

## A modification of atomic orbital theory and its application to $(1snl)^1L^\pi$ and $(nl^2)^1L^\pi$ excited states of He-like ions

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**Abstract.** A modification of the Slater's atomic orbital theory (AOT) is presented in this paper and applied to the calculation of energies for  $(1sns)^1S^e$ ,  $(1snp)^1P^o$ ,  $(1snd)^1D^e$  and  $(ns^2)^1S^e$ ,  $(np^2)^1D^e$ ,  $(nd^2)^1G^e$ ,  $(nf^2)^1I^e$ ,  $(ng^2)^1K^e$ ,  $(nh^2)^1M^e$  excited states of He-like ions up to  $Z = 12$ . The inadequacy of Slater's AOT for excited states of the atomic systems is discussed. The results obtained in the present work are in good agreement with available experimental and theoretical results.

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**Key words:** atomic orbital theory, screening constant, semi-empirical calculations, excited states, helium-like ions

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## 1 Introduction

Since the early experiment of Madden and Codling [1] and others [2] and theoretical explanation of Cooper, Fano and Prats [3], doubly-excited states (DES) of helium-like ions have been the intention of several studies. Greatest attention has been concentrated on the study of symmetric DES ( $nl^2$ ) where the electronic correlation effects may be predominant as shown by Fano [4]. Some of these symmetric DES in two-electron systems have been identified in the solar flare [5] and in the solar corona [6] and, revealed experimentally by the studies of double Rydberg resonances in negative ions of rare gases [7,8]. Besides, higher-energy Rydberg envelopes contain doubly-excited states which are generally labelled in the usual spectroscopic notation  $(Nl, nl)^{2S+1}L^\pi$  with  $n = N, N+1$  [9]. In this notation,  $N$  and  $n$  denote respectively the principal quantum numbers of the inner and the outer electron,  $l$  and  $l'$  their respective orbital quantum numbers,  $S$  the total

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spin,  $L$  the total angular momentum and  $\pi$  the parity of the system. The lowest-energy envelope ( $N = 1$ ) contains the singly-excited states  $(1s, nl)^{2S+1}L^\pi$  approaching the first ionization threshold which have been over the years, the intention of some computations [10–12].

As concern the methods applied in the treatment of the helium-like atoms' properties in excited states, several techniques of computation have been performed. Among these methods are the hyperspherical close-coupling method [11], the method of computing double sums over the complete hydrogen spectrum [12], the diagonalization approximation [13–16] the variational method using the Hylleraas-type wave function [17, 18], the time-dependent variation perturbation theory [19], the variational method using the Pekeris-type electronic wavefunctions [20], the density-functional theory [21], the complex rotation method [22]. In all these *ab initio* methods, energies for excited states of He-like ions can't be expressed in a simple analytical formula. However, most of the preceding methods require large basis-set calculations involving a fair amount of mathematics complexity. But, it is widely believed that there are distinct advantages to viewing problems of physics within the framework of simple analytical models. Such analytical procedures have been performed successfully in the case of the ground -state of helium -like ions by Bethe and Salpeter [22] who express an excellent semi-empirical expansion for the first ionization energy of two-electron systems whereas Slater [24] developed his atomic orbital theory in the framework of a general semi-empirical approach and expresses analytical the total energy of an electronic configuration given containing several electrons.

Recently, Sakho [25] presents screening constant by unit nuclear charge analytical method very suitable for ground-state [26] and doubly excited states [25, 27, 28] of the helium isoelectronic sequence. Besides, if single-exponent Slater function [29] and complex-exponent Slater-orbitals [30] are employed in the study of the properties of atoms and molecules, the AOT as presented by Slater [24] is not suitable for excited states of atomic systems.

As AOT of Slater [24] is a suitable analytical approach for the ground state of atoms and isoelectronic ions, it will be interesting to present a modification of the Slater's AOT for excited states of atoms -like ions. Such study is the intention of this paper considering the particularly case of helium -like systems. In Section 2 we present our modification of the atomic orbital theory of Slater [24] after discussing its inadequacy for excited states of atomic systems. In Section 3, the presentation and the discussion of our results in the case of  $(1sns)^1S^e$ ,  $(1snp)^1P^o$ ,  $(1snd)^1D^e$  and  $(ns^2)^1S^e$ ,  $(np^2)^1D^e$ ,  $(nd^2)^1G^e$ ,  $(nf^2)^1I^e$ ,  $(ng^2)^1K^e$ ,  $(nh^2)^1M^e$  excited states of He-like ions up to  $Z = 12$  are made. All our results are compared to available theoretical and experimental data.

## 2 Theory

### 2.1 Inadequacy of atomic orbital theory of Slater for excited states

In 1930, J. C. Slater [24] proposed an approached method of calculation of the energy and the ionic radius of atomic systems containing several electrons by the determination of the effective charge number  $Z^*$

$$Z^* = Z - \sum_j \sigma_{ij} = Z - \sigma_i, \quad (1)$$

where  $\sigma_{ij}$  denotes the screening coefficient of the  $j$  electron on the  $i$  electron and  $\sigma_i$  represents the screening coefficient relative to the  $i$  electron.

The AOT of Slater uses special hydrogenic wave-functions of type

$$\Psi_{nlm} = N_n \left( \frac{r}{a_0} \right)^{n^*-1} \exp\left(-\zeta \frac{r}{a_0}\right) Y_{lm}(\Theta, \varphi), \quad (2)$$

where  $N_n = (2\zeta)^{n+1/2} [(2n)!]^{-1/2}$  is the normalisation factor;  $\zeta = \frac{Z-\sigma_i}{n^*}$  denotes the exponent orbital;  $n^*$  designs the effective quantum number linked to the principal quantum number  $n$  by an empirical rule established by Slater [24],  $Y(\Theta, \varphi)$  are the spherical harmonics.

