CHEMICAL ENGINEERING TRANSACTIONS

VOL. 71, 2018

A publication of
AIDIC
The Italian Association
of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Xiantang Zhang, Songrong Qian, Jianmin Xu

ISBN 978-88-95608-68-6; **ISSN** 2283-9216

DOI: 10.3303/CET1871110

Energies and Quantum Defects of $1s^2ng$ States for Lithium-like Ions from Scandium to Zinc

Xin Liu, Jingchao Zhang*

Key Laboratory for Microstructural Material Physics of Hebei Province, School of Science, Yanshan University,
Qinhuangdao 066004, China
ysu-zjc@163.com

The non-relativistic energy and wave function of high angular momentum $1s^2ng$ ($5 \leq n \leq 8$) states of lithium-like isoelectronic sequence from ScXIX to ZnXXVIII are calculated using the full-core-plus-correlation (FCPC) method. Relativistic effects and mass polarization effects are considered as perturbations, and their corrections to system energy are estimated. In order to get hold of high-precision theoretical results, it is also necessary to consider the contribution of quantum electrodynamics (QED). Based on the single-channel quantum defect theory, the quantum defects of $1s^2ng$ Rydberg series are determined, and the results are in full compliance with its physical laws. Comparing the ionization potential obtained by the semi-empirical method with the FCPC method, it can be seen that the results are in good agreement. Consequently, the ionization potential can be extrapolated to the energy territory with larger principal quantum numbers to forecast the approximate value of unknown energy levels, which provides theoretical instruction for relevant studies.

1. Introduction

In recent years, owing to the promotion of demand in many high-tech fields and the development of experimental technologies, the generation of experimental devices of highly charged ion (HCI) based on photoionization and electron impact ionization not only makes the research in this field become one of the frontiers of international atomic physics, but also offers possibilities for understanding the universe and opening up important applications of HCI.(Gillaspy, 2001) Under the current quantum theory framework, the key to solving the multi-electron atom system is how to dispose of electronic association and relativistic effects. Pekeris made a comprehensive and in-depth study of the nature of two-electronic system using the Hylleras method.(Pekeris et al., 1962) Drake and Yan used multiple basis sets techniques in the Hylleras coordinate expansion.(Drake and Yan, 1995; Yan and Drake, 1995) Kelly first applied the Multibody Perturbation Theory (MBPT) to Be atoms in 1963.(Kelly, 1963) Wiese and Weiss studied the variation of oscillator strength with isoelectronic sequences using the 1/Z expansion method.(Wiese and Weiss, 1968) Layzer made a comprehensive calculation of the second-order energy correction.(Layzer et al., 1964) Vainshtein and Safronova calculated the energy structures of lowly excited states of the helium-like and lithium-like ions.(Vainshtein and Safronova, 1985) Marinescu, Sadeghpour, and Dalgarno used the model potential method to study the long-range interactions between alkali metal atoms and achieved expected results.(Marinescu et al., 1994) However, these methods constantly tangled with problems such as numerical convergence and low accuracy.

At present, a method named full-core-plus-correlation (FCPC) has been systematically performed on the structures and properties of the $1s^2nl$ states ($n \leq 9$, $l \leq 3$) for lithiumlike atoms, and accumulated a large amount of accurate and trusted theoretical data.(Ge et al., 2004; Li et al., 2013; Hu and Wang, 2008; Hu and Wang, 2009; Li and Wang, 2014; Wang et al., 2005) A challenging issue is whether the identical precision is also conceivable for highly excited states and particularly for the states of high angular momentum.

In this work, all the numerations are written using the Fortran language program devised by Dr. Kwong T. Chung's group. (Chung, 1991; Chung, 1992) This paper extends the theoretical approach to reckon the nonrelativistic energies of $1s^2ng$ states from ScXIX to ZnXXVIII by the Rayleigh-Ritz method. The quantum

Please cite this article as: Liu X., Zhang J., 2018, Energies and quantum defects of 1s2ng states for lithium-like ions from scandium to zinc, Chemical Engineering Transactions, 71, 655-660 DOI:10.3303/CET1871110

defects of the Rydberg series are obtained, which enabled a reliable prediction of the highly excited energy of the ion. As is known to all, a dependable theoretical prediction of energies and quantum defects is especially imperative because high precision measurements are hard to achieve,and the experimental data on high angular momentum ions available in the literature is also unsatisfactory. On various occasions, credible theoretical prediction for these momentous data is apparently of significance.

