

Modified Atomic Orbital Calculations of Energy of the ($2s^2\ ^1S$) Ground-State, the ($2p^2\ ^1D$); ($3d^2\ ^1G$) and ($4f^2\ ^1I$) Doubly Excited States of Helium Isoelectronic Sequence from H^- to Ca^{18+}

Malick Sow^{1*}, Ibrahima Sakho², Boubacar Sow¹, Abdou Diouf¹, Youssou Gning¹, Babou Diop¹, Matabara Dieng³, Abdourahmane Diallo⁴, Mamadou Diouldé Ba⁴, Jean Kouhissoré Badiane⁴, Mamadi Biaye⁵, Ahmadou Wagué¹

¹Department of Physics, Atoms Lasers Laboratory, Faculty of Sciences and Technologies, University Cheikh Anta Diop, Dakar, Senegal

²Department of Physics, UFR Sciences et Technologies, University of Thiès, Thiès, Senegal

³UFR SATIC, University Alioune DIOP de Bambey, Bambey, Senegal

⁴Department of Physics, UFR of Sciences and Technologies, University Assane Seck of Ziguinchor, Ziguinchor, Senegal

⁵Department of Physics and Chemistry, Faculty of Sciences and Technologies of Training and Education, University Cheikh Anta Diop, Dakar, Senegal

Email: *malick711.sow@ucad.edu.sn

How to cite this paper: Sow, M., Sakho, I., Sow, B., Diouf, A., Gning, Y., Diop, B., Dieng, M., Diallo, A., Ba, M.D., Badiane, J.K., Biaye, M. and Wagué, A. (2020) Modified Atomic Orbital Calculations of Energy of the ($2s^2\ ^1S$) Ground-State, the ($2p^2\ ^1D$); ($3d^2\ ^1G$) and ($4f^2\ ^1I$) Doubly Excited States of Helium Isoelectronic Sequence from H^- to Ca^{18+} . *Journal of Applied Mathematics and Physics*, 8, 85-99.

<https://doi.org/10.4236/jamp.2020.81007>

Received: December 3, 2019

Accepted: January 3, 2020

Published: January 6, 2020

Copyright © 2020 by author(s) and Scientific Research Publishing Inc.

This work is licensed under the Creative Commons Attribution International License (CC BY 4.0).

<http://creativecommons.org/licenses/by/4.0/>



Open Access

Abstract

We report in this paper the ground-state energy $2s^2\ ^1S$ and total energies of doubly excited states $2p^2\ ^1D$, $3d^2\ ^1G$, $4f^2\ ^1I$ of the Helium isoelectronic sequence from H^- to Ca^{18+} . Calculations are performed using the Modified Atomic Orbital Theory (MAOT) in the framework of a variational procedure. The purpose of this study required a mathematical development of the Hamiltonian applied to Slater-type wave function [1] combining with Hyllebras-type wave function [2]. The study leads to analytical expressions which are carried out under special MAXIMA computational program. This first proposed MAOT variational procedure, leads to accurate results in good agreement as well as with available other theoretical results than experimental data. In the present work, a new correlated wave function is presented to express analytically the total energies for the $2s^2\ ^1S$ ground state and each doubly $2p^2\ ^1D$, $3d^2\ ^1G$, $4f^2\ ^1I$ excited states in the He-like systems. The present accurate data may be a useful guideline for future experimental and theoretical studies in the ($n\ell$) systems.

Keywords

Modified Atomic Orbital Theory, Variational Calculations, Correlated

1. Introduction

The resolution of the Schrödinger equation gives for the ground-state of the Helium atom the value $E = 108.8$ eV. The experimental result being equal to $E_0 = -79.0$ eV, one conceives that one takes into account the electronic correlation term, overestimating, numerous studies provided evidence of the importance of the electronic correlation in the ground-state and in the doubly excited state of He-like series [3] [4] [5].

For the ground states, energy calculations of Helium isoelectronic sequence are performed by using several correlated wavefunction and an analytical technique calculation. Thus, Moore [6], Radzig and Smirnov [7] and Arnaud [8] measured the ground state energies $E(1s^2\ ^1S)$ of two-electron systems with atomic number Z ($2 \leq Z \leq 10$). Combining the perturbation theory [9] to the Ritz variational method [10], Sakho *et al.*, [11] set in motion a technic of analytical calculation of the ground state energy $E(1s^2\ ^1S_0)$, the first ionization energy $J(1s^2\ ^1S_0)$ and the radial correlation expectation value $\langle r_{12}^{-1} \rangle(1s^2\ ^1S_0)$ for the Helium-like ions from Hydrogen ion H^- ($Z = 1$) to silicon Si^{12+} ($Z = 14$). Utpal and Talukdar [12] used an analytical approach to also calculate the ground-state energies of helium isoelectronic sequence from Hydrogen ion H^- ($Z = 1$) up to the silicon ion Si^{12+} ($Z = 14$). For some methods using variational wavefunction like Hylleraas's one, a good approximation of the eigenvalues is obtained when the minima of the function $(\frac{dE}{d\alpha})$, with α a variational parameter, E is the energy) converges with

the increasing values of the dimension D and when the function $E = f(\alpha, D)$ exhibits a plateau [2]. For other methods using a non variational wavefunction [13], the ground-state energy of He-like ions is determined by the use of proper core boundary conditions correct behavior for $r_{12} \rightarrow 0$ and $r_{12} \rightarrow \infty$ and by taking recourse to a perturbative method. For some methods using an analytical technique calculation, some authors were interested in the setting in work of calculation techniques permitting one to succeed to an analytical expression of the ground-state energy of the He-like ions. Thus, an analytical calculation for the ground-state energy and radial expectation values of Helium isoelectronic sequence is managed by using a wavefunction of the type of Bhattacharyya [12] [14]. Besides, developing the orbital atomic theory, Slater in [15] introduced the notions of screen constant σ and effective quantum number n^* for the calculation of the energy of an electronic configuration given containing N electrons.

