{12})$ by considering the Schrödinger equation in some specific domain. For the singly excited $(1s)(nl)$ states, consider a wave function of the form

$$\Psi(\vec{r_1}, \vec{r_2}) = \Phi_\pm(r_1, r_2) f_\pm(r_{12}) \tag{2.4.35}$$

$$\Phi_\pm(r_1, r_2) = \Phi_1^Z(r_1)\Phi_n^{Z-1}(r_2) \pm \Phi_n^{Z-1}(r_1)\Phi_1^Z(r_2)$$

where Φ_n^z are the hydrogenic wave functions with nuclear charge Z and principal quantum number n. Substituting this in Eq. (2.2.1) leads to

$$\left[(1/r_{12} - 1/r_2)\Phi_1^Z(r_1)\Phi_n^{Z-1}(r_2) \pm (1/r_{12} - 1/r_1) \right.$$

$$\left. \times \Phi_n^{Z-1}(r_1)\Phi_1^Z(r_2) \right] f_\pm(r_{12}) - \Phi_\pm(r_1, r_2)\nabla_{12}^2 f_\pm(r_{12}) - 2\left[\vec{\nabla}_{12}\Phi_\pm(r_1, r_2)\right] \cdot \vec{\nabla}_{12} f_\pm(r_{12})$$

$$= \left\{ E + Z^2/2 + \left[(Z-1)^2/2n^2 \right] \right\}\Psi(\vec{r_1}, \vec{r_2}) \tag{2.4.36}$$

Since the $(1s)(nl)$ energies are close to the sum of the hydrogenic energies

$$E = -Z^2/2 - (Z-1)^2/(2n^2) \tag{2.4.37}$$

It is neglected the term on the right-hand side in Eq.(2.4.36) For the singlet states, since $\Phi_\pm(r_1, r_2)$ is symmetric under the interchange of $\vec{r_1}$ and $\vec{r_2}$, it contains only even power terms in r_{12}. Therefore,

$$\left(\frac{1}{r_{12}} - \frac{1}{r_1} \right) f_+ - \nabla_{12}^2 f_+ = O(r_{12}) \tag{2.4.38}$$

where $O(r_{12}) \to 0$ for $r_{12} \to 0$. Using an expansion for f_+ in Eq. (2.4.38), we get from the first two terms

$$f_+ = 1 + q_1 r_{12} + q_2 r_{12}^2 + ... \qquad q_1 = 1/2, \ q_2 = -\frac{1}{6}(1/r_1 - 1/2) \tag{2.4.39}$$

The first relation is the cusp condition in (Eq. 2.2.11). Comparing the expansion in Eq. (2.4.39) with the expansion of $f_+(r_{12})$ in Eq.(2.4.26), it is obtained that

$$\lambda_+ = \frac{2}{3}(1/r_1 - 1/2) \tag{2.4.40}$$

It is required that this equation is satisfied for $r_1 = 4/[3(Z - 1/3)]$. The reason for this choice of r_1 is that the inner electron is found mainly in the region of $1/Z$ and $2/Z$ and it is taken r_1 to be about $(4/3Z)$ and include some screening effect. Using this value of r_1 in Eq.(2.4.40) one obtains

$$\lambda_+ = (Z - 1)/2 \qquad (2.4.41)$$

For the triplet state, when the two electrons are close to each other, it can be written

$$\Phi_-(r_1, r_2) = \vec{r}_{12} \cdot \vec{R}\Phi(R), \qquad \vec{R} = \vec{r}_1 + \vec{r}_2 \qquad \text{for } r_{12} \to 0 \qquad (2.4.42)$$

Substituting this in Eq.(2.4.36) leads to

$$-\nabla_{12}^2 f_- - (2/r_{12})(\partial f / \partial r_{12}) + (1/r_{12} - 1/r_1)f_- = O(r_{12}) \qquad (2.4.43)$$

Using an expansion for f_- in Eq.(2.4.43),

$$f_- = 1 + q_1 r_{12} + q_2 r_{12}^2 + \dots , \qquad q_1 = 1/4, \quad q_2 = -\frac{1}{10}(1/r_1 - 1/4) \qquad (2.4.44)$$

