Energy levels of $1s^2nd$ ($n \leq 9$) states for lithium-like ions*

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The full-core plus correlation method with multi-configuration interaction wave functions is extended to the calculation of the non-relativistic energies of $1s^2nd$ ($n \leq 9$) states for the lithium isoelectronic sequence from $Z = 11$ to 20. Relativistic and mass-polarization effects on the energy are calculated as the first-order perturbation correction. The quantum-electrodynamics correction is also included. The fine structure splittings are determined from the expectation values of spin–orbit and spin–other-orbit interaction operators in the Pauli–Breit approximation. Combining the term energies of lowly excited states obtained with the quantum defects calculated by the single channel quantum defect theory, each of which is a smooth function of energy and approximated by a weakly varying function of energy, the ion potentials of highly excited states ($n \geq 6$) are obtained with the semi-empirical iteration method. The results are compared with experimental data in the literature and found to be closely consistent with the regularity.

Keywords: lithium-like ions, excited states, quantum defect theory, quantum defect

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1. Introduction

The lithium atom has been served as a test system for various theoretical developments for a long time, aiming at the accurate determination of atomic and molecular properties. As far as an atomic system is concerned, it can be regarded as a few-electron system, so it is hopeful for obtaining accurate results for a variety of properties. In addition, the lithium-like ion is one of the simplest systems and offers the possibility of studying core, valence and valence-core interactions, and it is also an interesting system for investigating the role of correlations among the electrons.

The energy structure of lithium-like systems makes them suited for accurate spectroscopic studies. For example, the lifetime for the 2p $^2P^O$ state in lithium has been measured with a number of different techniques, including the bam-gas-laser method.[1] The Li isotope shift for the 2s ^{2}S–2p $^2P^O$ transition has been measured accurately with Doppler-free frequency modulation spectroscopy.[2] However, there are few available theoretical investigations on highly charged lithium-like ions in the literature.

More recently, a series of variational calculations on lithium and lithium-like ions with full-core plus correlation (FCPC) method has been performed.[3,4] In earlier papers, calculations of the energy levels and the oscillator strengths for all levels $n \leq 9$ in low-Z lithium-like ions of the elements BeII, BIII, CIV, NV, OVI, FVII, NeVIII using the FCPC method including mass polarization, quantum-electrodynamics (QED) and relativistic corrections were presented, and the accuracy obtained for the excited states was well satisfied.[5–7] Now, this method has been successfully used to calculate the energy levels and the oscillator strengths of nl ($n \leq 9$, l=s, p) states of lithium-like systems along the isoelectronic sequence.[8–11]

In the present paper, the method is extended to the calculation of the excitation energies, the ion potentials and the fine structure splittings of $1s^2nd$ ($n \leq 9$) states for the lithium-like ions from NaIX to CaXVIII. Those states have been studied very little so far. In order to test the accuracy of the method presented, the calculated results are compared with experimental data available in the literature. For all of the ions considered, the comparisons indicate that all of the discrepancies lie in the measurement error range of the experimental data.

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All of the computations in this work are carried out with a program in Fortran language composed by Dr. Kwong T. Chong's group, its detail has been described in Ref. [3]. The results obtained in this work are in atomic units (a.u.). However, accurate experimental data are mostly given in cm^{-1}. Therefore, to make a definitive comparison with the experiment, the excitation energies and fine structure splittings of the $1s^2 n\,d$ states ($n \leq 9$) from Na IX to Ca XVIII evaluated are converted into cm^{-1} using the reduced Rydberg constant.