The wave-functions of Slater are solution of the Schrödinger's equation where the Hamiltonian operator is in the form

$$\hat{H} = -\frac{\hbar^2}{2m} \Delta + \hat{V}(r). \quad (3)$$

In this equation, the potential energy operator  $\hat{V}(r)$  is in the shape

$$\hat{V}(r) = -e^2 \frac{(Z-\sigma_i)}{r} + \frac{\hbar^2}{2m} \frac{n^*(n^*-1)}{r^2}. \quad (4)$$

The eigenvalue corresponding to the eigenfunctions given by Eq.(2) is in the form

$$E = -\frac{me^4}{2\hbar^2} \frac{(Z-\sigma_i)^2}{(n^*)^2}. \quad (5)$$

In rydbergs, this result can be written as follows

$$E = -\frac{(Z-\sigma_i)^2}{(n^*)^2}. \quad (6)$$

For two-electron systems which interest our study, total energy in the view point of Slater's AOT is given by

$$E = -2 \frac{(Z-\sigma_i)^2}{(n^*)^2}. \quad (7)$$

On the other hand, the parameters  $\sigma_i$  and  $n^*$  are evaluated by using the Slater's rules. The value of  $n^*$  is linked to that of the principal quantum number  $n$  along these lines

$$\begin{array}{cccccc} n & \dots\dots\dots & 1 & 2 & 3 & 4 & 5 & 6 \\ n^* & \dots\dots\dots & 1 & 2 & 3 & 3.7 & 4 & 4.2 \end{array} \quad (8)$$

The screening coefficient  $\sigma_i$  are determined by dividing the atomic orbital in groups: (1s) (2s2p) (3s3p) (3d) (4s4p) (4d) (4f) (5s5p) and so on. Then, the value of  $\sigma_i$  is evaluated like so

$$\begin{aligned} (1s) &= 0.30(1s - 1), \\ (2p) &= (2s) = 0.85(1s) + 0.35(2s + 2p - 1), \\ (3p) &= (3s) = 1.00(1s) + 0.85(2s + 2p) + 0.35(3s + 3p - 1), \\ (4p) &= (4s) = 1.00(1s + 2s + 2p) + 0.85(3s + 3p + 3d) + 0.35(4s + 4p - 1), \\ (3d) &= 1.00(1s + 2s + 2p + 3s + 3p) + 0.85(2s + 2p) + 0.35(3d - 1). \end{aligned} \quad (9)$$

For the calculation of the screening coefficient for a given configuration, one must replace 1s, 2s, 2p, 3d, etc., in the second members of the above relations, by the number of electrons occupying the corresponding orbital. For example, in the particularly case of the ground state,  $\sigma = 0.30(2 - 1) = 0.30$ . Although the AOT of Slater is an approach analytical method, it permits to put into evidence the successive ionization energies of atoms, the energetical classification of the different AO (*the most stable electronic configuration corresponds to that of the lowest energy*) and also permits to justify the Klechkowsky's rule with respect to the filling's order of the 1s, 2s, 2p, 3s, 3p, 4s, 3d..., electronic configurations.

But, the AOT in its original formalism is not suitable for the study of excited states of atoms for mainly two reasons: Firstly, for excited states with  $n > 3$ , the effective quantum number  $n^*$  stills not a whole number (for  $n = 4$ ,  $n^* = 3.7$  and for  $n = 6$ ,  $n^* = 4.2$ ) as revealed by Eq. (8). This will influence for example in the energy value of symmetric DES ( $nl^2$ ) where  $n$  is a whole number; Secondly, for excited states, the screening coefficient  $\sigma$  conserves the same value for all orbitals. Using Eq. (9) one can see that:  $\sigma(2p) = \sigma(2s) = \sigma(3s) = \sigma(3p) = \dots = \sigma(4s) = \sigma(4p) = \sigma(3d) = 0.35$ . This indicates that the orbitals (2p) and (2s) have the same value of total energy. The predictions for (3s), (3p), (3d) and (4s), (4p), (4d), (4f) are of similar.

## 2.2 Modification of atomic orbital theory

The preceding observations show that, to formulate a modification of Slater's AOT for excited states, one must only reconsider the values of  $n^*$  and  $\sigma$ . In this purpose, we replace in the Slater's orbital wave-functions given by Eq.(2) and in the potential energy operator given by Eq.(4), the effective quantum number  $n^*$  by the principal quantum number  $n$ . Considering separately the atomic orbital noted here ( $\nu l$ ),  $\nu$  a principal quantum number,

the eigenvalue energy for ( $\nu l$ ) is using Eq.(6)

$$E(\nu l) = -\frac{[Z - \sigma(l)]^2}{\nu^2}. \quad (10)$$

For an atomic system of several electrons  $N$ , the total energy is given by (in rydbergs)

$$E = -\sum_{i=1}^N \frac{[Z - \sigma_i(l)]^2}{\nu_i^2}. \quad (11)$$

### 2.3 Applications

Application 1: Total energies for  $(1s, nl)^1 L^\pi$  singly excited states of helium-like ions

For two-electron systems, we obtain from Eq. (11)

$$E = -\frac{[Z - \sigma_1(l)]^2}{\nu_1^2} - \frac{[Z - \sigma_2(l)]^2}{\nu_2^2}.$$