The first relation follows from the cusp condition in Eq.(2.2.11). Comparing the expansion in Eq.(2.4.44) with the expansion of $f_-(r_{12})$ in Eq.(2.4.26),

$$\lambda_- = \frac{4}{5}(1/r_1 - 1/4) \qquad (2.4.45)$$

Since $1/r_1$ is the dominant term, this expression is larger than λ_+ in Eq.(2.4.40). by a factor of about 6/5, and for simplicity it is taken that

$$\lambda_- = 6\lambda_+/5 - 3(Z - 1)/5 \qquad (2.4.46)$$

where the expression for λ_+ in Eq.(2.4.41) is used.

Now the energies of the states can be computed using the model wave functions. Excited $(1s)(ns)$ states:

For excited $(1s)(ns)$ states, the wave function in Eq. (2.4.25) is used to deduce the energy from the Hamiltonian in Eq (2.2.1):

$$E = \langle \Psi H \Psi \rangle / \langle \Psi | \Psi \rangle \qquad (2.4.47)$$

The shift parameter c_0 in the wave function $\Phi(r)$ in Eq. (2.4.25) is determined by the relation in Eq. (2.4.29), which ensures the asymptotic behavior in Eq. (2.2.2). The parameter B_0 in the coalescence function $g_0(r)$ in Eq. (2.4.27) is determined by the relation in Eq. (2.4.31) obtained from the coalescence condition in Eq. (2.2.8). Finally, the parameters $\lambda_\pm$ in the correlation functions $f_\pm(r_{12})$ are determined by the relations in Eqs. (2.4.41) and (2.4.46). The remaining free parameter is the exponent b in the coalescence function in Eq. (2.4.27), which is determined by using the virial relation in Eq. (2.2.12). The quantities a_1 and u_1 in Eq. (2.4.25) are related to the ionization energy E_1 as in Eq. (2.2.2), which is related to the total energy as in Eq. (2.2.3). The energy E is therefore determined self-consistently by iteration, such that the input value of E in Eq. (2.2.3) is equal to the output value in Eq.(2.4.47). It has been given that the values of b, the calculated values of the energy, the normalization constant A in Eq. (2.4.25), and of $\langle r_1 \rangle, \langle r_{12} \rangle$, in Table 2.4. They are close to the known accurate values $[39,40]$.

Table 2.4. The values of the parameter b in the coalescence function in Eq. (2.4.27) , normalization constant A in Eq. (2.4.25) , the predicted values of the energy, the expectation values $\langle r_1 \rangle, \langle r_{12} \rangle$ and accurate values from Ref.[40] given in brackets, for $(1s)(2s)$ and $(1s)(3s)$ states

		$(1s)(2s)^1 S$	$(1s)(2s)^3 S$	$(1s)(3s)^1 S$	$(1s)(3s)^3 S$
He	b	1.14	1.41	0.91	0.83
	A	0.2957	0.3599	0.1681	0.2263
	$-E$	2.1455	2.1751	2.0615	2.0686
		(2.1460)	(2.1752)	(2.0613)	(2.0687)
	$\langle r_1 \rangle$	3.025	2.552	6.482	5.865
	$\langle r_{12} \rangle$	5.373	4.443	12.24	11.01
Li$^+$	b	2.00	9.5	1.35	1.31
	A	1.289	1.388	0.7091	0.8238
	$-E$	5.0381	5.1103	4.7332	4.7519
		(5.0409)	(5.1107)	(4.7338)	(4.7521)
	$\langle r_1 \rangle$	1.673	1.496	3.479	3.235
	$\langle r_{12} \rangle$	2.899	2.560	6.481	5.998

Excited $(1s)(np)$ states:

For the $(1s)(np)^{1,3} P$ states, the wave function in Eq. (2.4.32) is used to calculate the energy as in Eq. (2.4.47). The parameter B_1 in the coalescence function $g_1(r)$ in Eq. (2.4.33) is determined by the relation in Eq. (2.4.34) obtained from the coalescence condition in Eq. (2.2.8) for the outer electron wave function $l = 1$. The correlation parameter $\lambda_\pm$ is determined by the relations in Eqs.(2.4.41) and (2.4.46). The remaining free parameter is the exponent b in the coalescence function in Eq. (2.4.33), which is determined by using the virial relation in Eq. (2.2.12), except in the case of $(1s)(np)^3 P$ states for which b is determined by minimizing the energy. Even in this case, the virial ratio in Eq. (2.2.12) comes out to be -1.99 , which ensures good quality of the wave function. The parameter a_1 in Eq.(2.4.32) is related to the ionization energy as in Eq. (2.2.2), which is determined self-consistently by iteration, such that the input value of E in Eq.(2.2.3) is equal to the output value in Eq. (2.4.47). It has been given that the values of b, the calculated values of the energy, the normalization constant A in

Eq. (2.4.32), and of $\langle r_1 \rangle, \langle r_{12} \rangle$, in Table 2.5. They are close to the known accurate values [39,40].

Table 2.5. The values of the parameter b in the coalescence function in Eq. (2.4.33) , normalization constant A in Eq. (2.4.32) , the predicted values of the energy, the expectation values $\langle r_1 \rangle, \langle r_{12} \rangle$ and accurate values from Ref. [40] given in brackets, for $(1s)(2p)$ and $(1s)(3p)$ states

		$(1s)(2p)^1 P$	$(1s)(2p)^3 P$	$(1s)(3p)^1 P$	$(1s)(3p)^3 P$
He	b	0.96	0.87	0.95	1.15
	A	0.1146	0.1178	0.0664	0.0699
	$-E$	2.1235	2.1326	2.0551	2.0577
		(2.1238)	(2.1332)	(2.0551)	(2.0577)
	$\langle r_1 \rangle$	2.925	2.730	6.698	6.521
	$\langle r_{12} \rangle$	5.165	4.803	12.67	12.33
Li^+	b	1.57	1.21	1.53	2.03
	A	1.172	1.191	0.6872	0.7222
	$-E$	4.9928	5.0263	4.7201	4.7295
		(4.9933)	(5.0277)	(4.7202)	(4.7305)
	$\langle r_1 \rangle$	1.520	1.428	3.405	3.329
	$\langle r_{12} \rangle$	2.586	2.442	6.331	6.188

We see that the predictions of these wave functions for the energies and $\langle r_1 \rangle$, $\langle r_{12} \rangle$, are in close agreement with the values obtained from elaborate calculations [39,40]. This emphasizes the importance of the local properties in the development of accurate model wave functions which give a clear perspective of their physical structure.

CHAPTER 3

ALTERNATIVE TREATMENTS FOR TWO-ELECTRON ATOMS

In the first section of this chapter, we have attempted to solve Schrödinger equation for atoms having two electrons in an alternative framework. However, after some algebraic work we have realized that supersymmetric quantum mechanics (SUSYQM)[30] in its present form cannot be used properly due to the correlation term. Nevertheless, this failure directs us to introduce another prescription to solve bound state energies and wave functions of helium and helium-like atoms which is discussed and presented in the second section. This successful method leads us to present appropriate screening parameters, to our knowledge such discussion has not appeared in the related literature.

3.1. An Attempt to Solve The Related Problem

As mentioned above, one can easily sees that SUSY QM treatment technique is not appropriate for solving such systems under consideration because of the correlation term appearing due to the interaction between the electrons. To see this drawback, which is significant to develop an effective model in the following section, we proceed with (in atomic units)

$$H = H_0 + H_1 \tag{3.1.1}$$

where

$$H_0 = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - (Z - \beta)\left(\frac{1}{r_1} + \frac{1}{r_2}\right) \tag{3.1.2}$$

 and

$$H_1 = \frac{1}{r_{12}} - \beta \left(\frac{1}{r_1} + \frac{1}{r_2} \right) \quad . \tag{3.1.3}$$

In the above equations r_1, r_2 are the positions of electrons with respect to the nucleus having a charge of Z with infinite mass, and r_{12} is the distance between electrons. For those electronic configurations of the system in which two electrons are at unequal distances from the nucleus, the outer electron should experience a smaller effective charge than the inner one. In other words, each electron is partially screened from screening the full charge of the nucleus due to the presence of the other electron. This would suggest introducing an appropriate parameter, β, in the calculations.