On the basis of his theory, Slater expresses analytically the total energy of an atomic system of N electrons according to σ and n^* determined from rules that he established. The analytical formula of Slater permits the simple calculation of the ground-state energy of He-like ions for which $N = 2$, $\sigma = 0.30$ and $n^* = 1$.

For the doubly excited states in He-like ions, since the early experiment [16] and theoretical explanation [17], Doubly Excited States (DES) of Helium isoelectronic sequence have been the target of a number of theoretical approaches. Greatest attention have been concentrated on studying symmetric DES (n^2) with excited electrons having equal values of principal quantum number n (intrashell states) where the electronic correlation effect may be predominant [18]. The investigations of the intrashell states of two-electrons systems are advanced and due to the group theoretical method [19] which allowed intrashell states to be approximatively classified and some of these properties studied [20]. Theoretical investigations of (n^2) doubly excited states are performed by using various method. The projection operator method and group theoretical methods [20] have been used for energies calculations of the $2s^2$, $2p^2$ states in Helium-like ions. Time independent variational perturbation [21] was applied for total energies calculations of the $2s^2$, $2p^2$ and $3d^2$ states in He, Li^+ , Be^{2+} and B^{3+} . The correlation part of the energies for the $2s^2$, $2p^2$, $3s^2$, $3p^2$, $3d^2$ states in He isoelectronic series have been investigated by using perturbation theory [4]. The Screening Constant by Unit Nuclear charge (SCUNC) method [22] used a semi-empirical procedure to calculate $(ns^2)^1S$, $(np^2)^1D$ and $(Nsnp)^1P^o$ excited state of He-like ions. Recently the Modified Atomic Orbital Theory (MAOT) has been applied successfully in the studies of high lying $^{1,3}P^o$ of He-like ions [1]. In this paper, we apply the first MAOT variational procedure, to calculate the ground-state energy $2s^2^1S$ and the total energies of the singlet DES $2p^2^1D$, $3d^2^1G$ and $4f^2^1I$ of He isoelectronic sequence from H^- to Ca^{18+} . In addition, for the first time in our knowledge, we have also calculated theoretical the screening constant σ_{theo} which is compared with experimental Slater screening constant (σ_{exp}) determined from his rule. Our present procedure leads to analytical expression which are carried out under MAXIMA computational program. Our energies positions are compared to other available theoretical and experimental data.

2. Theory

2.1. Brief Description of the MAOT Formalism

In the framework of Modified Atomic Orbital Theory (MAOT), total energy of ($\nu\ell$)-given orbital is expressed in the form [1] [23]:

$$E(\nu\ell) = -\frac{[Z - \sigma(\ell)]^2}{\nu^2} \quad (1)$$

For an atomic system of several electrons M , the total energy is given by (in Rydberg):

$$E = -\sum_{i=1}^M \frac{[Z - \sigma_i(\ell)]^2}{\nu_i^2}$$

With respect to the usual spectroscopic notation $(N\ell, N\ell')^{2S+1}L^{\pi}$, this equation becomes

$$E = -\sum_{i=1}^M \frac{\left[Z - \sigma_i \left({}^{2S+1}L_J \right) \right]^2}{\nu_i^2} \quad (2)$$

In the photoionization study, energy resonances are generally measured relatively to the E_∞ converging limit of a given $({}^{2S+1}L_J)nL$ -Rydberg series. For these states, the general expression of the energy resonances is given by the formula [24] presented previously (in Rydberg units):

$$E_n = E_\infty - \frac{1}{n^2} \left\{ Z - \sigma_1 \left({}^{2S+1}L_J \right) - \sigma_2 \left({}^{2S+1}L_J \right) \times \frac{1}{n} - \sigma_2^\alpha \left({}^{2S+1}L_J \right) \times (n-m) \times (n-q) \sum_k \frac{1}{f_k(n, m, q, s)} \right\}^2 \quad (3)$$

In this equation m and q ($m < q$) denote the principal quantum numbers of the $({}^{2S+1}L_J)nL$ -Rydberg series of the considered atomic system used in the empirical determination of the $\sigma_k({}^{2S+1}L_J)$ -screening constants, s represents the spin of the nL -electron ($s = 1/2$), E_∞ is the energy value of the series limit generally determined from the NIST atomic database, E_n denotes the corresponding energy resonance, and Z represents the nuclear charge of the considered element. The only problem that one may face by using the MAOT formalism is linked to the determination of the $\sum_k \frac{1}{f_k(n, m, q, s)}$ term. The correct expression of this term

is determined iteratively by imposing general Equation (3) to give accurate data with a constant quantum defect values along all the considered series. The value of α in the σ_2 of the last term is fixed to 1 and 2 during the iteration. The quantum defect δ is calculated from the standard formula

$$E_n = E_\infty - \frac{RZ_{core}^2}{(n-\delta)^2} \Rightarrow \delta = n - Z_{core} \sqrt{\frac{R}{(E_\infty - E_n)}} \quad (3 \text{ bis})$$

In this Equation (3 bis), R is the Rydberg constant, Z_{core} represents the electric charge of the core ion.

Z_{core} is directly obtained by the photoionization process from an atomic X system $X + h\nu \rightarrow X^{p+} + pe^-$

$f_k = f_k \left({}^{2S+1}L_J, n, s, m, q \right)$ are screening constants to be evaluated empirically with k taking the values from 1 to q .

L_j : denote the considered quantum state (S, P, D, F, \dots).