2. Theory

This paper uses Slater-type basis sets, the FCPC wave function for lithium-like isoelectronic sequence can be represented in the form:

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

The concrete expressions for Φ_{1s1s} and $\Phi_{n(i),l(i)}$ can be found in Ref. (Chung, 1991; Chung, 1992) and will not be repeated here.

Summation of all three electrons with a single electron operator and adding the electrostatic Coulomb interaction potential between the electrons yields the non-relativistic Hamiltonian operator of the system,

$$H_0 = \sum_{i=1}^{3}\left[-\frac{1}{2}\nabla_i^2 - \frac{Z}{r_i}\right] + \sum_{\substack{i,j=1\\ i<j}}^{3}\frac{1}{r_{ij}}, \tag{2}$$

Where r_i is the distance between the i-th electron and the nucleus, and r_{ij} is the distance between the i-th electron and the j-th electron, and the sum of $i < j$ over all electron pairs.

Under the Pauli-Breit approximation, (Bethe and Salpeter, 1957) various relativistic modified operator and mass polarization term are available,

$$H' = H_1 + H_2 + H_3 + H_4 + H_5\ . \tag{3}$$

Where the explicit representation of each item can be shown in Ref. (Chung, 1991; Chung, 1992).

The non-relativistic energies of the 1s^2-core and 1s^2*n*g states are acquired by minimizing the expectation value of their corresponding non-relativistic Hamiltonian operator H_0:

$$\delta E_0 = \delta\langle H_0\rangle = \delta\frac{\langle\Psi|H_0|\Psi\rangle}{\langle\Psi|\Psi\rangle}. \tag{4}$$

The modification of relativity and mass polarization effect are treated as the first-order perturbation theory,

$$\Delta E = \langle\Psi|H'|\Psi\rangle = \langle\Psi|H_1 + H_2 + H_3 + H_4 + H_5|\Psi\rangle. \tag{5}$$

Consequently, the total energy of 1s^2*n*g state along the sequence is

$$E_{\mathrm{tot}} = E_0 + \Delta E. \tag{6}$$

For the sake of getting accurate ionization energy, the contribution of the QED effect should also be included. When computing the ionization potential of the system, the revision of the QED effect from the 1s^2-core is essentially offset, so merely the QED contribution of the valence electrons needs to be taken into consideration. This part of correction can be estimated by using the corresponding hydrogen-like pattern (Bethe and Salpeter, 1957):

$$\Delta E_{\mathrm{QED}} = \frac{4Z_{\mathrm{eff}}^4\alpha^3}{3\pi n^3}\left\{\delta_{l,0}\left[\ln(Z_{\mathrm{eff}}\alpha)^{-2} + \frac{11}{24} - \frac{1}{5}\right] - \ln\left[\frac{k_0(nl)}{Z_{\mathrm{eff}}^2 R_\infty}\right] + \frac{3}{8}\frac{C_{lj}}{(2l+1)}\right\}, \tag{7}$$

Where

$$\begin{aligned} C_{lj} &= (l+1)^{-1}, j = l + 1/2, \\ C_{lj} &= -l^{-1}, j = l - 1/2. \end{aligned} \tag{8}$$

α is a fine structure constant. Obviously, the first term in Eq. (7) is a amendment to the average energy of the configuration, which can only cause the shift of the energy center of gravity of the *LS* spectral term. (Erickson and Yennie, 1965) For the system we have discussed, the value of the Bethe logarithm term $K_0(nl)$ is taken from literature (Drake and Swainson, 1990). The second term in Eq. (7) is the QED correction for fine structure splitting. (Erickson and Yennie, 1965)
The ionization potential (*IP*) of $1s^2ng$ states is derived from the following equation

$$IP\left(1\mathrm{s}^2\, n\mathrm{g}\right) = E_{\mathrm{tot}}(1\mathrm{s}^{2\,1}\mathrm{S}) - E_{\mathrm{tot}}(1\mathrm{s}^2\, n\mathrm{g}^2\mathrm{G}) - \Delta E^{\mathrm{g}}_{\mathrm{QED}}(n\mathrm{g}). \tag{9}$$