In this equation, the first term in the right hand side corresponds to the energy of the 1s-orbital (then  $\nu_1 = 1$ ) whereas the second term gives the energy of the  $nl$ -orbital (so  $\nu_2 = n$ ). In that case total energy for  $(1s, nl)^1 L^\pi$  singly excited states of helium-like ions is in the form

$$E(1s, nl) = -[Z - \sigma(l)]^2 - \frac{1}{n^2}[Z - \sigma'(l)]^2, \quad (12)$$

where the screening constants  $\sigma$  and  $\sigma'$  are evaluated empirically. For  $(1s, nl)^2$ , Eq. (12) gives respectively when  $l$  ranges between 0 and 2

$$E(1s, ns; ^1 S^e) = -[Z - \sigma_s]^2 - \frac{1}{n^2}[Z - \sigma'_s]^2, \quad (13)$$

$$E(1s, np; ^1 P^o) = -[Z - \sigma_p]^2 - \frac{1}{n^2}[Z - \sigma'_p]^2, \quad (14a)$$

$$E(1s, nd; ^1 D^e) = -[Z - \sigma_d]^2 - \frac{1}{n^2}[Z - \sigma'_d]^2. \quad (14b)$$

In these equations, we have done the changes  $\sigma(l=0) = \sigma_s$ ,  $\sigma'(l=0) = \sigma'_s$ ;  $\sigma(l=1) = \sigma_p$ ,  $\sigma'(l=1) = \sigma'_p$  and  $\sigma(l=2) = \sigma_d$ ,  $\sigma'(l=2) = \sigma'_d$ .

By use of experimental total energy [10] of  $(1s2p)^1 P^o$ ,  $(1s3p)^1 P^o$ , and that of  $(1s3d)^1 D^e$ ,  $(1s4d)^1 D^e$ -levels of the helium atom, Eq.(14) give for  $\sigma_p$  and  $\sigma_d$  negative values (see Appendix).

As the  $\sigma$ -screening constant is essentially positive, total energies for  $(1snp)^1 P^o$  and  $(1snd)^1 D^e$  excited states are expressed as follows

$$E(1s, np; ^1 P^o) = -Z^2 - \frac{1}{n^2}[Z - \sigma_p]^2, \quad (15)$$

$$E(1s, nd; ^1 D^e) = -Z^2 - \frac{1}{n^2}[Z - \sigma_d]^2. \quad (16)$$

Using the experimental energy values (in atomic units) of the helium atom  $E(1s2s;^1S^e) = -2.14597$  and  $E(1s3s;^1S^e) = -2.06127$  [10], Eq.(13) expressed in rydbergs (1a.u. = 2Ryd.) gives for He

$$\begin{cases} (2-\sigma_s)^2 + \frac{1}{4}(2-\sigma'_s)^2 = 4.29194, \\ (2-\sigma_s)^2 + \frac{1}{9}(2-\sigma'_s)^2 = 4.12254. \end{cases}$$

Resolving these equations, one obtains  $\sigma_s = 0.003247636$  and  $\sigma'_s = 0.895608765$ .

In the same way, from Ref. [10] we pull the experimental energy  $E(1s4p;^1P^o) = -2.03110$  and  $E(1s4d;^1D^e) = -2.03131$  of the helium atom. Using these values, Eqs. (15) and (16) yield respectively

$$\begin{cases} E(1s,4p;^1P^o) = 4 + \frac{1}{16}[2-\sigma_p]^2 = 4.0622, \\ E(1s,4d;^1D^e) = 4 + \frac{1}{16}[2-\sigma_d]^2 = 4.06262. \end{cases}$$

The resolution of these equations gives  $\sigma_p = 1.002402887$  and  $\sigma_d = 0.999040460$ .

The total energy of  $(1s, nl)^1L^\pi$  excited states ( $l=0-2$ ) in He-like ions are expressed with a good approximation as follows (in rydbergs)

$$E(1s, ns;^1S^e) = -[Z - 0.003247636]^2 - \frac{1}{n^2}[Z - 0.895608765]^2, \quad (17)$$

$$E(1s, np;^1P^o) = -Z^2 - \frac{1}{n^2}[Z - 1.002402887]^2, \quad (18)$$

$$E(1s, nd;^1D^e) = -Z^2 - \frac{1}{n^2}[Z - 0.999040460]^2. \quad (19)$$

Application 2: Total energies for  $(nl^2)^1L^\pi$  symmetric doubly excited states of helium-like ions

Following the idea of Slater [24], we divide the atomic orbital into two groups:  $(ns^2; np^2)$ ;  $(nd^2; nf^2)$ , and so on. In these two groups, the screening constant is assumed to vary as follows

For  $(ns^2; np^2)$ :

$$\sigma(l) = al + b. \quad (20)$$

For  $(nd^2; nf^2)$ :

$$\sigma(l) = -a \cdot (n_{low}/l) + 2b. \quad (21)$$

In Eq.(21),  $n_{low}$  denotes the principal quantum number of the lowest level of the considered atomic orbital. For  $nd^2$ , the lowest level is  $3d^2$ , then  $n_{low} = 3$ ; for  $nf^2$  the lowest level is  $4f^2$ , then  $n_{low} = 4$ .

Using Eqs.(20) and (21), total  $(nl^2)$  DES of helium-like ions are expressed in the form (in rydbergs)

For  $(ns^2; np^2)$ :

$$E(nl^2) = -\frac{2}{n^2} \times [Z - (al + b)]^2. \quad (22)$$

Table 1: Experimental and theoretical values of total energy in singly excited states  $(1sns)^1S^e$ ,  $n \leq 4$  of He-like systems up to  $Z = 12$ . All energies are reported in eV (1 Ryd = 13.605698 eV).