2.2. Variational Procedure of Calculations

For the $2s^2 \ ^1S$ ground state and each doubly excited states $2p^2 \ ^1D$, $3d^2 \ ^1G$, $4f^2 \ ^1I$, we constructed the basis wave functions below by combining Slater-type wave function [1] and Hylleraas-type wave functions [2]:

$$\phi_{jkmn}(\mathbf{r}_1, \mathbf{r}_2) = (r_1 r_2)^{(v-1)} \times \exp \left(- \left(\frac{Z - \sigma}{\nu \times a_0} \right) (r_1 + r_2) \right) (r_1 + r_2)^j (r_1 - r_2)^k |\mathbf{r}_1 - \mathbf{r}_2|^m \quad (4)$$

We considered parameter

$$\xi = \frac{Z - \sigma}{\nu \times a_0} \quad (5)$$

and Z, σ, ν and a_0 are respectively the nucleus charge number, the screening constant, the principal quantum number and Bohr's radius

$$\phi_{jkmn}(\mathbf{r}_1, \mathbf{r}_2) = (r_1 r_2)^{(\nu-1)} \times \exp(-\xi(r_1 + r_2)) (r_1 + r_2)^J (r_1 - r_2)^K |r_1 - r_2|^M \quad (6)$$

$$\text{With } |r_1 - r_2| = \sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos \theta_{12}}$$

where \mathbf{r}_1 and \mathbf{r}_2 denote the positions of the two electrons;

r_1 and r_2 are respectively used for $|\mathbf{r}_1|$ and $|\mathbf{r}_2|$, J, K, M are Hylleraas parameters with $(J, K, M \geq 0)$.

J takes into account the distance of the two electrons from the nucleus.

K takes into account the approximation of the two electrons from the nucleus.

M takes into account the distance between the two electrons.

From Equation (5) the screening constant can be expressed

$$\sigma = Z - a_0 \nu \xi \quad (7)$$

The final form of the wave function of the singlet doubly excited state can be written as follow:

$$\Psi_n(\mathbf{r}_1, \mathbf{r}_2) = \sum_{jkm} \beta_{jkm} \phi_{jkmn}(\mathbf{r}_1, \mathbf{r}_2) \quad (8)$$

where the coefficients β_{jkm} are determined by solving the Schrödinger equation:

$$H\Psi_n(\mathbf{r}_1, \mathbf{r}_2) = E\Psi_n(\mathbf{r}_1, \mathbf{r}_2) \quad (9)$$

where the Hamiltonian operator H has the form:

$$H = T + C + W \quad \text{with} \quad (10)$$

$$T = \frac{-\hbar^2}{2m} (\nabla_1 + \nabla_2); \quad C = -\left(\frac{Ze^2}{r_1} + \frac{Ze^2}{r_2} \right); \quad W = \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \quad (11)$$

where T is the kinetic energy, C is the Coulomb potential between the atomic nucleus and the two electrons, W is the Coulomb interaction between electrons.

In the Hamilton operator we neglected all magnetic and relativistic effects together with the motion of the atomic nucleus.

In this Equation (11), Z is the nuclear charge ∇_1 is the Laplacian with reference to the coordinates of the vector radius \mathbf{r}_1 which detect the position of the electron 1. ∇_2 Laplacian defines the coordinates of the vector radius \mathbf{r}_2 which detect the position of the electron 2 and $|\mathbf{r}_1 - \mathbf{r}_2|$ inter-electronic distance.

The representation of the Schrödinger equation on the non-orthogonal basis leads to the general eigenvalue equation [25];

$$\sum_{(j,k,m),(j'k'm')} (H_{JKMnl} - EN_{JKMnl}) = 0 \quad (12)$$

With $J = j + j'$; $K = k + k'$; $M = m + m'$

$$N_{JKMnl} = \langle \phi_{jkmnl} | \phi_{j'k'm'nl} \rangle: \text{ is the normalization factor} \quad (13)$$

$$H_{JKMnl} = \langle \phi_{jkmnl} | H | \phi_{j'k'm'nl} \rangle: \text{ is the matrix elements of Hamilton operator (14)}$$

E : is the eigenvalue of the energy

$$H_{JKMnl} = T_{jkm,j'k'm'nl} + C_{JKMnl} + W_{JKMnl} \quad (15)$$

$T_{jkm,j'k'm'nl}$: is the matrix elements of the kinetic Energy operator of the two electrons

C_{JKMnl} : is the matrix elements of the Coulombian interaction Energy operator between the nucleus and the two electrons

W_{JKMnl} : is the matrix elements of the Coulombian interaction Energy operator between the two electrons

Thus following the form of the basis wave function above (4), we have constructed for each state a special wave function and then calculated the matrix elements N_{JKMnl} , C_{JKMnl} , W_{JKMnl} , $T_{jkm,j'k'm'nl}$

For example on $2p^2$ states: $n = \nu = 2; l = 1$

The wave function is written as follow:

$$\phi_{jkm21}(\mathbf{r}_1, \mathbf{r}_2) = (r_1 r_2) \times \exp(-\xi(r_1 + r_2))(r_1 + r_2)^J (r_1 - r_2)^K |\mathbf{r}_1 - \mathbf{r}_2|^M \quad (16)$$

The matrix elements of the normalization factor is written as follow:

$$N_{JKM21} = \langle \phi_{jkm21} | \phi_{j'k'm'21} \rangle \quad (17)$$

$$N_{JKM21} = \iiint d^3 r_1 d^3 r_2 \phi_{jkm21}(\mathbf{r}_1, \mathbf{r}_2) \times \phi_{j'k'm'21}(\mathbf{r}_1, \mathbf{r}_2) \quad (18)$$

$$N_{JKM21} = \iiint d^3 r_1 d^3 r_2 (r_1 r_2)^2 (r_1 + r_2)^J (r_1 - r_2)^K |\mathbf{r}_1 - \mathbf{r}_2|^M \times \exp(-2\xi(r_1 + r_2)) \quad (19)$$

$$\text{With } \iiint d^3 r_i = \int r_i^2 dr_i \int_0^\pi \sin \theta_i d\theta_i \int_0^{2\pi} d\varphi_i = 4\pi \int r_i^2 dr_i \quad (i = 1, 2) \quad (20)$$