On the grounds of quantum defect theory (QDT), (Fano and Rau, 1986; Friedrich, 1991) the quantum defect μ_{Nk} of $1s^2ng$ system with energy E_n satisfying the following relationship:

$$E_n = -\frac{(Z-N+1)^2}{2(n^*)^2} = -\frac{(Z-N+1)^2}{2(n-\mu_{nK})^2}, \tag{10}$$

Where $n^* = n - \mu_{nK}$, μ_{nK} is called quantum defect along Rydberg series. From the QDT, (Fano and Rau, 1986; Friedrich, 1991) the quantum defect of high excited state can be expanded as follows:

$$\mu_{nK} = \mu_0 + h_1 E + h_2 E^2. \tag{11}$$

The coefficients μ_0 , h_1 , h_2 are determined by the energy values of the three lowest configurations of the Rydberg series achieved by the FCPC method. Using the undetermined coefficients μ_0 , h_1 , h_2, together with the quantum defect obtained by Eq. (10), the term energy of any excited states along the Rydberg series of $1s^2ng$ ($n \geq 10$) states from ScXIX to ZnXXVIII can be reckoned.

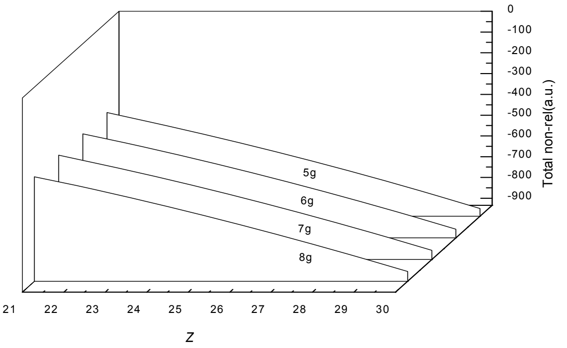

Figure 1: 3D waterfall of non-relativistic energies changes with nuclear charge number Z for $1s^2ng$ ($5 \leq n \leq 8$) states from ScXIX to ZnXXVIII (in a.u.)

3. Results and discussion

In the present paper, when calculating the $1s^2$ core energy, a total of 222 basis functions are developed. For the high angular momentum $1s^2ng$ state, the valence electron effect in the three-electron wave function is picked out by seven terms. The CI wave function selects seven subwaves, the number of entries from 707 to 721. In the variational calculation, the determination of partial wave terms are accomplished through the debugging for parameters and optimization for procedures, meanwhile the most reasonable combination is selected to attain the objective of high-precision theoretical calculation. The dimensions of such duration equations have dropped from 2261*2261, 2275*2275 to 714*714, 728*728, respectively. This greatly reduces the amount of computation. The problem of numerical calculation instability caused by excessive number of basic function items can be avoided, and the operation velocity can be greatly refined.
Figure 1 depicts the 3D waterfall of non-relativistic energy of $1s^2ng$ ($5 \leq n \leq 8$) states from ScXIX to ZnXXVIII changes with the nuclear charge *Z*. It is convenient to see that with an increasing nuclear charge number *Z*,

the non-relativistic energy of $1s^25g$, $1s^26g$, $1s^27g$, $1s^28g$ states diminishes monotonously, the rate of descent gradually becomes faster and has a similar tendency for each excited state.