2. Theory

The full-core plus correlation method used at present follows that of Ref. [3] closely, its details will not be repeated again. The variational wave function of the $1s^2 n\,d$ ($n \leq 9$) states for the lithium isoelectronic sequence, using square-integrated Slater-type basis sets, is given by

$$\Psi(1,2,3) = A\Big[\Phi_{1s1s}(1,2)\sum_i d_i r_3^i \,\mathrm{e}^{-\beta r_3} Y_{l(i)}(3)\,\chi(3) + \sum_i C_i \Phi_{n(i),l(i)}(1,2,3)\Big], \quad (1)$$

where A is the anti-symmetrization operator. In the first term on the right-hand side of Eq. (1), the factor multiplied with Φ_{1s1s} is the linear combination of the Slater orbital for the valence electron and Φ_{1s1s} is a predetermined $1s^2$-core wave function and represented in terms of a configuration interaction basis set. The second term on the right-hand side accounts for three-electron correlation and the relaxation of the core.

The non-relativistic energies of the $1s^2$-core and $1s^2 n\,d$ states are calculated by minimizing the expectation value as follows:

$$\delta E_0 = \delta\langle H_0\rangle = \delta\frac{\langle\Psi|H_0|\Psi\rangle}{\langle\Psi|\Psi\rangle}, \quad (2)$$

where H_0 is the non-relativistic Hamiltonian.

The corrections from the relativistic and mass-polarization effects are expressed as

$$\Delta E = \langle\Psi|H'|\Psi\rangle. \quad (3)$$

The perturbation operator, H', includes corrections from kinetic energy, the Darwin term, the electron–electron contact term, the mass-polarization term and orbit–orbit interaction. Thus, the total energy including the corrections is

$$E_{\mathrm{tot}} = E_0 + \Delta E. \quad (4)$$

For the system with larger Z value, the correction from the QED effect should also be considered. This correction can be evaluated for the valence $n\,d$ electron by using the hydrogenized formula with an effective nuclear charge Z_{eff}.[12]

The excitation energy of the excited states $1s^2 n\,d$, including corrections of the relativistic, mass-polarization and QED effect, is the energy above the ground state. That is,

$$\text{Excitation energy}(1s^2 n\,d) = \mathrm{IP}(1s^2 2s) - \mathrm{IP}(1s^2 n\,d). \quad (5)$$

As is well known, most of the fine structure splittings of the excited states come from the main physical reasons, the spin–orbit and the spin–other-orbit interactions. In the calculation of fine structure splitting, the *LSJ* coupling scheme is used. The energy for the fine structure obtained by computing the expectation values of spin–orbit and the spin–other-orbit operators, namely H_{so} and H_{soo}, and the QED correction to the fine structure splitting estimated from Ref. [3] are given

$$\Delta E_{\mathrm{fs}}^J = \langle LSJM_J|H_{\mathrm{so}} + H_{\mathrm{soo}}|LSJM_J\rangle + \Delta E_{\mathrm{QED}}^J(n\,d), \quad (6)$$

$$\Delta E_{\mathrm{QED}}^J(n\,d) = \Delta E_{\mathrm{QED}}^{5/2} - \Delta E_{\mathrm{QED}}^{3/2} = \frac{Z_{\mathrm{eff}}^4\,\alpha^3}{4\pi\,n^3}. \quad (7)$$

In the calculations of highly excited states or continuum states, the levels between different states become smaller and smaller, it is difficult to obtain accurate energy levels with the traditional variational method. In order to verify the accuracy of the results calculated in this work, the quantum defect theory is taken into consideration, which has been successfully used to calculate the energy levels of highly excited or continuum states of some atomic and molecule systems. For the lithium-like isoelectronic sequence, from the discrete region to the near-threshold region, the $1s^2$-core excited energy is very high so that the interactions among the channels are small enough to be neglected. Hence the behaviours of the highly excited states can be described well with the single-channel quantum defect theory.