The matrix elements of the Coulombian interaction Energy operator between the nucleus and the two electrons is written as follow:

$$C_{JKMnl} = \langle \phi_{jkm21}(\mathbf{r}_1, \mathbf{r}_2) | C | \phi_{j'k'm'21}(\mathbf{r}_1, \mathbf{r}_2) \rangle \quad (21)$$

$$C_{JKM21} = \langle \phi_{jkm21}(\mathbf{r}_1, \mathbf{r}_2) | -Ze^2 \left(\frac{1}{r_1} + \frac{1}{r_2} \right) | \phi_{j'k'm'21}(\mathbf{r}_1, \mathbf{r}_2) \rangle \quad (22)$$

$$C_{JKM21} = -Ze^2 \iiint d^3 r_1 d^3 r_2 \phi_{jkm21}(\mathbf{r}_1, \mathbf{r}_2) \left(\frac{1}{r_1} + \frac{1}{r_2} \right) \phi_{j'k'm'21}(\mathbf{r}_1, \mathbf{r}_2) \quad (23)$$

The matrix elements of the Coulombian interaction Energy operator between the two electrons is expressed as follow:

$$W_{JKM21} = \langle \phi_{jkm21}(\mathbf{r}_1, \mathbf{r}_2) | \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} | \phi_{j'k'm'21}(\mathbf{r}_1, \mathbf{r}_2) \rangle \quad (24)$$

$$W_{JKM21} = \iiint d^3 r_1 d^3 r_2 \phi_{jkm21}(\mathbf{r}_1, \mathbf{r}_2) \left(\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right) \phi_{j'k'm'21}(\mathbf{r}_1, \mathbf{r}_2) \quad (25)$$

The matrix elements of the kinetic Energy operator of the two electrons is ex-

pressed as follow:

$$T_{jkm,j'k'm'21} = \left\langle \phi_{jkm21}(\mathbf{r}_1, \mathbf{r}_2) \left| \frac{-\hbar^2}{2m} (\nabla_1 + \nabla_2) \right| \phi_{j'k'm'21}(\mathbf{r}_1, \mathbf{r}_2) \right\rangle \quad (26)$$

Calculations for the other matrix elements of other states were obtained in the same procedure.

The mathematical development of the Hamiltonian applied to each wave function of each states leads to simplified analytical expressions which are carried out under MAXIMA computational program.

Concerning the screening constant σ and the variational parameter ξ , the procedure is as follow:

From the Slater condition $0.3 \leq \sigma \leq 1$, and taken into account Equation (5), the parameter ξ can be expressed as follow:

$$\frac{Z-1}{n} \leq \xi \leq \frac{Z}{n} \quad (27)$$

In order to obtain the theoretical screening constant σ_{theo} , the exponential parameter ξ and the minimum eigenvalue in which we are interested, the analytical expressions of each matrix elements of each state are carried out by our self MAXIMA computational program.

MAXIMA is a computer algebra system for the manipulation of symbolic and numerical expressions, including differentiation, integration, ordinary differential equations, and matrix elements. MAXIMA yields high precision numeric results by using exact fractions, arbitrary precision integers, and variable precision floating point numbers. Our MAXIMA source code is compiled on windows systems.

At the beginning, the variational parameter ξ is determined as shown (27). For each value of Z and n , we know a limited area of the variational parameter ξ . Thus for each value of Z , n and ξ , the program calculated directly the screening constant σ as shown the Equation (7) and then the eigenvalue E . To obtain the minimum eigenvalue and the theoretical screening constant in which we are interested and quoted in tables 1 - 4, the variational parameter ξ and the Hylleraas parameters (J, K, M) are slightly varied that exhibit a plateau for the energy.

3. Results and Discussions

The main results of our calculations for the theoretical screening constant, the variational parameter ξ and energies concerning the $1s^2\ ^1S$ ground-state and the Doubly Excited State for $2p^2\ ^1D$, $3d^2\ ^1G$ and $4f^2\ ^1I$ of helium isoelectronic sequence are quoted respectively in **Tables 1-4**. Our present results are compared with other theoretical calculations and experimental data. Then our results are converted into Rydberg for direct comparison by using the infinite Rydberg $1\text{Ry} = 0.5\ \text{a.u} = 13.605698\ \text{eV}$. **Table 1** shows a comparison of the present calculation for the $1s^2\ ^1S$ ground-state energy with the experimental data [6] [7] [8], and the theoretical results [9] [10] [11] [12] [15]. In addition the theoretical screening

Table 1. Variational parameter ξ and ground energies for $1s^2\ ^1S$ states of Helium isoelectronic sequence. The values are reported in Rydberg (Ry). $1\text{Ry} = 13.605698\text{ eV}$. The screening constant sigma ($\sigma_{theo} = 0.3101$).

	Theory								Experiment	
	ξ	$-E^{MAOT}$	$-E^{Sakho}$	$-E^P$	$-E^C$	$-E^D$	$-E^{Slater}$	$-E^U$	$-E^{exp}$	$-E^{a,b}$
H ⁻	0.6899	1.0098	1.1406			1.0164		0.9745		
He	1.6899	5.7951	5.8872	5.8071	5.8078	5.7784	5.7799	5.7233	5.8063	5.8071 ^a
Li ⁺	2.6899	14.5063	14.6401	14.5593	14.5615	14.5321	14.6049	14.4726	14.4645	14.5593 ^b
Be ²⁺	3.6899	27.2554	27.3907	27.3113	27.3150	27.2844	27.4260	27.2224	27.2238	27.3120 ^b
B ³⁺	4.6899	43.9813	44.1403	44.0616	44.0690	44.0352	44.2542	43.9720	43.9815	44.0683 ^b
C ⁴⁺	5.6899	64.7582	64.8904	64.8125	64.8228	64.7860	65.0896	64.7221	64.7449	64.8294 ^b
N ⁵⁺	6.6899	89.5054	89.6403	89.5624	89.5779	89.5367	89.9314	89.4720		89.5999 ^b
O ⁶⁺	7.6899	118.3513	118.3908	118.2886	118.3342	118.2872	118.7803	118.2952		118.3834 ^b
F ⁷⁺	8.6899	151.0853	151.1403	151.0631	151.0903	151.0374	151.6357	150.9721		151.2366 ^b
Ne ⁸⁺	9.6899	187.9563	187.8903	187.8840	187.8477	187.7874	188.4974	187.7221		188.0050 ^b
Na ⁹⁺	10.6899	228.6006	228.6395		228.6056	228.5373	228.9797	228.4719		
Mg ¹⁰⁺	11.6899	273.4513	273.3906		273.3648	273.2877	273.7801	273.2222		
Al ¹¹⁺	12.6899	322.0992	322.1407		322.1245	322.0378	322.5802	321.9724		
Si ¹²⁺	13.6899	374.9353	374.8907		374.8855	374.7878	375.3802	374.7224		
P ¹³⁺	14.6899	431.4453								
S ¹⁴⁺	15.6899	492.1952								
Cl ¹⁵⁺	16.6899	556.9453								
Ar ¹⁶⁺	17.6899	625.6953								
K ¹⁷⁺	18.6899	698.4452								
Ca ¹⁸⁺	19.6899	775.1954								