The non-relativistic quantum defects of $1s^2ng$ states for lithium-like ScXIX, as a typical example, are plotted in Figure 2. It is not difficult to see that the quantum defect have grown slowly with the change in the pricipal quantum number. This is due to the fact that for the $1s^2ng$ state, the valence electron energy enlarged with an increasing pricipal quantum number. The valence electrons get closer to the $1s^2$-core, the penetration effect of the valence electrons on the $1s^2$-core and the polarization effect of the core gradually enhanced simultaneously. For instance, the non-relativistic quantum defect of $1s^25g$ state is 0.0005540, and the numerical value for $1s^26g$ state is 0.0009685, which increases in order and tends to be flat steadily. Wang reported the quantum defects of $1s^25s$, $1s^25p$, $1s^25d$ states of ScXIX ion with the value of 0.04685, 0.01613, 0.00284, respectively.(Wang et al., 2005) Comparing with the outcomes of $1s^25g$ state in this article, it is indicated that quantum defect decreases with the increasing of angular quantum number. This is because when the number of angular quantum grows, the external barrier builted by the centrifugal potential increases, which made the penetrating ability of the valence electrons weakened, and the short-range non-coulomb interaction between the valence electron and the $1s^2$-core also reduced, as a consequence the quantum defect is droped off. The energy expansion coefficients of quantum defects from ScXIX to ZnXXVIII are shown in Table 1.

Integrating Eqs. (10) with (11) , the ionization potentials of the lithium-like isoelectronic sequence for highly excited states $1s^2ng$ ($6 \le n \le 8$) are obtained from the semi-emprical iteration method. In order to further verify the accuracy of the energies calculated with the iteration method, a comparison of the semi-empirical method and FCPC methods are listed in Table 2. Taking the $1s^26g$ state of ScXIX for example, the ionization energy of the semi-empirical method is 5.015214 a.u., while the result of the FCPC method is 5.015341 a.u., their relative discrepancy is 0.0025%. As for the $1s^27g$ state, the two results are 3.684518 a.u. and 3.684620 a.u., individually. The relative deviation is 0.0028%.It is evident that the results obtained by the semi-empirical method have high accuracy. In this paper, the energy values of the main quantum number n are 10, 20, 30, 50, and 100 severally, and the relevant information are shown in Table 3.

Figure 3 reflects the extrapolation of energy along the Rydberg sequence in the excited states for different lithium-like systems more intuitively. It was indicated that when the main quantum number n is small, the energy changes rapidly. When n is around 30, the energy varies tardily and gradually approaches a constant.

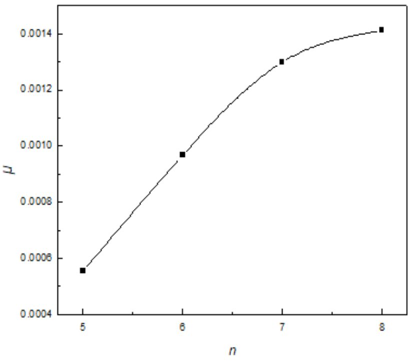

Figure 2: Quantum defects of $1s^2ng$ ($5 \le n \le 8$) states for ScXIX.

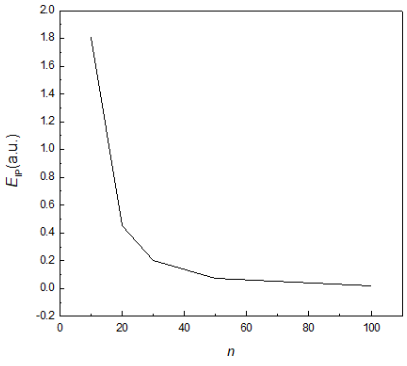

Figure 3: Extrapolation of ionization potentials under semi-empirical method for ScXIX (in a.u.).

Table 1: Coefficients in the expansions of quantum defects for $1s^2ng$ states of lithium-like systems from ScXIX to ZnXXVIII.

Z	μ_0	h_1	h_2	Z	μ_0	h_1	h_2
21	0.00012449	-0.00038187	0.00004656	26	0.00342373	-0.00044126	0.00001629
22	0.00199073	-0.00033961	0.00002098	27	0.00375971	-0.00042221	0.00001157
23	0.00213572	-0.00126341	0.00011470	28	0.00035953	-0.00024181	0.00001781
24	0.00009870	-0.00028489	0.00002387	29	0.00215794	-0.00007773	0.00000188
25	0.00607823	-0.00151415	0.00011014	30	0.00158655	-0.00050222	0.00002277

Table 2: Comparisons of ionization potentials for $1s^2ng$ ($n \geq 6$) states obtained from the FCPC method and semi-empirical method from ScXIX to ZnXXVIII. (in a.u.)