The contributions of relativistic effects in highly charged ions are significantly increased compared with those in neutral atoms. For this reason it is natural to describe the interaction of the valence electron with the core in terms of the relativistic quantum defect.[13]

The term energy of excited state can be expressed by the relativistic quantum defect theory as

$$E_{nk} = mc^2 \left\{ \frac{1}{[1 + (Z_c\alpha/n^*)^2]^{1/2}} - 1 \right\}, \quad (8)$$

where α is the fine structure constant, n^* is the effective quantum number,

$$n^* = n - \mu_{nk}, \quad (9)$$

Z_c is the charge of the core, mc^2 is the electron rest energy (in atomic units, $mc^2 = \alpha^{-2}$) and μ_{nk} is quantum defect.

According to the single-channel quantum theory, the quantum defect of the highly excited state should be a smooth function of energy and approximated by a weakly varying function of energy in the following form:

$$\mu_{nk} = \mu_0 + h_1 E + h_2 E^2. \quad (10)$$

The coefficients μ_0, h_1 and h_2 for each series are determined by the value μ_{nk} obtained from Eq. (8). Treating Eqs. (8) and (10) as a system equation for E_{nk} and μ_{nk}, the quantum defect μ_{nk} and the term energy E_{nk} for highly excited states ($n \geq 10$) can be determined by the semi-empirical (S.E.) iteration method.

3. Results and discussion

For the $1s^2$-core states of the lithium-like systems, the wave function with 222-terms in seven components is used in Eq. (1). Eight d_i terms and 502 terms of $\Phi_{n(i)l(i)}$ with 10 partial waves are used in the calculation of the $1s^2n\,d$ energy. The energy convergence pattern for $1s^2n\,d$ states is quite similar for each n along this isoelectronic sequence. With the wave functions obtained above, the excitation energies of the $1s^2n\,d$ states ($n \leq 9$) from Na IX to Ca XVIII are evaluated with Eq. (5) and listed in Table 1. The experimental data available in the literature are also given in this table. For $1s^2n\,d$ states ($n \leq 9$), it is shown that most of excitation energies of $1s^2n\,d$ states ($n \leq 9$) for lithium-like systems are in excellent agreement with experimental data available in the literature, although the experimental uncertainties in Refs. [14]–[18] are several hundreds of cm^{-1}, or even more. It indicates that the agreement between the results obtained and available experimental data is satisfactory for these states. As far as experimental and theoretical data are concerned, there exist no new data available in some cases up to now yet. It is hoped that some interest in highly accurate experimental measurements or exactly theoretical calculations may be aroused due to the present predictions.

Table 1. Excitation energies for $1s^2n\,d$ ($3 \leq n \leq 9$) states of lithium-like systems from $Z = 11$ to 20 (in cm^{-1}).

Z	States	This work	Exp.[14−16]	Z	States	This work	Exp.[17]
11	$1s^23d$	1430282		16	$1s^23d$	3311027	
	$1s^24d$	1862726			$1s^24d$	4357409	
	$1s^25d$	2062906			$1s^25d$	4841833	
	$1s^26d$	2171369			$1s^26d$	5103472	
	$1s^27d$	2237153			$1s^27d$	5262129	
	$1s^28d$	2279473			$1s^28d$	5365095	
	$1s^29d$	2308642			$1s^29d$	5435670	
12	$1s^23d$	1744007		17	$1s^23d$	3781471	
	$1s^24d$	2277876			$1s^24d$	4982694	
	$1s^25d$	2525013			$1s^25d$	5538817	
	$1s^26d$	2658843	2658800		$1s^26d$	5839037	
	$1s^27d$	2739775	2739600		$1s^27d$	6021179	
	$1s^28d$	2792307			$1s^28d$	6139384	
	$1s^29d$	2828314			$1s^29d$	6220410	
13	$1s^23d$	2088822		18	$1s^23d$	4283783	
	$1s^24d$	2734796			$1s^24d$	5650546	
	$1s^25d$	3033854	3033700		$1s^25d$	6283325	
	$1s^26d$	3196401	3196400		$1s^26d$	6624651	
	$1s^27d$	3294305	3294300		$1s^27d$	6831905	
	$1s^28d$	3358096	3358100		$1s^28d$	6966382	
	$1s^29d$	3400740			$1s^29d$	7058584	

Table 1. (*Continued*).