E^{MAOT} : Energy E of the Modified Atomic Orbital Theory (MAOT), present work. E^{Sakho} (Sakho, 2006) [11]; E^P (Pekeris, 1962); E^C (Drake, 1988) [9]; E^{Slater} (Minkine, 1982) [15]; $E^{a,b}$ Experimental data (Radzig, 1985 [7]; Arnaud, 1993) [8]; E^{exp} (Moore, 1971) [6]; E^D (Utpal and Talukdar, 1999) [12]; E^U (Roothaan *et al.*, 1960) [10].

constant $\sigma_{theo} = 0.3101$ is also presented and agree very good with the experimental screening constant of Slater $\sigma_{Slater} = 0.30$ determined from his rule ($\sigma_{Slater} = 0.30$ for $1s^2$ state, $n = 1$). For H⁻ ($Z = 1$), our results at -1.0098 Ry are compared with those of [10] [11] [12], respectively at -1.14069 Ry; -1.01648 Ry and -0.97459 Ry and it can see the good agreement. Comparison indicates that MAOT results agree well with each other up to $Z = 10$. For $10 < Z \leq 14$, our results are compared with those of [10] [11] [15]. Comparison indicates that for $Z = 14$, our total energy at -374.9353 Ry agree with [11] at -374.89072 Ry, with [9] at -374.88558 Ry, with [15] at -375.38022 Ry and with [10] at -374.72241 Ry. Generally, this good agreement enables to expect our results with MAOT calculation for ground-state energy up to $Z = 20$ to be accurate.

In **Table 2**, we presented the theoretical screening constant $\sigma_{theo} = 0.3512$ and reported the value of the variational parameter ξ and total energies for $2p^2\ ^1D$

Table 2. Parameter ξ and total energies E for doubly excited $2p^2\ ^1D$ states. The values are reported in Rydberg (Ry). $1\text{Ry} = 13.605698\ \text{eV}$. The screening constant sigma ($\sigma_{theo} = 0.3512$).

	Theory							Experiment	
	ξ	$-E^{MAOT}$	$-SCUNC$	$-E^{BIA}$	$-E^r$	$-E^s$	$-E^b$	$-E^{r,f}$	$-E^{Ray}$
H ⁻	0.3244	0.2335							
He	0.8244	1.3841	1.4052	1.4097			1.4266	1.4052 ^e	1.3728
Li ⁺	1.3244	3.5398	3.5418	3.5565	3.5110	3.5411	3.5565	3.5396 ^f	3.3906
Be ²⁺	1.8244	6.6838	6.6788	6.6993	6.6545	6.6751	6.6861		6.5097
B ³⁺	2.3244	10.8132	10.8153	10.8403	10.7976	10.8072	10.8160		10.6266
C ⁴⁺	2.8244	15.9892	15.9514	15.9793			15.9455		
N ⁵⁺	3.3244	22.0819	22.0885	22.1186			22.0753		
O ⁶⁺	3.8244	29.1999	29.2252	29.2568			29.2046		
F ⁷⁺	4.3244	37.3396	37.3615	37.3946			37.3350		
Ne ⁸⁺	4.8244	46.5156	46.4981	46.5327			46.4643		
Na ⁹⁺	5.3244	56.6209							
Mg ¹⁰⁺	5.8244	67.7463							
Al ¹¹⁺	6.3244	79.9033							
Si ¹²⁺	6.8244	93.0931							
P ¹³⁺	7.3244	107.2076							
S ¹⁴⁺	7.8244	122.3587							
Cl ¹⁵⁺	8.3244	138.4988							
Ar ¹⁶⁺	8.8244	155.6603							
K ¹⁷⁺	9.3244	173.8364							
Ca ¹⁸⁺	9.8244	193.0401							

E^{MAOT} : Energy E of the Modified Atomic Orbital Theory (MAOT), present work. SCUNC (Sakho, 2008) [22]; E^{BIA} (Biaye et al., 2005) [2]; E^{Ray} Experimental data (Ray et al., 1991) [21]; E^r (Roy et al., 1997) [26]; E^s (Ho and Bhatia, 1991) [27]; E^b (Ivanov and Safronova, 1993) [4]; E^r Experimental data (Hicks and Comer, 1975) [28]; E^f Experimental data (Diehl et al., 1999) [29].

doubly excited states of He-like ions up to $Z = 20$. For this state, comparison shows that MAOT results agree well with the theoretical results of [2] [4] [21] [22] [26] [27] and also the experimental data of [28] [29]. For $Z \leq 10$, comparison indicates that results agree well with each other. In addition, we calculated the energy of the ion Hydrogen H⁻ where there is no available data for comparison. For $Z = 10$, our results at $-46.5156\ \text{Ry}$ are compared with those of [2] [4] [22] respectively at $-46.49816\ \text{Ry}$; $-46.53271\ \text{Ry}$ and $-46.46435\ \text{Ry}$. Thus, this good agreement allowed us to expect our results up to $Z = 20$ to be also accurate.

