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Modified atomic orbital theory applied to the calculation of high-lying $_2(K,T)_n^{\pm}\ ^{1,3}P^{\circ}$ Rydberg series of He-like ions

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ABSTRACT

The $_2(1,0)_n^{-}\ ^1P^{\circ}$, $_2(1,0)_n^{+}\ ^3P^{\circ}$, $_2(1,0)_n^{+}\ ^1P^{\circ}$, and $_2(1,0)_n^{-}\ ^3P^{\circ}$ intershell Rydberg series of the helium-like ions are investigated in the framework of the modified Atomic Orbital Theory (MAOT). Highlying energy resonances of He and excitation energy of the helium-like Li^+ up to $n = 10$ are tabulated. In addition, total energy positions for lowlying states ($n \le 4$) of the helium-isoelectronic sequence with $Z = 2, 3, \cdots 10$ are also presented. All the current results agreed well with the published values. The data listed in this paper may be useful guideline for future experimental and theoretical studies in high-lying $^{1,3}P^{\circ}$ autoionizing states of two-electron systems.

Keywords: Atomic Orbital Theory; Screening Constant; Semi-Empirical Calculations; Autoionizing States; Rydberg Series; Helium-Like Ions

1. INTRODUCTION

Studies of excited states in two electron systems have been an active field of research both experimentally and theoretically since the earlier synchrotron radiation source experiment of Madden and Codling on He [1]. At present, the description of the properties of the excited states in the helium isoelectronic series is done in the framework of the new classification scheme with the label $_n(K,T)_N^{A\ 2S+1}L^{\pi}$. In this notation, N and n denote respectively the principal quantum numbers of the inner and of the outer electron, S the total spin, L the total angular momentum, π the parity of the system, K and T are angular correlation quantum numbers and A represents the radial correlation quantum number of the two electrons. Besides, this designation incorporates singly excited states and both intrashell and intershell excited states in the helium-like ions. A given channel μ is labelled by $\mu = (K,T)_N^{A\ 2S+1}L^{\pi}$ as originally used by Herrick and Sinanoglu [2,3] with the following assignment of K and T for a given N, L and π

$T = 0, 1, 2, \cdots, \min(L, N-1)$.

$K = N-1-T, N-3-T, \cdots, -(N-1-T)$.

These assigned values of K and T depend not on the total angular spin S. Besides, T is roughly speaking the projection of L onto the interelectronic axis and describes then the orientations between the orbitals of the two electrons and K is related to cosinus of the interelectronic angle as $K \approx -\langle r_< \cos\theta_{12}\rangle$ where $r_<$ denotes the radius of the inner electron. Physically, the larger the positive value of K, the value of $-\langle\cos\theta_{12}\rangle$ is closer to unity. In addition, A can take the values +1 or −1 and 0 only [4,5]. For the $A = +1$ states, the two electrons tend to approach or to move away from the nucleus in phase and for $A = -1$ states, the two electrons have out-of-phase such that, when one electron approaches the nucleus, the other tends to move away from it [4,5]. For $A = 0$ states, they are little radial correlation between the two electrons and they are similar to singly excited states [4,5].

In the description of the autoionizing states in two electron systems, various methods are used. Among these methods are the saddle-point complex-rotation method [6], the close-coupling method [7], the truncated-diagonalization method [8], the complex-coordinate rotation [9-11], the computing double sum over the complete hydrogen spectrum [12], the screening constant by unit nuclear charge formalism [13-15], the Debye screening model [16]. Except for the screening constant by unit nuclear charge method based on a semi-empirical formalism, most of the preceding methods present special theoretical and computational problems. To overcome these problems, we apply in this paper the modified atomic orbital theory (MAOT) we present recently [17,18]. The MAOT formalism is then used to study the $_2(1,0)_n^{-}\ ^1P^{\circ}$, $_2(1,0)_n^{+}\ ^3P^{\circ}$, $_2(0,1)_n^{+}\ ^1P^{\circ}$, and

${}_2(0,1)_n^{-}\,{}^3P^{\circ}$ intershell Rydberg series of the helium-like ions up to $Z = 10$ and $n = 10$.