Z	*n*	FCPC	Semi-Emp.	*Z*	*n*	FCPC	Semi-Emp.
21	6	5.015341	5.015214	22	6	5.556947	5.556825
	7	3.684620	3.684518		7	4.082745	4.082623
	8	2.821308	2.820899		8	3.126145	3.125886
23	6	6.127654	6.127521	24	6	6.724318	6.724217
	7	4.501578	4.501409		7	4.940079	4.939305
	8	3.446784	3.446050		8	3.782813	3.782039
25	6	7.349425	7.349218	26	6	8.002497	8.002227
	7	5.399677	5.399422		7	5.879890	5.879650
	8	4.134725	4.134570		8	4.499289	4.501989
27	6	8.683350	8.683117	28	6	9.392206	9.392106
	7	6.380352	6.380152		7	6.900286	6.900078
	8	4.885378	4.885222		8	5.284031	5.282755
29	6	10.128975	10.128622	30	6	10.893183	10.893012
	7	7.441912	7.441723		7	8.002228	8.002004
	8	5.698089	5.697668		8	6.127957	6.125973

Table 3: Extrapolation of ionization potentials obtained by the semi-empirical method (in a.u.).

Z	*n*	Semi-Emp.	*Z*	*n*	Semi-Emp.	*Z*	*n*	Semi-Emp.	*Z*	*n*	Semi-Emp.
21	10	1.8052390	23	10	2.2050410	25	10	2.6465040	27	10	3.1265960
	20	0.4512630		20	0.5511687		20	0.6615890		20	0.7815186
	30	0.2005582		30	0.2449701		30	0.2939995		30	0.3473059
	50	0.0722004		50	0.0881929		50	0.1058251		50	0.1250185
	100	0.0180501		100	0.0220491		100	0.0264532		100	0.0312523

4. Conclusion

In this paper, we have extended the FCPC method to figure up the nonrelativistic energies of high angular momentum $1s^2ng$ states along the isoelectronic sequence from ScXIX to ZnXXVIII. The quantum defects of $1s^2ng$ states for Rydberg series have been determined. The accuracy of the semi-empirical method is entirely dependent on the precision of the coefficients in Eq. (10), and the accuracy of these coefficients rest upon the precision of the low excited state energy, therefore the exact and believable low excited state energy is the basis of achieving precise calculations with the semi-empirical method. While the FCPC method has obvious advantages in the calculation of low excited state energy levels in lithium-like systems, its theoretical results are more reliable and accurate than the experimental results. Hence we are convinced that the energy structures of high excited states for lithium-like system by using the semi-empirical method has a high resolution. As a consequence, we have completed the calculation of the energy of any excited state of $1s^2ng$ states of the lithium-like Rydberg series, and obtained more satisfactory results. The lithium-like system require more accurate experimental measurements and our research will make a significant contribution to the exploration and understanding of these high angular momentum systems.

Acknowledgments

Project supported by the National Natural Science Foundation of China (Grant No 21603185). We are grateful to Dr Kwong T. Chung for his hospitality.

References

Bethe H.A., Salpeter E.E., 1957, Quantum Mechanics of One-and Two-electon Systems, Berlin: Springer, DOI: 10.1007/978-3-642-45869-9_2

Chung K.T., 1991, Ionization potential of the lithiumlike $1s^22s$ states from lithium to neon, Physical Review A, 44(9), 5421-5433, DOI:10.1103/PhysRevA.44.5421

Chung K.T., 1992, Ionization potential for the lithiumlike $1s^22s$ states from Na Ⅸ to Ca ⅩⅧ, Physical Review A, 45(11), 7766-7773, DOI: 10.1103/PhysRevA.45.7766

Drake G.W.F., Swainson R.A., 1990, Bethe logarithms for hydrogen up to *n*=20, and approximations for two-electron atoms, Physical Review A, 41(3), 1243-1246, DOI: 10.1103/PhysRevA.41.1243