Assuming that

$$\left\langle \frac{1}{r_{12}} \right\rangle = \beta \left\langle \frac{1}{r_1} + \frac{1}{r_2} \right\rangle \tag{3.1.4}$$

the Hamiltonian, $\langle H_1 \rangle = \langle \Psi(r_1, r_2) | H_1 | \Psi(r_1, r_2) \rangle$, incorporating a perturbation due to the correlation term vanishes. In this case, Eq. (3.1.2) gains a physical importance, the solution of which reflects also the correlation effects indirectly. This is in agreement with the well known fact from the literature that the inclusion of electron correlation in the Hamiltonian accounts for the screening precisely.

Consequently, the Hamiltonian is formed as below,

$$H = H_0 = -\frac{1}{2} \nabla_1^2 - \frac{1}{2} \nabla_2^2 - (Z - \beta) \left(\frac{1}{r_1} + \frac{1}{r_2} \right)$$

The unperturbed Hamiltonian, H_0, is separable and hence the corresponding Schrödinger equation is solved analytically. Each of these independent electron picture is the same as the Schrödinger equation for the Hydrogen atom, leading to the full unperturbed solutions. In SUSY QM, the eigenfunctions of these electrons are

$$\Phi_1 = r_1 e^{-(Z-\beta)r_1} \qquad \text{and} \qquad \Phi_2 = r_2 e^{-(Z-\beta)r_2} \tag{3.1.5}$$

for 1. electron and 2. electron, respectively, that can be inferenced easily from [30].

For the first electron, the appropriate supperpotential is

$$W_{\Phi_1} = -\frac{1}{\sqrt{2}}\frac{\Phi_1'}{\Phi_1} \quad . \tag{3.1.6}$$

We can have the partner potential, $V_{-(\Phi_1)}$, for Φ_1

$$V_{-(\Phi_1)} = W_{\Phi_1}^{\ 2} - \frac{1}{\sqrt{2}}W_{\Phi_1}'$$

$$V_{-(\Phi_1)} = \frac{(Z-\beta)^2}{2} - \frac{(Z-\beta)}{r_1} \tag{3.1.7}$$

For the second electron, the appropriate superpotantial is

$$W_{\Phi_2} = -\frac{1}{\sqrt{2}}\frac{\Phi_2'}{\Phi_2}$$

$$W_{\Phi_2} = -\frac{1}{\sqrt{2}}\left(-(Z-\beta) + \frac{1}{r_2} \right) \tag{3.1.8}$$

and for Φ_2 the partner potential $V_{-(\Phi_2)}$ is

$$V_{-(\Phi_2)} = W_{\Phi_2}^{\ 2} - \frac{1}{\sqrt{2}}W_{\Phi_2}' \quad ,$$

$$V_{-(\Phi_2)} = \frac{(Z-\beta)^2}{2} - \frac{(Z-\beta)}{r_2}. \tag{3.1.9}$$

The total partner potential , $V_{-(\Phi)}$, is

$$V_{-(\Phi)} = V_{-(\Phi_1)} + V_{-(\Phi_2)} = \frac{(Z-\beta)^2}{2} - \frac{(Z-\beta)}{r_1} + \frac{(Z-\beta)^2}{2} - \frac{(Z-\beta)}{r_2},$$

$$V_{-(\Phi)} = (Z-\beta)^2 - \frac{(Z-\beta)}{r_1} - \frac{(Z-\beta)}{r_2} \quad . \tag{3.1.10}$$

We know that the difference between the partner potential and the potential of the system equals to the ground state energy. That's

$$V_{-(\Phi)} = V - E_0 \tag{3.1.11}$$

and

$$E_0 = E_{01} + E_{02} = -\frac{(Z-\beta)^2}{2} - \frac{(Z-\beta)^2}{2} = -(Z-\beta)^2 \qquad (3.1.12)$$

The ground state energies of $H^-, He, Li^+, Be^{2+}, B^{3+}$ using Eq. (3.1.12) are fairly in agreement with the experimental results. However, these results are not reliable from the physical point of view since a specific value of the screening parameter (5/16) has been used throughout the calculations. We suggest a physically more reliable model in the next section.