Then, in this paper, energies for high-lying ${}^{1,3}P^{\circ}$ autoionizing states of He-like ions below the $N = 2$ hydrogenic thresholds are tabulated using the modified atomic orbital theory (MAOT) in the framework of a semi-empirical procedure. The results up to $Z = 10$ compare well to some theoretical results. In addition, it is also demonstrated in the present work, the adequacy of the MAOT's formalism to separately identify the classification (+, –) of the ${}_n(K,T)_N^{A\ 2S+1}L^{\pi}$ Rydberg states without complex calculations. The data quoted in this work may be of interest for future experimental and theoretical investigations in high-lying ${}^{1,3}P^{\circ}$ Rydbergs series of two-electron systems.

In Section 2, we present the theoretical procedure adopted in this work.

In Section 3, we present and discuss the results obtained, compared with available theoretical and experimental data.

2. THEORY

2.1. General Formalism of the MAOT Method for Excited States of Two Electron Systems

In the framework of Modified Atomic Orbital Theory (MAOT), total energy of a $(n\ell)$-given orbital is expressed in the form [17,18]

$$E(n\ell) = -\frac{\left[Z - \sigma(\ell)\right]^2}{n^2}. \tag{1}$$

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

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

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

$$E = -\sum_{i=1}^{M}\frac{\left[Z - \sigma_i\left({}^{2S+1}L^{\pi}\right)\right]^2}{n_i^2}. \tag{2}$$

With regard to the new classification scheme, **Eq.2** takes the form

$$E\left[{}_N(KT)_n^A\right] = -\sum_{i=1}^{M}\frac{\left[Z - \sigma_i(KTNn, A)\right]^2}{n_i^2}$$

For two electron systems which are the intention of the present work, we obtain

$$E\left[{}_N(KT)_n^A\right] = -\frac{\left[Z - \sigma(KTNn, A)\right]^2}{N^2} - \frac{\left[Z - \sigma'(KTNn, A)\right]^2}{n^2} \tag{3}$$

2.2. Energies for ${}_2(K,T)_n^{\pm}\,{}^{1,3}P^{\circ}$ Doubly Excited States of He Isoelectronic Sequence

Total energies for ${}_2(1,0)_n^{-}\,{}^1P^{\circ}$, ${}_2(1,0)_n^{+}\,{}^3P^{\circ}$, ${}_2(0,1)_n^{+}\,{}^1P^{\circ}$, and ${}_2(0,1)_n^{-}\,{}^3P^{\circ}$ autoionizing states of two-electron systems are respectively given by

$$E\left[{}_2(1,0)_n^{-}\,{}^1P^{\circ}\right] = -\frac{1}{4}\left[Z - \sigma_1(1,0-) + \sigma_1(1,0-)\times\frac{(n-3)(n-4)}{n^2}\right]^2 - \frac{1}{n^2}\left[Z - \sigma_2(1,0-) + \sigma_2(1,0-)\times\frac{(n-3)(n-4)}{(n-1)^2+1}\right]^2 \tag{4.a}$$

$$E\left[{}_2(1,0)_n^{+}\,{}^3P^{\circ}\right] = -\frac{1}{4}\left[Z - \sigma_3(1,0+) + \sigma_3(1,0+)\times\frac{(n-3)(n-4)}{n^2}\right]^2 - \frac{1}{n^2}\left[Z - \sigma_4(1,0+) + \sigma_4(1,0+)\times\frac{(n-3)(n-4)}{(n+1)^2}\right]^2 \tag{4.b}$$

$$E\left[{}_2(0,1)_n^{+}\,{}^1P^{\circ}\right] = -\frac{1}{4}\left[Z - \sigma_5(0,1+) + \sigma_5(0,1+)\times\frac{(n-3)(n-4)}{n^2}\right]^2 - \frac{1}{n^2}\left[Z - \sigma_6(0,1+) + \sigma_6(0,1+)\times\frac{(n-3)(n-4)}{(2n+1)^2}\right]^2 \tag{4.c}$$

$$E\left[{}_2(0,1)_n^{-}\,{}^3P^{\circ}\right] = -\frac{1}{4}\left[Z - \sigma_7(0,1-) + \sigma_7(0,1-)\times\frac{(n-3)(n-4)}{n^2}\right]^2 - \frac{1}{n^2}\left[Z - \sigma_8(0,1-) + \sigma_8(0,1-)\times\frac{(n-3)(n-4)}{(n-1)^2}\right]^2 \tag{4.d}$$