Z	States	This work	Exp.[14−16]	Z	States	This work	Exp.[17]
14	$1s^2$3d	2464837		19	$1s^2$3d	4818050	
	$1s^2$4d	3233596			$1s^2$4d	6361033	
	$1s^2$5d	3589478			$1s^2$5d	7075418	
	$1s^2$6d	3781966	3782700		$1s^2$6d	7460431	
	$1s^2$7d	3898521	3899150		$1s^2$7d	7694408	
	$1s^2$8d	3974163	3974800		$1s^2$8d	7846258	
	$1s^2$9d	4026033	4026722		$1s^2$9d	7950374	
15	$1s^2$3d	2872186		20	$1s^2$3d	5384478	
	$1s^2$4d	3774413			$1s^2$4d	7114375	
	$1s^2$5d	4192093	4192300		$1s^2$5d	7915330	
	$1s^2$6d	4419425	4419350		$1s^2$6d	8345605	8345000
	$1s^2$7d	4554644			$1s^2$7d	8608991	8610000
	$1s^2$8d	4643421			$1s^2$8d	8779185	
	$1s^2$9d	4704287			$1s^2$9d	8894384	8894400

The fine-structure splittings of $1s^2n\,d$ ($n \leq 9$) states for the lithium-like ions from $Z = 11$ to 20 are calculated with Eqs. (6) and (7), the comparisons among results calculated, other theoretical results[19] and experimental results[20] are given in Table 2 and plotted in Fig. 1. It is interesting to find that the excellent agreement between results calculated in this work and theoretical results of Ref. [19] for $1s^2n\,d$ ($3 \leq n \leq 5$) states from $Z = 11$ to 20 is obtained and the discrepancy is well below 10 cm^{-1}. However, the agreement between the calculated results and experimental ones are not satisfactory, especially for Na IX $1s^2$4d and $1s^2$6d states. For $1s^2$4d state of Na IX, the theoretical results are both 100 cm^{-1}, i.e., they are equal to each other. However, the experimental result is 320 cm^{-1}, it is higher than the theoretical result, even higher than the experimental result of $1s^2$3d state in Ref. [20], 200 cm^{-1}, and it is equal to the experimental result of $1s^2$4d state of MgX, 320 cm^{-1}. As for the $1s^2$6d state of Na IX, the result calculated is 30 cm^{-1}, and the experimental result is 160 cm^{-1}, it is also higher than the experimental result of $1s^2$5d state, 50 cm^{-1}. Such situations are also for the $1s^2$4d state of KXVII, CaXVIII and $1s^2$5d state of KXVII. As is well known, the fine structure splitting decreases slowly while the principal quantum number n increases gradually along the Rydberg series for an atom or ion, and it will increase rapidly with the increase of nuclear charge Z along the isoelectronic sequence. It is noticeable the fine structure splittings of $1s^2n\,d$ ($n \leq 9$) states obtained in this work follow a well-behaved isoelectronic curve. On the contrary, the experimental data deviate from the isoelectronic regularity of fine-structure splitting drastically. It is suggested that some of the experimental data of Ref. [20] are probably too large to be neglected. These experimental data are unreasonable and their reliabilities are open to suspicion. The reason is that these unusual data are probably due to misidentification, so there may be large error bar in the observed optical lines in some cases, which are undistinguished from each other accurately or mistaken for each other. In most cases, there are no experimental data available in the literature to be compared with theoretical results. It is believed that the present predictions may provide valuable reference data for highly accurate experimental measurements and theoretical calculations in the future.