States	Z											
	2	3	4	5	6	7	8	9	10	11	12	
1s2s	$E^a$	58.395	137.249	250.118	397.001	577.898	792.810	1041.736	1324.676	1641.630	1992.598	2377.581
	$E^b$	58.395	137.176	249.972	396.781	577.605	792.444	1041.296	1324.163	1641.044	1991.939	2376.848
	$E^c$	58.528	137.255	249.997	396.753	577.527	790.307	1041.106	1323.919	1640.746	1991.587	2376.442
	$E^d$	58.395				577.481				1640.721		
1s3s	$E^a$	56.090	128.881	231.907	365.168	528.663	722.394	946.359	1200.559	1484.995	1799.665	2144.569
	$E^b$	56.090	128.805	231.756	364.941	528.361	722.016	945.906	1200.030	1484.390	1798.985	2143.814
	$E^c$	56.078	128.801	231.759	364.952	528.380	722.042	945.940	1200.072	1484.440	1799.042	2143.879
	$E^d$	56.090				528.386				1484.443		
1s4s	$E^a$	55.283	125.952	225.533	354.026	511.431	697.748	912.977	1157.118	1430.172	1732.138	2063.015
	$E^b$	55.307	125.920	225.445	353.882	511.232	697.493	912.667	1156.752	1429.751	1731.661	2062.483
	$E^c$	55.238	125.976	225.536	354.009	511.394	697.690	912.899	1157.020	1430.053	1731.999	2062.856
	$E^e$	55.337										

<sup>a</sup> Present work, values calculated using Eq. (17).

<sup>b</sup> Ref. [25].

<sup>c</sup> Ref [12].

<sup>d</sup> Ref. [20].

<sup>e</sup> Experimental data [10].

For  $(nd^2;nf^2)$ :

$$E(nl^2) = -\frac{2}{n^2} \times [Z - \{-a \cdot (n_{low}/l) + 2b\}]^2. \quad (23)$$

Using experimental data [31] of total energy of the helium atom for  $(2s^2)$  equals to - 21.19 eV and that of  $(2p^2)$  equals to - 19.12 eV, the coefficients  $a$  and  $b$  in Eq.(18) are determined by resolving the following equations (using 1Ryd = 13.605698 eV)

$$\begin{cases} E(2s;^1S^e) = \frac{2}{4}[2-b]^2 & = 1.557435716, \\ E(2p;^1D^e) = \frac{2}{4}[2-a-b]^2 & = 1.405293576. \end{cases}$$

We find then:  $b = 0.235\ 100\ 163$  and  $a = 0.088\ 419\ 251$ .

Using these results, Eqs. (22) and (23) give respectively

For  $(ns^2;np^2)$ :

$$E(nl^2) = -\frac{2}{n^2} \times [Z - (0.088419251l + 0.235100163)]^2. \quad (24)$$

For  $(nd^2;nf^2)$ :

$$E(nl^2) = -\frac{2}{n^2} \times [Z - \{-0.088419251 \cdot (n_{low}/l) + 0.470200327\}]^2. \quad (25)$$

Table 2: Experimental and theoretical values of total energy in singly excited states  $(1snp)^1P^o$ ,  $n \leq 4$  of He-like systems up to  $Z = 12$ . All energies are reported in eV (1 Ryd = 13.605698 eV).

States	Z											
	2	3	4	5	6	7	8	9	10	11	12	
1s2p	$E^a$	57.808	136.024	248.255	394.500	574.759	789.032	1037.320	1319.622	1635.938	1986.268	2370.613
	$E^b$	57.793	135.995	248.212	394.442	574.687	788.946	1037.219	1319.506	1635.808	1986.124	2370.454
	$E^c$	58.158	136.122	248.100	394.093	574.100	788.121	1036.157	1318.206	1634.270	1984.348	2368.440
	$E^d$	57.793										
	$E^e$	57.793										
1s3p	$E^a$	55.927	128.484	231.275	364.301	527.562	721.058	944.789	1198.755	1482.956	1797.391	2142.062
	$E^b$	55.924	128.477	231.265	364.288	527.546	721.039	944.766	1198.729	1482.926	1797.359	2142.026
	$E^c$	56.068	128.627	231.421	364.288	527.714	721.213	944.947	1198.916	1483.119	1797.558	2142.231
	$E^d$	55.923										
	$E^e$	55.924										
1s4s	$E^a$	55.269	125.845	225.332	353.732	511.044	697.268	912.404	1156.452	1429.412	1731.284	2062.069
	$E^b$	55.270	125.844	225.332	353.732	511.043	697.267	912.403	1156.451	1429.411	1731.284	2062.068
	$E^c$	55.275	125.831	225.299	353.679	510.972	697.176	912.293	1156.322	1429.263	1731.116	2061.881
	$E^e$	55.268										

<sup>a</sup> Present work, values calculated using Eq. (18).

<sup>b</sup> Ref. [25].

<sup>c</sup> Ref. [12].

<sup>d</sup> Ref. [20].

<sup>e</sup> Experimental data [10].

Table 3: Experimental and theoretical values of total energy in singly excited states  $(1snd)^1D^e$ ,  $n \leq 4$  of He-like systems up to  $Z = 12$ . All energies are reported in eV (1 Ryd = 13.605698 eV).