For the empirical evaluation of the σ_i-screening constants in **Eq.4**, we use the experimental energy results of electron ejected of Hicks and Comer [19] and photo-absorption experiments of Madden and Codling [1] on He along with photoionisation experimental values of Diehl *et al.* [20] of Li^+ quoted in **Table 1**. These energies are measured with respect to the ground state of the corresponding system. On the basis of these experimental data, the σ_i-semi-empirical screening constants are evaluated using **Eq.4**. The results obtained are listed in the last column of **Table 1**.

3. RESULTS AND DISCUSSIONS

The results of the present calculations for the energy resonances of $^{1,3}P^{\circ}$ states below the $N = 2$ hydrogenic thresholds are listed in **Tables 2-4**. In **Table 2**, we present a comparison of energy resonance of $_2(0,1)_n^{+\ 1}P^{\circ}$, $_2(1,0)_n^{+\ 3}P^{\circ}$, $_2(1,0)_n^{-\ 1}P^{\circ}$ and $_2(0,1)_n^{-\ 3}P^{\circ}$ autoionizing states of the helium atom obtained from the present

Table 1. Experimental energy resonances (E) of $_2(K,T)_n^{\pm\ 1,3}P^{\circ}$ doubly excited states of He and Li^+ used to evaluate empirically the σ_i-screening constants in **Eq.4**. The empirical data of the σ_i-parameters are quoted in last column of the table. The energy values are reported in eV. For energy conversion, the ground state energy of He at −79.01 eV and that of Li^+ equals to −198.09 eV are used along with the infinite rydberg: $1Ry = 13.605698$ eV.

	Experiments			Empirical values of the $\sigma_i(K,T,A)$-parameters	
	He		Li+		
State	Madden and Codling [1]	Hicks and Comer [19]	Diehl *et al.* [20]		
$_2(0,1)_3^{+\ 1}P^{\circ}$	63.655 ± 0.007			σ_1 (1,0, –)	0.038204997
$_2(0,1)_4^{+\ 1}P^{\circ}$	64.466 ± 0.007			σ_2 (1,0, –)	0.553951354
$_2(0,1)_3^{-\ 1}P^{\circ}$	62.758 ± 0.010			σ_3 (1,0, +)	0.024933760
$_2(0,1)_4^{-\ 1}P^{\circ}$	64.141± 0.016			σ_4 (1,0, +)	0.675656002
$_2(0,1)_3^{+\ 3}P^{\circ}$		63.09 ± 0.03		σ_5 (0,1, +)	0.007688938
$_2(0,1)_4^{+\ 3}P^{\circ}$		64.25 ± 0.03		σ_6 (0,1, +)	0.892656813
$_2(0,1)_3^{-\ 3}P^{\circ}$			63.09 ± 0.03	σ_7 (0,1, –)	0.033717048
$_2(0,1)_4^{-\ 3}P^{\circ}$			64.25 ± 0.03	σ_8 (0,1, –)	0.686479011

Table 2. Comparison of our results from the present modified atomic orbital theory (MAOT) with other theoretical results of $_2(0,1)_n^{+\ 1}P^{\circ}$, $_2(0,1)_n^{+\ 3}P^{\circ}$, $_2(0,1)_n^{-\ 1}P^{\circ}$ and $_2(0,1)_n^{-\ 3}P^{\circ}$ autoionizing states of the helium atom: saddle-point complex-rotation method (SPCR), Chen [6]; close-coupling method (CC), Oza [7]; truncated-diagonalization method (TDM), Conneely and Lipsky [8], complex coordinate rotation (CCR), Ho [9], Screening constant by unit nuclear charge (SCUNC) results, Sakho [15], results from Debye screening model (DSM), Kar and Ho [16].