Drake G.W.F., Yan Z.C., 1995, Asymptotic-expansion method for the evaluation of correlated three-electron integrals, Physical Review A, 52(5), 3681-3685, DOI: 10.1103/PhysRevA.52.3681

Erickson G.W., Yennie D.R., 1965, Radiative level shifts I. Formulation and lowest order lamb shift, Annals of Physics, 35(2), 271-313, DOI: 10.1016/0003-4916(65)90081-3

Fano U., Rau A.R.P., 1986, Atomic Collision and Spectra, New York:Academic, DOI: 10.1063/1.2811640

Friedrich H., 1991, Theoretical Atomic Physics, Berlin: Springer, DOI: 10.1007/3-540-29278-0

Ge Z.M., Wang Z.W., Zhou Y.J., 2004, Theoretical calculation of ionization potential and term energy of the ground states $1s^22s$ of lithium-like systems from Z=21 to 30, Acta Physica Sinica, 53(1), 42-46.

Gillaspy J.D., 2001, Highly charged ions, Journal of Physics B: Atomic, Molecular and Optical Physics, 34 (19), R93-R130, DOI: 10.1088/0953-4075/34/19/201

Hu M.H., Wang Z.W., 2008, Behavious of the excited states $1s^2np$ along lithium isoelectronic sequence from Z=11 to 20, Chinese Physics B, 17(3), 908-914, DOI:10.1088/1674-1056/17/3/028

Hu M.H., Wang Z.W., 2009, Oscillator strengths for 2^2s-n^2p transitions of the lithium isoelectronic sequence from Z=11 to 20, Chinese Physics B, 18(6), 2244-2249.

Kelly H.P., 1963, Correlation effects in atoms, Physical Review, 131(2), 684, DOI: 10.1103/PhysRev.131.684

Layzer D., Horak Z., Lewis M.N., Thompson D.P., 1964, Second-order Z-dependent theory of many-electron atoms, Annals of Physics, 29(1), 101-124, DOI: 10.1016/0003-4916(64)90192-7

Le K.A., 2018, Optimisation of Energy Usage in Ceramic Kiln Using Pinch Technique, Chemical Engineering Transactions, 63, 313-318, DOI: 10.3303/CET1863053

Li J.Y., Ding D.J., Wang Z.W., 2013, Excited-state energies and fine structure of highly charged lithiumlike ions, Physical Review A, 88, 042511, DOI: 10.1103/PhysRevA.88.042511

Li J.Y., Wang Z.W., 2014, Ionization energies and term energies of the ground states $1s^22s$ of lithium-like systems, Chinese Physics B, 23(1), 013201, DOI:10.1088/1674-1056/23/1/013201

Marinescu M., Sadeghpour H.R., Dalgarno A., 1994, Dispersion coefficients for alkali-metal dimers, Physical Review A, 49(2), 982-988, DOI: 10.1103/PhysRevA.49.982

Pekeris C.L., Schiff B., Lifson H., 1962, Fine structure of the 2^3P and 3^3P states of helium, Physical Review, 126(3), 1057, DOI: 10.1103/PhysRev.126.1057

Vainshtein L.A., Safronova U.I., 1985, Energy levels of He- and Li-like ions (states $1snl$, $1s^2nl$ with n=2-5), Physica Scripta, 31(6), 519, DOI: 10.1088/0031-8949/31/6/012

Wang Z.W., Yang D., Hu M.H., Han Q.J., Li J.Y., 2005, Transition energy and oscillator strength of Sc^{18+} ion, Chinese Physics, 14(8), 1559-1565, DOI: 10.1088/1009-1963/14/8/015

Wiese W.L., Weiss A.W., 1968, Regularities in atomic oscillator strengths, Physical Review, 175(1), 50-65, DOI: 10.1103/PhysRev.175.50

Yan Z.C., Drake G.W.F., 1995, Theoretical lithium $2^2S \rightarrow 2^2P$ and $2^2P \rightarrow 3^2D$ oscillator strengths, Physical Review A, 52, R4316, DOI: 10.1103/PhysRevA.52.R4316