States	Z											
	2	3	4	5	6	7	8	9	10	11	12	
1s3d	$E^a$	55.937	128.504	231.306	364.342	527.613	721.119	944.860	1198.836	1483.047	1797.493	2142.173
	$E^b$	55.979	128.538	231.332	364.361	527.626	721.124	994.858	1198.827	1483.031	1797.469	2142.142
	$E^c$	55.937										
	$E^d$	55.937										
1s4d	$E^a$	55.275	125.856	225.349	353.755	511.072	697.302	912.443	1156.490	1429.452	1731.341	2062.131
	$E^b$	55.282	125.872	225.361	353.755	511.072	697.302	912.443	1156.497	1429.463	1731.341	2062.131
	$E^c$	55.275										
	$E^d$	55.275										

<sup>a</sup> Present work, values calculated using Eq. (19).

<sup>b</sup> Ref. [12].

<sup>c</sup> Ref. [11].

<sup>d</sup> Experimental data [10].

### 3 Results and discussion

Results obtained in the present study for total energies are displayed in Tables 1-7. Calculations using Eqs.(17), (18) and (19), give the results of total energies for  $(1sns)^1S^e$ ,  $(1snp)^1P^o$  and  $(1snd)^1D^e$  singly excited states of He isoelectronic series with  $n \leq 4$  and



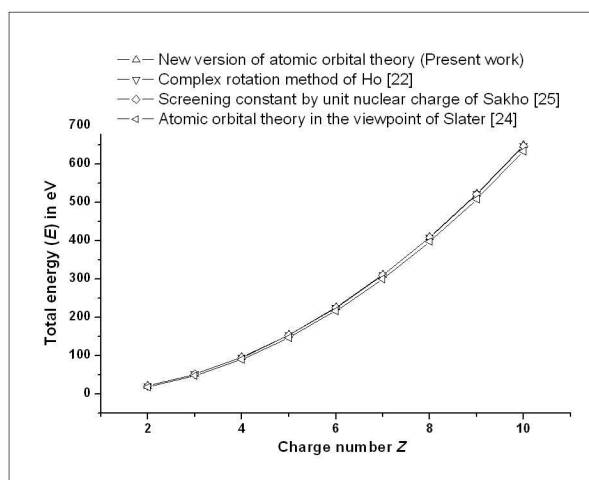


Figure 1: Comparison of atomic orbital theory of Slater and its new version with some other results for  $2s^2$ -energy level. The influence of the screening constant  $\sigma$  is observed.

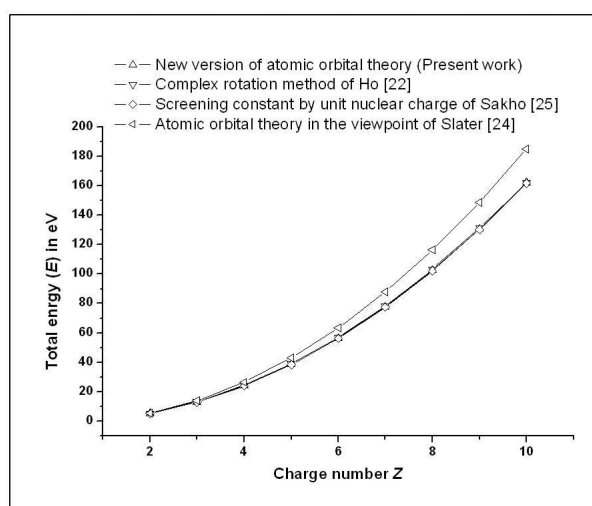


Figure 2: Comparison of atomic orbital theory of Slater and its new version with some other results for  $4s^2$ -energy level. The influence of both screening constant  $\sigma$  and effective quantum number  $n^*$  is observed.

$Z \leq 12$ . The results obtained are listed in Tables 1-3 compared with theoretical results quoted in Refs. [11, 12, 20, 25] and with experimental data [10]. Comparison shows that the semi-empirical expressions given by Eqs. (17) and (18) reproduce with a good accuracy experimental data [10] of total energy for  $(1s4s)^1S^e$ ,  $(1s2p)^1P^o$  and  $(1s3p)^1P^o$  excited states of the helium atom. The relative errors (as compared to the experimental values) are respectively about 0.09%, 0.02% and 0.005% respectively. For the  $(1s3d)^1D^e$  - level, Eq. (18) gives exactly the experimental value [10] for the helium atom. As regards He-

Table 4: Total energies for  $(ns^2)^1S^e$ ,  $n \leq 7$  symmetric doubly excited states of He - like ions up to  $Z = 12$ . All energies are reported in eV (1 Ryd = 13.605698 eV).