		-E (a.u.)						
classifications		MAOT	SPCR	CC	TDM	CCR	SCUNC	DSM
$(N, n\alpha)$	$_2(K,T)_n^{\pm\ 13}P^{\circ}$							
(2, 3*a*)	$_2(0,1)_3^{+\ 1}P^{\circ}$	0.56429	0.56407	0.56401	0.56292	0.56408	0.56420	0.56408
(2, 4*a*)	$_2(0,1)_4^{+\ 1}P^{\circ}$	0.53448	0.53436	0.53436	0.53386	0.53436	0.53445	0.53436
(2, 5*a*)	$_2(0,1)_5^{+\ 1}P^{\circ}$	0.52165	0.52150	0.52149	0.52125	0.52150	0.52153	0.52149
(2, 6*a*)	$_2(0,1)_6^{+\ 1}P^{\circ}$	0.51482	0.51473	0.51472		0.51473	0.51473	
(2, 7*a*)	$_2(0,1)_7^{+\ 1}P^{\circ}$	0.51071	0.51072	0.51067		0.51074	0.51072	
(2, 3*a*)	$_2(0,1)_4^{+\ 3}P^{\circ}$	0.58505	0.58467	0.584 65	0.583 35		0.586 11	0.58467
(2, 4*a*)	$_2(0,1)_4^{+\ 3}P^{\circ}$	0.54242	0.54284	0.542 83	0.542 20		0.543 02	0.54284
(2, 5*a*)	$_2(0,1)_5^{+\ 3}P^{\circ}$	0.52569	0.52571	0.525 71	0.525 38		0.525 88	0.52571

Continued

(2, 6*a*)	$_2(0,1)_6^{+\ 3}P^\circ$	0.51716	0.51711				0.517 30	
(2, 7*a*)	$_2(0,1)_7^{+\ 3}P^\circ$	0.51212	0.51221				0.512 38	
(2, 3*b*)	$_2(0,1)_3^{-\ 1}P^\circ$	0.59725	0.59707	0.59707	0.59656	0.59707	0.59753	0.59707
(2, 4*b*)	$_2(0,1)_4^{-\ 1}P^\circ$	0.54643	0.54649	0.54646	0.54620	0.54649	0.54651	0.54649
(2, 5*b*)	$_2(0,1)_5^{-\ 1}P^\circ$	0.52826	0.52729	0.52729	0.52713	0.52729	0.52726	0.52730
(2, 6*b*)	$_2(0,1)_6^{-\ 1}P^\circ$	0.51861	0.51794	0.51793	0.51784	0.51793	0.51792	
(2, 7*b*)	$_2(0,1)_7^{-\ 1}P^\circ$	0.51265	0.51267			0.51267	0.51269	
(2, 3*b*)	$_2(0,1)_3^{-\ 3}P^\circ$	0.57914	0.57903	0.57902	0.578 53		0.58022	0.57903
(2, 4*b*)	$_2(0,1)_4^{-\ 3}P^\circ$	0.53720	0.53956	0.53950			0.53961	0.53956
(2, 5*b*)	$_2(0,1)_5^{-\ 3}P^\circ$	0.52377	0.52395	0.52211			0.52366	0.52395
(2, 6*b*)	$_2(0,1)_6^{-\ 3}P^\circ$	0.51640	0.51608				0.51574	
(2, 7*b*)	$_2(0,1)_7^{-\ 3}P^\circ$	0.51162	0.51155				0.51123	

Table 3. Comparison of our results from the present modified atomic orbital theory (MAOT) for some $_2(K,T)_n^{\pm\ 1,3}P^\circ$ autoionizing states of the helium isoelectronic sequence with complex-coordinates rotation method (CCR), Ho [10] and computing double sum method (CDS) over the complete hydrogen spectrum Ivanov and Safronova [12]. Screening constant by unit nuclear charge (SCUNC) results [15]. All results are expressed in atomic units.