Table 3.1. The ground state energies within the frame of Eq.(3.1.12)

Atom	Present Results(au)	Accurate Energy(au)
H^-	-0.472656	-0.5277
He	-2.847656	-2.9037
Li^+	-7.222656	-7.2799
Be^{2+}	-13.59766	-13.6555
B^{3+}	-21.97266	-22.0309

3.2. Accurate Calculations for Two-Electron Atoms

Physically, the parameter, β, introduced above screens the nuclear charge and produces a change in the wavefunctions corresponding to the interaction of the each electron with the nucleus. Bearing in mind that the interelectronic interaction is repulsive, one may think of this repulsion resulting in some kind of positional displacement for the electronic wavefunctions. This justifies the claim put forward with Eqs. (3.1.2) and (3.1.4) that correlation can also be accounted for by introducing a correct screening parameter.

In this section of the work, for both the ground state and excited states of He and He-like atoms, the accurate values of screening parameter, β, is obtained. Additionally, the relation between the parameter and some expected values of these atoms is exhibited. The values computed are aggrement with the literature, which proves that the treatment is reliable.

3.2.1. Accurate calculations for the ground state of two-electron atoms

To proceed, in the ground state of these atoms we consider the form of the exact energy

$$E = -(Z)^2 + \Delta E \qquad (3.2.1)$$

where $\beta = 0$ and ΔE is the correction term to the energy value within the consideration of electron correlation, and

$$E = E_0 = -(Z - \beta)^2 = -(Z)^2 - \beta^2 + 2Z\beta \qquad (3.2.2)$$

in case of screening, leading to a connection between energy expressions

$$\Delta E = -\beta^2 + 2Z\beta \qquad (3.2.3)$$

of different physical considerations.

In order to provide an insight into the physical nature of the screening parameter, we obtain

$$\beta_{1,2} = Z \pm \sqrt{Z^2 - \Delta E} \qquad (3.2.4)$$

using Eq. (3.2.3). Though mathematically we have arrived at two roots for β, the substitution of Eq. (3.2.3) into (3.2.4) and a careful study of Eq. (3.1.12) direct us to choose the physically reasonable lower root due to the physical fact that $Z > \beta$. The dependence of β on nuclear charge Z, in Eq. (3.2.4), is in quite striking contrast with the previous calculations used trial functions where, in general, $\beta = 5/16$ irrespective of Z. The Eq. (3.2.4) thus justifies the discussion in [27]. As far as we know, this feature has not been perceived in an explicit way until now.

The accurate values of screening parameter for different atoms having two electrons are shown in Table 3.2. In calculating these parameters, exact energy values which are taken from the works in Refs. [13,14] are employed within the frame of Eqs. (3.2.1), (3.2.3) and (3.2.4).

Table 3.2. Exact screening parameters for the ground states of two-electron atoms in the range $1<Z<12$

Atom (^1S)	Exact Energy (au)	ΔE (Eq.3.2.1)	β (Eq.3.2.4)
H^-	-0.52775	0.47225	0.273535
He	-2.90372	1.09628	0.295969
Li^+	-7.27991	1.72009	0.301869
Be^{2+}	-13.65556	2.34444	0.304656
B^{3+}	-22.03097	2.96903	0.306283
C^{4+}	-32.40624	3.59376	0.307352
N^{5+}	-44.78144	4.21856	0.308106
O^{6+}	-59.15659	4.84341	0.308667
F^{7+}	-75.53171	5.46829	0.3091018
Ne^{8+}	-93.90680	6.09320	0.3094479
Na^{9+}	-114.28188	6.71812	0.3097296
Mg^{10+}	-136.65694	7.34306	0.3099640