		Z										
States		2	3	4	5	6	7	8	9	10	11	12
$2s^2$	$E^a$	21.19	52.00	96.43	154.45	226.09	311.32	410.17	522.62	648.67	788.33	841.60
	$E^b$	21.17	51.86	96.15	154.05	225.53	310.63	409.33	521.64	647.55		
	$E^c$	20.77	51.11	96.45	156.10	227.23	312.14	410.37	523.04	649.16	790.38	845.50
	$E^d$	21.19	51.76	95.93	153.71	225.09	310.08	408.68	520.88	646.68		
	$E^e$	18.52	47.77	90.63	147.09	217.16	300.84	398.12	509.01	633.50	771.60	923.30
	$E^f$		51.98									
$3s^2$	$E^a$	9.42	23.11	42.86	68.65	100.48	138.37	182.30	232.27	288.30	350.37	418.49
	$E^b$	9.63	23.41	43.24	69.11	101.03	138.99	183.01	233.07	289.18		
	$E^c$	9.21	23.41	44.11	71.38	105.23	145.65	192.65	246.24	306.41	373.16	446.48
	$E^d$	9.42	23.00	42.63	68.31	100.04	137.81	181.63	231.50	287.41		
	$E^e$	8.23	21.23	40.28	65.37	96.52	133.71	176.94	226.22	281.55	342.93	410.35
$4s^2$	$E^a$	5.30	13.00	24.11	38.61	56.52	77.83	102.54	130.65	162.17	197.08	235.40
	$E^b$	5.47	13.23	24.45	39.04	57.03	78.43	103.21	131.41	162.01		
	$E^c$	4.89	12.24	22.94	37.02	54.50	75.37	99.54	127.31	158.39	192.88	230.77
	$E^d$	5.30	12.94	23.98	38.43	56.27	77.52	102.17	130.22	161.67		
	$E^e$	5.41	13.96	26.48	42.98	63.45	87.90	116.32	148.72	185.10	225.45	269.77
$5s^2$	$E^a$	3.39	8.32	15.43	24.71	36.17	49.81	65.63	83.62	103.79	126.13	150.66
	$E^d$	3.39	8.28	15.35	24.59	36.01	49.61	65.39	83.34	103.47		
	$E^e$	4.63	11.94	22.66	36.77	54.29	75.21	99.53	127.25	258.37	192.90	230.82
$6s^2$	$E^a$	2.35	5.78	10.71	17.16	25.12	34.59	45.57	58.07	72.07	87.59	104.62
	$E^a$	1.73	4.24	7.87	12.61	18.46	25.41	33.48	42.66	52.95	64.35	76.86

<sup>a</sup> Present work, values calculated using Eq. (24).

<sup>b</sup> Ref. [22].

<sup>c</sup> Ref. [17].

<sup>d</sup> Ref. [25].

<sup>e</sup> AOT results according to Slater, values calculated from Eq. (7).

<sup>f</sup> Experimental data [31].

like ions with  $3 \leq Z \leq 12$ , it can be seen that our results are in good agreement as well as with hyperspherical close-coupling computations of Tang *et al.* [11], double sums over the total hydrogen spectrum of product of radials integrals computations of Ivanov and Safronova [12], analytical calculations of Arias de Saavedra *et al.* [20] than with screening constant by unit charge calculations of Sakho [25]. The agreement between the present calculations for  $1s3d$  and  $1s4d$  levels and that of Ivanov and Safronova [12] it seen to be very satisfactory for  $Z = 2-12$ . Tables 4-7 list total energies for symmetric DES  $(ns^2)^1S^e$ ,  $(np^2)^1D^e$ ,  $(nd^2)^1G^e$  and  $(nf^2)^1I^e$  with  $n \leq 7$  for He-like ions up to  $Z = 12$ . For these states, only the experimental value of  $\text{Li}^+$  and that of He used for the evaluation of the empirical constants  $a$  and  $b$  in Eq.(22) are found in the literature. In the experimental side, comparison indicates that, our total energies calculated from Eq.(24) for  $(2s^2)^1S^e$  and  $(2p^2)^1D^e$  levels agree well with available experimental result of  $\text{Li}^+$  obtained by Diehl *et al.* [31].

The relative errors (as compared again to the experimental data) are respectively about 0.04% and 1.18%. Besides, for theoretical results, a good agreement is observed comparing our total energies for  $(ns^2)^1S^e$  and  $(np^2)^1D^e$ ,  $n \leq 5$  to those of the available

Table 5: Total energies for  $(np^2)^1D^e$ ,  $n \leq 7$  symmetric doubly excited states of He - like ions up to  $Z = 12$ . All energies are reported in eV (1 Ryd = 13.605698 eV).

States	Z											
	2	3	4	5	6	7	8	9	10	11	12	
$2p^2$	$E^a$	19.12	48.73	91.95	148.77	219.20	303.24	400.88	512.13	636.98	775.44	927.50
	$E^b$	19.18	48.39	91.15	147.49	217.41	300.94	398.06	508.78	633.11	771.05	922.58
	$E^c$	19.12	48.19	90.87	147.15	217.03	300.53	397.63	508.33	632.64		
	$E^g$	19.41	48.39	90.97	147.16	216.95	300.35	397.35	507.97	632.18		
	$E^h$		48.18	90.82	147.04							
	$E^i$		47.77	90.54	146.91							
	$E^e$		48.16 <sup>e</sup>									
$3p^2$	$E^a$	8.50	21.66	40.87	66.12	97.42	134.77	178.17	227.61	283.10	344.64	412.22
	$E^b$	8.67	21.81	41.03	66.38	97.85	135.45	179.20	229.08	285.10	347.27	415.58
	$E^c$	8.50	21.42	40.38	65.40	96.46	133.57	176.72	225.92	281.17		
	$E^g$	8.99	22.11	41.28	66.50	97.76	135.07	178.43	227.83	283.29		
	$E^h$		21.67	40.79	65.94							
	$E^i$		21.83	41.09	66.41							
$4p^2$	$E^a$	4.78	12.18	22.99	37.19	54.80	75.81	100.22	128.03	159.24	193.86	231.87
	$E^b$	4.89	12.24	22.94	37.02	54.50	75.37	99.64	127.31	158.39	192.88	230.77
	$E^c$	4.78	12.05	22.72	36.79	54.26	75.13	99.41	127.08	158.16		
	$E^i$		12.38	23.26	37.54							
$5p^2$	$E^a$	3.06	7.80	14.71	23.80	35.07	48.52	64.14	81.94	101.92	124.07	148.40
	$E^c$	3.06	7.71	14.54	23.54	34.72	48.08	63.62	81.33	101.22		
	$E^i$		7.95	14.93	24.08							
$6p^2$	$E^a$	2.12	5.41	10.22	16.53	24.36	33.69	44.54	56.90	70.77	86.16	103.06
$7p^2$	$E^a$	1.56	3.98	7.51	12.14	17.89	24.75	32.72	41.81	52.00	63.30	75.71

<sup>a</sup> Present work, values calculated using Eq. (24).