	$^1P^\circ$ (2) $_2(0,1)_3^{-\ 1}P^\circ$ [(2, 3*b*)]			$^1P^\circ$ (3) $_2(0,1)_3^{+\ 1}P^\circ$ [(2, 3*a*)]				$^1P^\circ$ (6) $_2(0,1)_4^{+\ 1}P^\circ$ [(2, 4*a*)]		
Z	MAOT	CCR	SCUNC	MAOT	CCR	SCUNC	CDS	MAOT	SCUNC	CDS
2	0.59725	0.59707	0.59753	0.56429	0.56400	0.56420	0.58621	0.53448	0.53445	0.54077
3	1.42893	1.43052	1.42912	1.36596	1.36143	1.36439	1.39615	1.25802	1.25639	1.26705
4	2.62171	2.62515	2.62237	2.52874	2.51825	2.52574	2.56719	2.29406	2.29084	2.30583
5	4.17561	4.18090	4.17696	4.05263	4.03535	4.04821	4.09935	3.64259	3.63779	3.65711
6	6.09062	6.09781	6.09276	5.93764	5.91315	5.93181	5.99261	5.30363	5.29725	5.32089
7	8.36674	8.37581	8.36973	8.18375	8.15175	8.17652	8.24699	7.27717	7.26921	7.29716
8	11.00397	11.0149	11.0078	10.79098	10.7513	10.7823	10.86248	9.56320	9.55367	9.58594
9	14.00232	14.0151	14.0071	13.75932	13.7119	13.7493	13.8391	12.16174	12.1506	12.1872
10	17.36177	17.3765	17.36749	17.08877	17.0334	17.0773	17.1768	15.07278	15.0601	15.1010
	$^3P^\circ$ (2) $_2(0,1)_3^{+\ 3}P^\circ$ [(2, 3*a*)]			$^3P^\circ$ (3) $_2(0,1)_3^{-\ 3}P^\circ$ [(2, 3*b*)]				$_2(0,1)_4^{+\ 3}P^\circ$ (2, 4*a*)		
Z	MAOT	CCR	SCUNC	MAOT	CCR	SCUNC	CDS	MAOT	SCUNC	CDS
2	0.58505	0.58465	0.58611	0.57914	0.57903	0.58022	0.58621	0.54242	0.54302	0.53697
3	1.40652	1.40627	1.40671	1.39721	1.39851	1.39757	1.39615	1.27521	1.27313	1.26521
4	2.58910	2.58911	2.58871	2.57639	2.57925	2.57662	2.56719	2.32050	2.31584	2.30594
5	4.13280	4.13311	4.13194	4.11669	4.12112	4.11702	4.09935	3.67828	3.67108	3.65918
6	6.03760	6.03824	6.03633	6.01809	6.02409	6.01864	5.99261	5.34857	5.33885	5.32491
7	8.30352	8.30447	8.30186	8.28061	8.28816	8.28144	8.24699	7.33136	7.31913	7.30315
8	10.93054	10.9318	10.9285	10.90424	10.9133	10.90539	10.86248	9.62665	9.61191	9.59388
9	13.91868	13.9203	13.9163	13.88898	13.8996	13.89049	13.8391	12.23444	12.21720	12.19712
10	17.26793	17.2699	17.2652	17.23483	17.2470	17.23671	17.2085	15.15472	15.13499	15.11286

Table 4. Comparison of our results from the present modified atomic orbital theory (MAOT) for excitation energies of ${}_2(K,T)_n^{+\ 1,3}P^\circ$ and ${}_2(K,T)_n^{-\ 1,3}P^\circ$ autoionizing states of Li^+ complex—coordinate rotational (CCR) results Chung and Lin [11]. Here and in [11], the energy of each state is measured from the ground state of Li equals to—07.280521a.u with 1 a.u. (^{7}Li) = 27.20927 eV, which includes the reduced mass correction. Screening constant by unit nuclear charge (SCUNC) results [15]. All results are expressed in eV.