Clearly, β slightly increases with increasing Z. In addition, we observe that there is a universal relation between the reduced energy (E_0/ε) and the reduced screening parameter (β/Z) such that

$$\frac{E_0(Z,\beta)}{\varepsilon(Z,\beta=0)}=\frac{-(Z-\beta)^2}{-(Z)^2}=\left(1-\frac{\beta}{Z}\right)^2 \tag{3.2.5}$$

for $S-$ states. The present result indicates another interesting point. Here, Z behaves as a critical screening parameter for which the binding energy of the level, Eqs. (3.1.12), (3.2.2) and subsequently (3.2.5), in question becomes zero. It is of interest however to examine whether such a relationship is also valid for $\ell \neq 0$ states.

Afterall, we wish to generalize the framework of our discussion by focusing on Eq. (3.1.4), in which there are two unknowns: the positions of electrons with respect to the nucleus (r_1, r_2) and the distance between interacting electrons (r_{12}). It is therefore obvious that there is a need for a second equation to be able to estimate

these two unknown observables. By the use of Heisenberg's uncertainty relation, we propose a similar idea to that of Yukawa for the correlation between the electrons,

$$\Delta E \, \Delta t \approx \hbar \Rightarrow \Delta x = \langle r_{12} \rangle = c \, \Delta t \Rightarrow \langle r_{12} \rangle \approx \frac{\hbar c}{\Delta E} \tag{3.2.6}$$

Throughout the work presented here we work in atomic units, Eq. (3.2.6) is thus formed as $\langle r_{12} \rangle \approx 1/\Delta E$. During the electron-electron interaction, we can expect a considerable change in total energy $(E = \varepsilon + \Delta E)$, on average, due to the correlation (ΔE) visualized as in Eq.(3.2.6), keeping in mind that the time required a photon exchange between these charged particles is quite short due to the photon moving with the speed of light.

Therefore, in the light of Eqs. (3.1.4), (3.2.3) and (3.2.6) one gets

$$\left[\left\langle \frac{1}{r_1} + \frac{1}{r_2} \right\rangle \approx 2Z - \beta \right] \tag{3.2.7}$$

and with the use of either Eq. (3.2.2) or Eq. (3.2.5), the energy expression in a closed algebraic form is given as

$$E \approx \left[\left\langle \frac{1}{r_1} + \frac{1}{r_2} \right\rangle - Z \right]^2 \tag{3.2.8}$$

It is useful at this stage to remind ourselves that these results are in a very good agreement with a significant but ongoing discussion in the literature. In brief, Eq. (3.2.8) clarifies explicitly that for low Z values, when one of the electrons coalesces with the nucleus the radial distribution of the second electron extends over several atomic units. As the charge increases, the second electron moves nearer to the nucleus. The equations above, also agree with the Bohr's suggestion that the radius of hydrogen-like atoms is inversely proportional with the charge of the nucleus if electron-nucleus problem is treated independently without considering the correlation effect.

Additionally, Eqs. (3.2.7) and (3.2.8) also reveals that one needs either a reasonable parameter reletad to the screening effect or the accurate positions of electrons to obtain exact binding energies for the cases of interest. To end up this

discussion, we provide $\langle 1/r_1 + 1/r_2 \rangle$ values in Table 3.3 for the atoms appeared in Table 3.2 considering the corresponding exact β – values. The comparison of the present results, $\langle 1/r_1 + 1/r_2 \rangle$, with those of Refs.$[41,42,43]$ confirms the physics behind the idea proposed in Eq. (3.2.6)