<sup>b</sup> Ref. [17].

<sup>c</sup> Ref. [25].

<sup>g</sup> Ref. [12].

<sup>h</sup> Ref. [31].

<sup>i</sup> Ref. [21].

<sup>e</sup> Experimental data [30].

theoretical values quoted in Tables 4-7. For  $(6s^2)^1S^e$ ,  $(7s^2)^1S^e$ ,  $(6p^2)^1D^e$  and  $(7p^2)^1D^e$  no literature values have been found. As regards the  $(nd^2)^1G^e$  -levels, comparison shows also a good agreement with variational Hylleraas results of Biaye *et al* [17], density-functional-theory results of Roy *et al.* [21] and time-dependant perturbation theory results of Ray and Mukherjee [19]. A very good agreement is also noted between our results and that of Sinanoglu and Herrick [32] for  $3d^2$ -level of the helium atom. For  $(nf^2)^1I^e$  no experimental data and theoretical results are available when  $n \geq 5$ . For  $4f^2$ -level, comparison with available results of Biaye *et al.* [17] indicates a satisfactory agreement. But, for  $(ng^2)^1K^e$  and  $(nh^2)^1M^e$  levels, no experimental and theoretical results are available. On the other hand, the results quoted in Table 4 show the inadequacy of AOT in the

Table 6: Total energies for  $(nd^2)^1G^e$ ,  $n \leq 7$  symmetric doubly excited states of He - like ions up to  $Z = 12$ . All energies are reported in eV (1 Ryd = 13.605698 eV).

States	Z											
	2	3	4	5	6	7	8	9	10	11	12	
$3d^2$	$E^a$	8.35	21.43	40.55	65.72	96.94	134.21	177.52	226.87	283.28	343.73	411.23
	$E^b$	8.58	21.55	40.49	65.46	96.44	133.46	176.51	225.60	280.73	341.91	409.13
	$E^i$	7.96	20.74	39.57	64.44							
	$E^j$	8.49	21.15	39.84	64.56							
	$E^k$	8.35										
$4d^2$	$E^a$	4.70	12.05	22.81	36.97	54.53	75.49	99.85	127.62	158.78	193.35	231.32
	$E^b$	4.89	12.24	22.94	37.02	54.50	75.36	99.63	127.31	158.38	192.87	230.76
	$E^i$	4.70	12.06	22.82	36.98							
	$E^j$	5.31	12.52	23.33	37.55							
$5d^2$	$E^a$	3.01	7.71	14.60	23.66	34.90	48.31	63.91	81.67	101.62	123.74	148.04
	$E^i$	3.07	7.81	14.74	23.84							
$6d^2$	$E^a$	2.09	5.36	10.14	16.43	24.23	33.55	44.38	56.72	70.57	85.93	102.81
	$E^i$	2.15	5.46	10.28	16.61							
$7d^2$	$E^a$	1.53	3.94	7.45	12.07	17.80	24.65	32.60	41.67	51.85	63.13	75.53
	$E^i$	1.59	4.02	7.57	12.23							

<sup>a</sup> Present work, values calculated using Eq. (25).

<sup>b</sup> Ref. [17].

<sup>i</sup> Ref. [21].

<sup>j</sup> Ref. [19].

<sup>k</sup> Ref. [31].

Table 7: Total energies for  $(nf^2)^1I^e$ ,  $(ng^2)^1K^e$ , and  $(nh^2)^1M^e$ ,  $n \leq 7$  symmetric doubly excited states of He - like ions up to  $Z = 12$ . All energies are reported in eV (1 Ryd = 13.605698 eV).

States	Z											
	2	3	4	5	6	7	8	9	10	11	12	
$4f^2^1I^e$	$E^a$	4.62	11.92	22.63	36.74	54.25	75.16	99.47	127.18	158.30	192.81	230.73
	$E^b$	4.89	12.22	22.90	36.95	54.38	75.19	99.40	126.99	157.98	192.37	230.15
$5f^2^1I^e$	$E^a$	2.95	7.63	14.48	23.51	34.72	48.10	63.66	81.40	101.31	123.40	147.67
$6f^2^1I^e$	$E^a$	2.05	5.30	10.06	16.33	24.11	33.40	44.21	56.53	70.35	85.69	102.55
$7f^2^1I^e$	$E^a$	1.51	3.89	7.39	11.99	17.71	24.54	32.48	41.53	51.69	62.96	75.34
$5g^2^1K^e$	$E^a$	2.93	7.59	14.42	23.44	34.63	47.99	63.54	81.26	101.16	123.23	147.48
$6g^2^1K^e$	$E^a$	2.03	5.27	10.02	16.27	24.05	33.33	44.12	56.43	70.25	85.58	102.42
$7g^2^1K^e$	$E^a$	1.49	3.87	7.36	11.96	17.67	24.49	32.42	41.46	51.61	62.87	75.25
$6h^2^1M^e$	$E^a$	2.02	5.25	9.99	16.24	24.01	33.28	44.07	56.37	70.18	85.51	102.34
$7h^2^1M^e$	$E^a$	1.48	3.86	7.34	11.93	17.64	24.45	32.38	41.42	51.56	62.82	75.19

<sup>a</sup> Present work, values calculated using Eq. (25).

<sup>b</sup> Ref. [17].