Table 3 indicates the present MAOT calculation for the $3d^2\ ^1G$ DES that are compared with those of [2] [4] [21] [30] [31]. Here, except the ion Hydrogen H⁻ ($Z = 1$) where there is no available results, the agreements between the calculation are generally good up to $Z = 5$. Thus for $5 < Z \leq 10$, our results are compared with

Table 3. Parameter ξ and total energies E for doubly excited ($3d^2\ ^1G$) states. The values are reported in Rydberg (Ry). $1\text{Ry} = 13.605698\text{ eV}$. The screening constant sigma ($\sigma_{theo} = 0.3512$).

	Theory							
	ξ	$-E^{MAOT}$	$-E^{Sakho}$	$-E^a$	$-E^b$	$-E^c$	$-E^d$	$-E^{Ray}$
H ⁻	0.2162	0.0152	-	-	-	-	-	-
He	0.5495	0.6260	0.6104	0.6166	0.6308	0.6303	0.5849	0.6232
Li ⁺	0.8829	1.6004	1.5486	1.5538	1.5837	1.5618	1.5247	1.4601
Be ²⁺	1.2162	2.9529	2.9313	2.9320	2.9762	2.9377	2.9085	2.8421
B ³⁺	1.5495	4.7596	4.7585	4.7540	4.8105	4.7581	4.7360	4.6669
C ⁴⁺	1.8829	7.1927	7.0301	7.0180	7.0875	7.0229		
N ⁵⁺	2.2162	9.8973	9.7461	9.7280	9.8079	9.7321		
O ⁶⁺	2.5495	13.0334	12.9066	12.882	12.9718	12.8858		
F ⁷⁺	2.8829	16.5999	16.5116	16.4800	16.5797	16.4840		
Ne ⁸⁺	3.2162	20.5969	20.5609	20.5200	20.6316	20.5265		
Na ⁹⁺	3.5495	25.0246						
Mg ¹⁰⁺	3.8829	29.8814						
Al ¹¹⁺	4.2162	35.1721						
Si ¹²⁺	4.54959	40.8918						
P ¹³⁺	4.88293	47.0424						
S ¹⁴⁺	5.21626	53.6234						
Cl ¹⁵⁺	5.54959	60.6351						
Ar ¹⁶⁺	5.88293	68.0777						
K ¹⁷⁺	6.21626	75.9507						
Ca ¹⁸⁺	6.54959	84.2544						

E^{MAOT} : Energy E of the Modified Atomic Orbital Theory (MAOT), present work. E^{Sakho} (Sakho,2010) [30]; E^a (Bachau et al., 1991) [31]; E^b (Biaye,2005) [2]; E^c (Ivanov and Safronova, 1993) [4]; E^d (Ho, 1989) as quoted in (Biaye, 2005) [2]; E^{Ray} (Ray et al., 1991) [21].

those of [2] [4] [30] [31] and it can be seen that the present MAOT results agrees well with each other. Comparison indicates that ($Z = 10$) our results at -20.5969 Ry agrees very well with them respectively at -20.56099 Ry, -20.52000 Ry, -20.63354 Ry and -20.52658 Ry for [4]. In addition, the theoretical screening constant is also calculated ($\sigma_{theo} = 0.3512$). This good agreement allows us to expect our results with MAOT calculation for $3d^2\ ^1G$ doubly excited state up to $Z = 20$ to be accurate.

In **Table 4**, we present our calculation for the $4f^2\ ^1I$ doubly excited state and compare our results with theoretical results of [2] [30] and [32]. In our knowledge, experimental data are not available yet and also for the ion Hydrogen H⁻ ($Z = 1$). Here the agreements between the calculations are seen to be very satisfactory. As far as comparisons with the SCUNC results of [2] [30] and [32] are

Table 4. Parameter ξ and total energies E for doubly excited $4\ell^2 1I$ states. The values are reported in Rydberg (Ry). $1\text{Ry} = 13.605698 \text{ eV}$. The screening constant sigma ($\sigma_{theo} = 0.3508$).

	Theory				
	ξ	$-E^{MAOT}$	$-E^{Sakho}$	$-E^{Biaye}$	$-E^{Ho}$
H ⁻	0.1623	0.04848	-	-	-
He	0.4123	0.32906	0.32380	0.3591	0.34080
Li ⁺	0.6623	0.85937	0.83464	0.89778	
Be ²⁺	0.9123	1.63938	1.59547	1.68285	
B ³⁺	1.1623	2.66909	2.60631	2.71550	
C ⁴⁺	1.4123	3.95001	3.86714	3.99645	
N ⁵⁺	1.6623	5.47766	5.37798	5.52616	
O ⁶⁺	1.9123	7.25650	7.13881	7.30493	
F ⁷⁺	2.1623	9.28507	9.14965	9.33300	
Ne ⁸⁺	2.4123	11.56332	11.41048	11.61005	
Na ⁹⁺	2.6623	14.09130			
Mg ¹⁰⁺	2.9123	16.86898			
Al ¹¹⁺	3.1623	19.89637			
Si ¹²⁺	3.4123	23.17405			
P ¹³⁺	3.6623	26.70029			
S ¹⁴⁺	3.9123	30.47681			
Cl ¹⁵⁺	4.1623	34.50304			
Ar ¹⁶⁺	4.4123	38.77898			
K ¹⁷⁺	4.6623	43.30464			
Ca ¹⁸⁺	4.9123	48.07999			

E^{MAOT} : Energy E of the Modified Atomic Orbital Theory (MAOT), present work. E^{Sakho} (Sakho, 2010) [30]; E^{Biaye} (Biaye *et al.*, 2005) [2]; E^{Ho} (Ho, 1989) as quoted in (Biaye *et al.*, 2005) [2].

concerned, our results for $Z = 2$, at -0.32906 Ry , agree well with them respectively at -0.32380 Ry ; -0.35913 Ry and -0.34080 Ry . For $2 < Z \leq 10$, it can be seen the present MAOT results agrees with each other, and the agreement can be seen up to $Z = 10$ between our results at -11.56322 Ry and that from theoretical calculations [30] and [2] respectively at -11.41048 Ry , and -11.61005 . As a result, our listed data up to $Z = 20$ are expected to be also accurate. In addition the screening constant is also calculated $\sigma_{theo} = 0.3508$. The good agreement between the results quoted in **Tables 1-4** indicate the validity of this MAOT variational procedure and his merit to calculate the ($n\ell$) ground-state and doubly excite state energies.