Table 3.3. Locations of electrons with respect to the nucleus

for ground states of two-electron atoms in the range 1<Z<12

$Atom\ (^1S)$	$\langle 1/r_1 + 1/r_2 \rangle\ (Eq.3.2.7)$
H^-	1.726465
He	3.704031
Li^+	5.698131
Be^{2+}	7.695344
B^{3+}	9.693717
C^{4+}	11.692648
N^{5+}	13.691894
O^{6+}	15.691333
F^{7+}	17.690898
Ne^{8+}	19.690552
Na^{9+}	21.690270
Mg^{10+}	23.690036

3.2.2. Accurate Calculations for The Excited States of Two-Electron Atoms

Here, in order to generalize, we extend the present scenario to the excited states. For simplicity and clear understanding, it is basically assumed that an electron is in the ground state while the second one (outer electron) sits in the first excited state. As expected, only the outer electron is screened from seeing the original nuclear charge by the inner one. The Hamiltonian of the system is then formed as below

$$H = H_0 + H_1 \tag{3.2.9}$$

$$H_0 = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \left(\frac{Z}{r_1} + \frac{(Z-\beta)}{r_2}\right) \qquad (3.2.10)$$

$$H_1 = \frac{1}{r_{12}} - \frac{\beta}{r_2} \qquad (3.2.11)$$

The exact energy value in this case for the system considered can be expressed as

$$E = E_{10} + E_{2l} + \Delta E$$

$$E = -\frac{Z^2}{2} - \frac{Z^2}{2(n_r + l + 1)^2} + \Delta E \qquad (3.2.12)$$

$E_{10} = -\dfrac{Z^2}{2}$ for the inner electron; $E_{2l} = -\dfrac{Z^2}{2(n_r + l + 1)^2}$ for the outer electron

where n_r is radial quantum number, l is orbital quantum number and ΔE is the correction term to the energy value within the consideration of electron correlation. As discussed in the previous section, the corresponding total energy values can easily be expressed by the SUSYQM

$$E = -\frac{Z^2}{2} - \frac{(Z-\beta)^2}{2(n_r + l + 1)^2}$$

$$E = -\frac{Z^2}{2} - \frac{Z^2}{2(n_r + l + 1)^2} + \frac{-\beta^2 + 2Z\beta}{2(n_r + l + 1)^2} \qquad (3.2.13)$$

as result of that, using the same analogy in the earlier calculations where Eqs.(3.21)-(3.2.3), one can easily get

$$\Delta E = \frac{-\beta^2 + 2Z\beta}{2(n_r + l + 1)^2} \qquad (3.2.14)$$

Remembering Eq. (32.4) and using the exact energy values for different l, we can compute the screening parameter β in Eq.(3.2.11) such as

$$\beta = Z \pm \sqrt{Z^2 - 2(n_r + l + 1)^2 \Delta E} \qquad (3.2.15)$$

It is obvious that the lower β value is physically acceptable as discussed in detail in the ground state calculations. For clarity, the accurate values of screening parameter for different l in the first excited states of different atoms in the range 2<Z<10 are shown in Table 3.4. However, it is stressed that one can readily apply the present technique, if it is required, the other excited states without causing any problem.

In calculating these parameters, the exact energy values are taken from the works in Refs. [39] and used within the frame of Eqs. (3.2.12), (3.2.14) and (3.2.15).

Table 3.4: The exact screening parameter for different l in the first excited states of two-electron atoms in the range 2<Z<10. All values are in a.u.