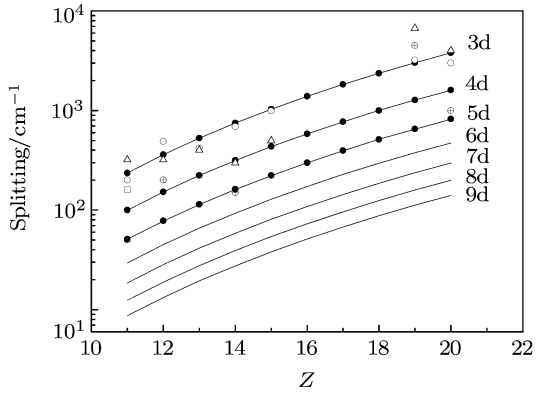


Fig. 1. Fine structure splittings for $1s^2n\,d$ ($3 \leq n \leq 9$) states of lithium-like systems from NaIX to CaXVIII, the solid lines are for the results obtained in this work, the black dots are for the theoretical results of Ref. [19] and other symbols are for experimental data of Ref. [20]. The symbols ◯, △, ⊕, □ denote the experimental data of $1s^2n\,d$ ($3 \leq n \leq 6$) states, respectively.

Table 2. Fine-structure splittings of $1s^2nd$ $(3 \leq n \leq 9)$ states for the lithium-like ions from $Z = 11$ to 20 (in cm^{-1}).

States	Z	This work	Other works[19]	Exp.[20]	Z	This work	Other works[19]	Exp.[20]
3d	11	237	236	200	16	1386	1387	
4d		100	100	320		584	585	
5d		51	51	50		299	300	
6d		30		160		173		
7d		19				109		
8d		12				73		
9d		9				52		
3d	12	361	360	490	17	1827	1829	
4d		152	152	320		770	772	
5d		78	78	200		394	395	
6d		45				228		
7d		28				144		
8d		19				96		
9d		13				68		
3d	13	528	528	420	18	2365	2369	
4d		223	223	400		1004	1000	
5d		114	114			514	512	
6d		66				295		
7d		41				186		
8d		28				125		
9d		20				88		
3d	14	748	748	690	19	3015	3021	3200
4d		315	316	300		1271	1275	6700
5d		161	162	150		650	653	4500
6d		93				376		
7d		59				237		
8d		39				159		
9d		28				112		
3d	15	1031	1031	990	20	3789	3798	3000
4d		434	435	500		1598	1603	4000
5d		222	223			818	821	1000
6d		129				473		
7d		81				299		
8d		54				200		
9d		38				140		

Combining Eqs. (8) and (10), the ion potentials for highly excited states $1s^2nd$ $(6 \leq n \leq 9)$ from $Z = 11$ to 20 are calculated again with the semi-empirical iteration method. In order to verify the accuracy of the results calculated with the iteration method, the comparisons between the semi-empirical method and FCPC methods are given in Table 3. As is shown, the accuracy of term energies of highly excited states relies partly on the expansion coefficients determined by the quantum defects and term energies of lowly excited states. It should be noted the results from the two methods, i.e., FCPC and the semi-empirical methods, are in good agreement with each other and the relative deviation is less than 10^{-4}. For Na IX $1s^26d_{3/2}$ states, the ion potential expended in this work is 1.125867 a.u., the same as one calculated with FCPC method, which is 1.125781 a.u. The absolute deviation between them is 0.000086 a.u. As for Na IX $1s^29d_{3/2}$ states, the results are 0.5002600 a.u. and 0.5002466 a.u. respectively, the absolute deviation is 0.0000134 a.u. It is reasonable to confirm the energies of highly excited states $(n > 9)$ can be predicted accurately with the reliable quantum defects μ_{nk} as input.

Table 3. Comparison of ionization potential for $1s^2 n\,d_{3/2,5/2}$ ($6 \leq n \leq 9$) states between the semi-empirical method and FCPC method for lithium-like system from $Z = 11$ to 20 (in a.u.).