4. Summary and Conclusion

In this work, the variational procedure of the Modified Atomic Orbital Theory

(MAOT) has been applied for the first time to the calculations of the ground-state energy $2s^2\ ^1S$ and excitation energies of the doubly $2p^2\ ^1D$, $3d^2\ ^1G$, $4f^2\ ^1I$ excited states of the Helium isoelectronic sequence from Hydrogen ion H^- to Calcium ion Ca^{18+} . It has demonstrated the possibilities to construct a new correlated wave function adapted to the correct description of the electron-electron correlations phenomena in the ground and in the doubly excited nl^2 states of the He-like systems. These very important results obtained in this work indicate the possibility to apply the MAOT variational procedure to the treatment of atomic spectra in two electron systems and probably in more complex atomic systems. The good results give also the possibility to analyze resonance energies via a very MAOT flexible procedure, in contrast to the complex procedures of experimental and theoretical methods based on the determination of the photoionization cross-section.

Acknowledgements

The authors are grateful to the Abdus Salam International Centre for Theoretical Physics, Trieste, Italy, the Orsay Institute of Molecular Sciences (OIMS), Paris, France and the Swedish International Development Agency (SIDA) for support.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

References

- [1] Sakho, I. (2012) Modified Atomic Orbital Theory Applied to the Calculation of High-Lying $2(K,T)n^{+1,3}P^0$ Rydberg Series of He-Like Ions. *Natural Science*, **4**, 73-78. <https://doi.org/10.4236/ns.2012.41011>
- [2] Biaye, M., Konté, A., Faye, N.A.B. and Wague, A. (2005) The Singlet Doubly Excited $(nl)^2$ States of Helium-Like Systems. *Physica Scripta*, **71**, 39. <https://doi.org/10.1088/0031-8949/71/1/006>
- [3] Wague, A. (1990) Electron Correlation Processes in Atomic Doubly Excited States Ionization. *LAMP Seminar ICTP*, Trieste, July 1990.
- [4] Ivanov, A.I. and Safronova, I.U. (1993) Calculation of the Correlation Part of the Energy of Two-Electron System. *Optics and Spectroscopy*, **75**, 506.
- [5] Ivanov, A.I. (1995) Analytical Properties of the Exact Energy of the Ground-State of a Two Electrons Atoms as Function of $1/Z$. *Physical Review A*, **52**, 3. <https://doi.org/10.1103/PhysRevA.52.1942>
- [6] Moore, C.E. (1971) Atomic Energy Levels (National Standard Reference Data Series, No. 35 U. S. GPO, Washington, D.C). Vol. 1, 4.
- [7] Radzig, A.A. and Smirnov, M.B. (1985) Reference Data on Atoms, Molecules and Ions. Springer, Berlin. <https://doi.org/10.1007/978-3-642-82048-9>
- [8] Arnaud, P. (1993) Cours de chimie physique. 3rd Edition, Dunod, Paris, Chapter 11, 88.
- [9] Drake, G.W. (1988) Theoretical Energies for the $n = 1$ and 2 States of the Helium Isoelectronic Sequence up to $Z = 100$. *Canadian Journal of Physics*, **66**, 586-611.

<https://doi.org/10.1139/p88-100>

- [10] Roothaan, C.C.J., Sachs, L.M. and Weiss, A.W. (1960) Analytical Self-Consistent Field Functions for the Atomic Configurations $1s^2$, $1s^2 2s$, and $1s^2 2s^2$. *Reviews of Modern Physics*, **32**, 186.
- [11] Sakho, I., et al. (2006) Calculation of the Ground-State Energy, the First Ionization Energy and the Radial Correlation Expectation Value for He-Like Atoms. *Physica Scripta*, **74**, 180-186. <https://doi.org/10.1088/0031-8949/74/2/005>
- [12] Utpal, R. and Talukdar, B. (1999) Electron Correlation for Helium-Like Atoms. *Physica Scripta*, **59**, 133. <https://doi.org/10.1238/Physica.Regular.059a00133>
- [13] Kleinekathöfer, U., Patil, S.H., Tang, K.T. and Toenies, J.P. (1996) Boundary-Condition-Determined Wave Function for the Ground State of Helium and Isoelectronic Ions. *Physical Review A*, **54**, 2840. <https://doi.org/10.1103/PhysRevA.54.2840>
- [14] Bhattacharyya, S., Bhattacharyya, A., Talukdar, B. and Deb, N.C. (1994) Analytical Approach to the Helium-Atom Ground State Using Correlated Wavefunctions. *Journal of Physics B: Atomic, Molecular and Optical Physics*, **29**, L147. <https://doi.org/10.1088/0953-4075/29/5/003>
- [15] Minkine, V., Simkine, B. and Miniaev, R. (1982) Théorie de la Structure Moléculaire. Mir, Paris, Chapter 3, 65.
- [16] Codling, K., Madden, R.P. and Ederer, D.L. (1967) Resonances in the Photo-Ionization Continuum of Ne I (20-150 eV). *Physical Review*, **155**, 26. <https://doi.org/10.1103/PhysRev.155.26>
- [17] Cooper, J.W., Fano, U. and Prats, F. (1963) Classification of Two-Electron Excitation Levels of Helium. *Physical Review Letters*, **10**, 518. <https://doi.org/10.1103/PhysRevLett.10.518>
- [18] Fano, U. (1983) Correlations of Two Excited Electrons. *Reports on Progress in Physics*, **46**, 97. <https://doi.org/10.1088/0034-4885/46/2/001>
- [19] Rau, P.R.A. (1990) Group Theoretical Treatments of Strongly Correlated Atomic Dynamics. *Reports on Progress in Physics*, **53**, 181. <https://doi.org/10.1088/0034-4885/53/2/002>
- [20] Herrick, R.D., Kellman, E.M. and Poliak, D.R. (1980) Supermultiplet Classification of Higher Intrashell Doubly Excited States of H^- and He. *Physical Review A*, **22**, 1517. <https://doi.org/10.1103/PhysRevA.22.1517>
- [21] Ray, D. and Mukherjee, P.K. (1991) Doubly Excited $^1S^e$, $^1D^e$ and $^1G^e$ States of He, Li^+ , Be^{2+} and B^{3+} . *Journal of Physics B: Atomic, Molecular and Optical Physics*, **19**, 1241-1249. <https://doi.org/10.1088/0953-4075/24/6/013>
- [22] Sakho, I. (2008) Screening Constant by Unit Nuclear Charge Calculations for $(n s^2)^1S^e$, $(np^2)^1D^e$ and $(N s n p)^1P^o$ Excited States of He-Like Systems. *The European Physical Journal D*, **47**, 37-44. <https://doi.org/10.1140/epjd/e2008-00018-2>
- [23] Sakho, I. (2013) Photoabsorption of H^- and He via the Modified Atomic Orbital Theory: Application to the 1P -Rydberg State. *Chinese Journal of Physics*, **51**, 209. <https://doi.org/10.6122/CJP.51.209>
- [24] Sakho, I. (2014) General Formalism of the Modified Atomic Orbital theory for the Rydberg Series of Atoms and Ions: Application to the Photoionization of Ne^+ . *Journal of Atomic and Molecular Sciences*, **5**, 206. <https://doi.org/10.4208/jams.110813.021414a>
- [25] Schmid, E.W., Spitz, G. and Losch, W. (1987) Theoretical Physics on the Personal Computer. Springer-Verlag, Berlin, Heidelberg, New York, London, Paris, Tokyo.
- [26] Roy, K.A., Singh, R. and Deb, M.B. (1997) Density-Functional Calculations for