Atom	$(1S2S)^1S$			$(1S2S)^3S$			$(1S2P)^1P$			$(1S2P)^3P$		
	Exact Energy	ΔE Eq(3.2.12)	β Eq.(3.2.15)	Exact Energy	ΔE Eq.(3.2.12)	β Eq.(3.2.15)	Exact Energy	ΔE Eq.(3.2.12)	β Eq.(3.2.15)	Exact Energy	ΔE Eq.(3.2.12)	β Eq.(3.2.15)
He	-2.1460	0.354	0.9193	-2.1752	0.3248	0.8161	-2.1238	0.3762	1.0048	-2.1332	0.3668	0.9677
Li^+	-5.0409	0.5841	0.9198	-5.1107	0.5143	0.7897	-4.9933	0.6317	1.0134	-5.0277	0.5973	0.9453
Be^{2+}	-9.1849	0.8151	0.9212	-9.2972	0.7028	0.7786	-9.1108	0.8892	1.0190	-9.1750	0.8250	0.9340
B^{3+}	-14.5785	1.0465	0.9223	-14.7339	0.8911	0.7726	-14.4773	1.1477	1.0228	-14.5731	1.0519	0.9276
C^{4+}	-21.2220	1.2780	0.9230	-21.4208	1.0792	0.7687	-21.0933	1.4067	1.0254	-21.2217	1.2783	0.9232
N^{5+}	-29.1154	1.5096	0.9236	-29.3577	1.2673	0.7661	-28.9591	1.6659	1.0273	-29.1205	1.5045	0.9202
O^{6+}	-38.2588	1.7412	0.9240	-38.5446	1.4554	0.7642	-38.0747	1.9253	1.0288	-38.2694	1.7306	0.9180
F^{7+}	-48.6521	1.9729	0.9243	-48.9816	1.6434	0.7627	-48.4402	2.1848	1.03	-48.6684	1.9566	0.9162
Ne^{8+}	-60.2953	2.2047	0.9246	-60.6686	1.8314	0.7616	-60.0556	2.4444	1.0309	-60.3175	2.1825	0.9148

In addition, recalling the previous subsection calculations regarding the Heisenberg's uncertainty relation to predict the distance between interacting electrons for the present case, we obtain

$$\langle r_{12} \rangle \approx \frac{\hbar c}{\Delta E} = \frac{2(n_r + l + 1)^2}{-\beta^2 + 2Z\beta} \qquad (3.2.16)$$

where $\hbar = c = 1$. Bearing Eq. (3.2.11) in mind, we have

$$\left\langle \frac{1}{r_2} \right\rangle = \frac{\Delta E}{\beta} = \frac{-\beta + 2Z}{2(n_r + l + 1)^2} \qquad (3.2.17)$$

where r_2 is the distance between the outer electron and nucleus. Using the exact values of β for different quantum states (as in Table 3.4), one can easily calculate the predictions for $\left\langle \frac{1}{r_2} \right\rangle$, which reproduces reasonable results when compared to those of other calculations [40].

CHAPTER 4

CONCLUSION

The helium atom and isoelectronic ions are universal examples which illustrate the properties of few-electron atoms and ions, and the complications introduced by many-particle systems. By the consideration of this essential point, we have been principally concerned in this work with finding correct secreening parameters for the systems considered. We have observed that for helium and its isoelectronic series the size of β scales with the nuclear charge. It has been also demonstrated that physically reasonable parameters can be included in the Hamiltonian rather than in the trial functions.

The screening factor is a refinement taking the screening of the nuclear charges by the electrons into account. Since a screening factor complicates in general the calculation of off-diagonal matrix elements, many theoretical techniques do not include this parameter in the wavefunction due to the structure of their framework. Therefore, one can expect that the results will be less accurate in cases where screening becomes important; i.e. at smaller internuclear distances of two-electron molecules, or for dissociation limits involving negative atomic ions, see Ref. $[23]$. However, the present approach would be helpful in removing such deficiencies. In addition, the relatively simple and compact form of the present wavefunction would be of interest for the calculation of electronic transition moments needed in dynamical studies, where intermediate and large internuclear distances are involved.

Clearly, considerable additional work is still needed to extend the present scenario to more complex cases of helium and its isoelectronic ions with the more physical consideration involving other physical parameters. Further, since the same β value has been chosen for both electrons, our method can be easily extended to doubly-excited configurations in which both the electrons occupy the same orbital.

With this considerations, we hope to stimulate further examples of applications of the present procedure in important problems in physics. Along this line the works are in progress.

As a final remark, with the wide application of the screened Coulomb potential families in different areas of physics, we believe that our discussion presented would also provide new insights to the research communities of atomic physics.

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PUBLICATIONS

1) M. Çapak and B. Gönül, Accurate solutions for two-electron atoms, submitted to *Physica Scripta* (2010)