			E (eV)				
State	MAOT	CCR	SCUNC	State	MAOT	CCR	SCUNC
		$^1P^\circ$				$^3P^\circ$	
${}_2(0,1)_3^+$	160.93097	161.0509	160.9629	${}_2(0,1)_3^+$	159.82727	159.8314	159.8114
${}_2(0,1)_4^+$	163.86789	163.9351	163.9019	${}_2(0,1)_4^+$	163.40019	163.4096	163.4464
${}_2(0,1)_5^+$	165.18079	165.2337	165.2172	${}_2(0,1)_5^+$	164.91783	164.9662	164.9849
${}_2(0,1)_6^+$	165.88875	165.9304	165.9194	${}_2(0,1)_6^+$	165.72018	165.7769	165.7823
${}_2(0,1)_7^+$	166.31626	166.3473	166.3384	${}_2(0,1)_7^+$	166.20227	166.2513	166.2493
${}_2(0,1)_8^+$	166.59484	166.6164	166.6084	${}_2(0,1)_8^+$	166.51684	166.5524	166.4644
${}_2(0,1)_9^+$	166.78662	166.8002	166.7926	${}_2(0,1)_9^+$	166.73419	166.7553	166.7473
		$^1P^\circ$				$^3P^\circ$	
${}_2(0,1)_3^-$	159.21762	159.1704	159.2016	${}_2(0,1)_3^-$	160.08063	160.0419	160.0602
${}_2(0,1)_4^-$	163.17450	163.2004	163.2550	${}_2(0,1)_4^-$	163.62036	163.5789	163.6071
${}_2(0,1)_5^-$	164.76855	164.8734	164.9079	${}_2(0,1)_5^-$	164.98422	165.0658	165.0942
${}_2(0,1)_6^-$	165.62991	165.7275	165.7469	${}_2(0,1)_6^-$	165.73689	165.8377	165.8609
${}_2(0,1)_7^-$	166.15893	166.2219	166.2319	${}_2(0,1)_7^-$	166.21001	166.2907	166.3084
${}_2(0,1)_8^-$	166.50818	166.5335	166.5378	${}_2(0,1)_8^-$	166.52840	166.5794	166.5925
${}_2(0,1)_9^-$	166.75018	166.7424	166.7432	${}_2(0,1)_9^-$	166.75248	166.7747	166.7841

modified atomic orbital theory (MAOT) with the saddle-point complex-rotation method (SPCR) [8], the close-coupling method [9], the truncated-diagonalization method (TDM) [10], the complex coordinate rotation (CCR) [21], the screening constant by unit nuclear charge (SCUNC) results [15] and with the data from Debye screening model (DSM) [16]. The calculations agree well with each other. **Table 3** indicates the present MAOT calculations for some ${}_2(K,T)_n^{+\ 1,3}P^\circ$ autoionizing states of the helium isoelectronic sequence (Z = 2 - 10) compared to the CCR data [13], the SCUNC results [15] and to the CDS calculations [12]. It is seen that the present results compared well to both CCR [13], SCUNC [15], and DSM [16] results. As far as the slight discrepancies between the MAOT results and that from CDS, they are mainly due to the fact that the formalism of Ivanov and Safronova [12] is done in the framework of the independent particles model which disregards the classification (+, –) of the supermultiplets investigated. This may point out the merit of the present MOAT formalism to identify separately the classification of the ${}_n(K,T)_N^{A\ 2S+1}L^\pi$ Rydberg states in the framework of a simple analytical procedure. The present calculated excitation energies of the ${}_2(0,1)_n^{+\ 1}P^\circ$, ${}_2(1,0)_n^{+\ 3}P^\circ$, ${}_2(1,0)_n^{-\ 1}P^\circ$ and ${}_2(0,1)_n^{-\ 3}P^\circ$ states of Li^+ are listed in **Table 4** and compared to the complex—coordinate rotational results of Chung and Lin [14]. These authors have included in their theory reduced mass and relativistic corrections (correction to kinetic energy, Darwin term) and stated that their calculated resonance energies are expected to be accurate within a few meV. Even if the present MAOT formalism is for non-relativistic theory and where no reduced mass corrections are included in the calculations, it can be seen a good agreement between the present results and the complex—coordinate rotational data [14]. As far as comparison with the SCUNC results is concerned, the agreement is seen to be also good. It should be mentioned that the good accuracy obtained in this paper indicates the adequacy of the MOAT formalism to treat the properties of the ${}_2(K,T)_n^{\pm\ 1,3}P^\circ$ autoionizing states of two electron systems. The good results presented in this work may be explain by the fact that the σ-fitting screening constants evaluated using experimental data incorporate implicitly relativistic corrections to the energy levels of the states investigated. In other words, the semi-empirical Formula (4) are not purely classical ex-

pressions. But, for sake of very good accuracy in the calculations, relativistic corrections and mass polarisation must be taken explicitly into account.

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