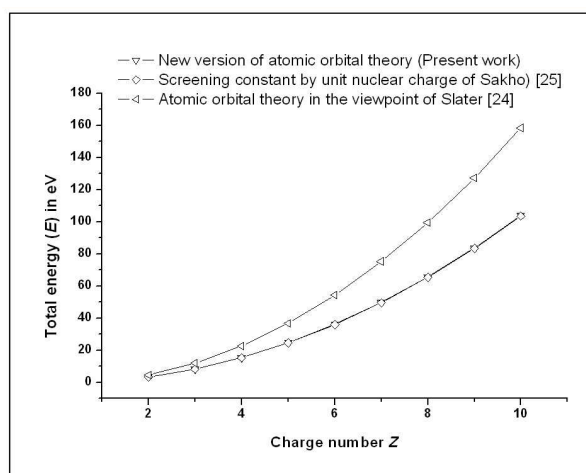


Figure 3: Comparison of atomic orbital theory of Slater and its new version with some other results for  $5s^2$ -energy level. Specific influence of effective quantum number  $n^*$  is observed.

view point of Slater [24] for excited states of helium-like ions and then for atomic systems. For  $(2s^2)$ -level for example, discrepancies between first version AOT results and accurate results reported in [22,25] increase when the charge number  $Z$  increases. These discrepancies are due to the definition of  $\sigma$ -screening constant which has not been defined by Slater [24] for excited states. This is clearly observed considering Fig. 1. These discrepancies are most accentuated in the case of  $4s^2$  and  $5s^2$  levels due to both influence of  $\sigma$ -screening constant and effective quantum number  $n^*$  as shown in Figs. 2 and 3. This may be generalized to any excited states where  $n^{*1} \neq n$ .

## 4 Conclusions

In this work, we have shown that atomic orbital theory in the view point of Slater's first formalism is not suitable for excited states of atomic systems. This confirms that AOT have been developed by Slater [24] only for total ground-state energies of atomic systems of several electrons. In addition, it has been demonstrated in this paper, the possibilities to formulate a modification of the first Slater's atomic orbital theory for the investigations of excited states of helium-like ions. The good accuracy obtain in this work for  $(nl^2)^1L^\pi$  and  $(1s, nl)^1L^\pi$  excited states in the framework of a nonrelativistic semi-empirical procedure, point out that, the present Modification of Atomic Orbital Theory may be extended as well as to singly triplet  $(1s, nl)^3L^\pi$  excited states than to doubly excited states with mixing configurations of type  $(Nl, nl')$  for two-electron systems and extended to excited states of other atomic systems like lithium isoelectronic series. Such investigations will present atomic orbital theory of Slater [24] as a complete theory suitable as well as for the ground -state than for excited states of atoms and there isoelectronic ions.

## 5 Appendix

We intend in this section to demonstrate the reasons that lead to Eqs. (15) and (16). Let us in this purpose, consider Eq. (14) remind below

$$E(1s,np;^1P^o) = -[Z - \sigma_p]^2 - \frac{1}{n^2} [Z - \sigma'_p]^2, \quad (14a)$$

$$E(1s,nd;^1D^e) = -[Z - \sigma_d]^2 - \frac{1}{n^2} [Z - \sigma'_d]^2. \quad (14b)$$

From Ref. [10], experimental total energies of  $(1s2p)^1P^o$ ,  $(1s3p)^1P^o$ ,  $(1s3d)^1D^e$  and  $(1s4d)^1D^e$ -levels of the helium atom are respectively (in atomic units) -2.123 87; -2.055 17, -2.055 65 and -2.031 31. Using these values Eq. (14) yield (knowing that 1a.u. = 2Ryd)

$$\begin{cases} (2 - \sigma_p)^2 + \frac{1}{4}(2 - \sigma'_p)^2 = 4.24774 \\ (2 - \sigma_p)^2 + \frac{1}{9}(2 - \sigma'_p)^2 = 4.11034 \end{cases} ,$$

$$\begin{cases} (2 - \sigma_p)^2 + \frac{1}{9}(2 - \sigma'_d)^2 = 4.11130 \\ (2 - \sigma_d)^2 + \frac{1}{16}(2 - \sigma'_d)^2 = 4.06262 \end{cases} .$$

Solving these equations we find respectively  $\sigma_p = -0.000\ 104\ 997$ ;  $\sigma'_p = 1.005\ 374\ 442$ ; and  $\sigma_d = -0.000\ 007\ 857$ ;  $\sigma'_d = 0.999\ 291\ 679$ .

Physically, the effective charge  $Z^* = Z - \sigma < Z$ . that means  $\sigma > 0$ . Then, in the view point of physical aspect, the results  $\sigma_p = -0.000104997$  and  $\sigma_d = -0.000007857$  are not acceptable. To viewing the problem, one can see that the absolute value  $|\sigma_p| = 0.000104997 \approx 0.000$  and  $|\sigma_d| = 0.000007857 \approx 0.000$ . these remarks permit to express total energies of  $(1snp)$  and  $(1snd)$  singlet excited states of He-like ions by putting into Eq. (14)  $\sigma_p = \sigma_d = 0$ . We find then for total energies of  $(1snp)^1P^o$  and  $(1snd)^1D^e$  singly excited states in helium isoelectronic sequence Eqs. (15) and (16) respectively reminded below

$$E(1s,np;^1P^o) = -Z^2 - \frac{1}{n^2} [Z - \sigma_p]^2,$$

$$E(1s,nd;^1D^e) = -Z^2 - \frac{1}{n^2} [Z - \sigma_d]^2.$$

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