- Doubly Excited States of He, Li⁺, Be²⁺ and B³⁺ (^{1,3}S^e, ³P^o, ^{1,3}D^e, ^{1,3}P^o, ¹G^e). *Journal of Physics B*, **30**, 4763. <https://doi.org/10.1088/0953-4075/30/21/014>
- [27] Ho, Y.K. and Bathia, A.K. (1991) Complex-Coordinate Calculation of ^{1,3}D Resonances in Two-Electron Systems. *Physical Review A*, **44**, 2895. <https://doi.org/10.1103/PhysRevA.44.2895>
- [28] Hicks, P.J. and Comer, J. (1975) Ejected Electron Spectroscopy of Autoionizing States Excited by Low Energy Electron Impact. *Journal of Physics B*, **8**, 1866. <https://doi.org/10.1088/0022-3700/8/11/022>
- [29] Diehl, S., Cubaynes, D., Bizau, J.P., Wuilleumier, F.J., Kenedy, E.T., Mosnier, J.P. and Morgan, T.J. (1999) New High-Resolution Measurements of Doubly Excited States of Li⁺. *Physica B*, **32**, 4193. <https://doi.org/10.1088/0953-4075/32/17/305>
- [30] Sakho, I. (2010) Calculations of (nl)² and (3lnl') Autoionizing States in Two-Electron Systems. *Physica Scripta*, **82**, Article ID: 035301. <https://doi.org/10.1088/0031-8949/82/03/035301>
- [31] Bachau, H., Martin, F., Riera, A. and Yanez, M. (1991) Resonance Parameters and Properties of Helium-Like Doubly Excited States: 2 ≤ Z ≤ 10. *Atomic Data and Nuclear Data Tables*, **48**, 167-212. [https://doi.org/10.1016/0092-640X\(91\)90006-P](https://doi.org/10.1016/0092-640X(91)90006-P)
- [32] Ho, Y.K. (1989) Resonances in Helium Atoms Associated with the N=4 and N=5 He⁺ Thresholds. *Zeitschrift für Physik D*, **11**, 277-281. <https://doi.org/10.1007/BF01438499>

List of the Symbols

σ_{theor} : (theo = theory): screening constant σ determined theoretically

E : Energy

H : Hamilton operator

N : Normalization factor

T : Kinetic Energy

W : Coulombian interaction potential operator between the two electrons

C : Coulombian interaction potential between the nucleus and the two electrons

∇_i : denotes the Laplacian operator ∇ with reference to the coordinates of the vector radius r_i which detect the position of the electron i .

∇_1 : is the Laplacian with reference to the coordinates of the vector radius r_1 which detect the position of the electron 1.

∇_2 : Laplacian defines the coordinates of the vector radius r_2 which detect the position of the electron 2.

r_i = denotes the position r of the electron i relative to the nucleus

r_1 and r_2 = denote respectively the position r of the electron 1 and the electron 2 relative to the nucleus.

$|r_1 - r_2|$: is an inter-electronic distance.

θ_i, φ_i = angular variables of the electron i

S : total spin

\hbar = reduced Planck constant such as $\hbar = h/2\pi$ with h the Planck constant

N = principal quantum number

l = orbital quantum number

Θ_{12} : angle between electron 1 and electron 2.

ξ : variational parameter zeta, a Greek alphabet

H^- : Hydrogen ion

He: Helium atom

Li^+ : Lithium ion

Be^{2+} : Beryllium ion

B^{3+} : Boron ion

C^{4+} : Carbon ion

N^{5+} : Nitrogen ion

O^{6+} : Oxygen ion

F^{7+} : Fluorine ion

Ne^{8+} : Neon ion

Na^{9+} : Sodium ion

Mg^{10+} : Magnesium ion

Al^{11+} : Aluminium ion

Si^{12+} : Silicon ion

P^{13+} : Phosphorus ion

S^{14+} : Sulfur ion

Cl^{15+} : Chlorine ion

Ar^{16+} : Argon ion

K^{17+} : Potassium ion

Ca^{18+} : Calcium ion