		$J = 3/2$		$J = 5/2$	
Z	States	Semi-empirical	FCPC	Semi-empirical	FCPC
11	6d	1.125867	1.125781	1.125733	1.125647
	7d	0.8270787	0.8270357	0.8269942	0.8269511
	8d	0.6331812	0.6331598	0.6331246	0.6331031
	9d	0.5002600	0.5002466	0.5002202	0.5002068
12	6d	1.389886	1.3898711	1.3896811	1.3896662
	7d	1.021050	1.0210423	1.020921	1.0209133
	8d	0.7816864	0.7816827	0.7815999	0.78159615
	9d	0.6175940	0.6175947	0.6175333	0.61753399
13	6d	1.681874	1.681830	1.681455	1.681529
	7d	1.235535	1.235527	1.235283	1.235338
	8d	0.9458823	0.9458885	0.9457179	0.9457619
	9d	0.7473174	0.7473391	0.7472041	0.7472501
14	6d	2.001760	2.001605	2.001334	2.001179
	7d	1.470512	1.470438	1.470244	1.470171
	8d	1.125762	1.125725	1.125583	1.125546
	9d	0.8894296	0.8894154	0.8893033	0.8892893
15	6d	2.349360	2.349230	2.348775	2.348644
	7d	1.725865	1.725803	1.7254971	1.725434
	8d	1.3212491	1.321227	1.321003	1.320980
	9d	1.043877	1.043867	1.043703	1.043694
16	6d	2.724888	2.724717	2.724101	2.723929
	7d	2.001718	2.001636	2.001222	2.001139
	8d	1.532422	1.532380	1.532090	1.532047
	9d	1.210711	1.210690	1.210478	1.210455
17	6d	3.128284	3.128083	3.127250	3.127044
	7d	2.298040	2.297942	2.297389	2.297288
	8d	1.759262	1.759213	1.758826	1.758775
	9d	1.389923	1.389896	1.389616	1.389587
18	6d	3.559523	3.559323	3.558179	3.557984
	7d	2.6148191	2.614729	2.613973	2.613882
	8d	2.001763	2.001719	2.001197	2.001153
	9d	1.581507	1.581488	1.581109	1.581089
19	6d	4.018710	4.018487	4.016997	4.016773
	7d	2.952114	2.951961	2.951035	2.950887
	8d	2.259963	2.259870	2.2592401	2.259146
	9d	1.785489	1.785458	1.784981	1.784947
20	6d	4.505745	4.505561	4.503589	4.503406
	7d	3.309872	3.309784	3.308515	3.308427
	8d	2.533829	2.533787	2.532920	2.532879
	9d	2.001848	2.001829	2.001209	2.001190

4. Conclusions

In this work, we concentrate on the extension of accurate predictions of energy and fine structure splitting of the lithium-like ions with higher nuclear charge and in the higher energy region along the isoelectronic sequence.

The results indicate that the calculated excitation energies and fine structure splittings of the $1s^2 n\,d$ states ($n \leq 9$) for the systems from $Z = 11$ to 20 are in good agreement with most experimental data available in the literature. In the cases of Na IX, KXVII,

CaXVIII $1s^2 4d$ states and the Na IX $1s^2 6d$ state, there are noticeable discrepancies between the results obtained in this work and experimental data. We hope that our results may arouse some interest in making highly accurate experimental measurement.

Based on the energies and the wave functions of $1s^2 n\,d$ lowly excited states of lithium-like ions, the quantum defects for Rydberg series of these ions can be calculated and approximated by a weakly varying function of energy. With the quantum defects used as input in calculation, the ion potentials for highly excited states ($6 \leq n \leq 9$) are calculated again by the iteration method, the relative deviation is within 0.0076. Thus, the accurate predictions make it possible to predict the highly excited energy below the threshold region of these systems and the results should be reasonable and accurate. The results obtained show that the method used in this work is effective for energy level calculations of the lithium-like systems with higher nuclear charge along the isoelectronic sequence, the reliable predictions will enrich the basic data greatly and provide a useful reference for the study in spectral and other regions.

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