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Energy and fine structure of $1s^2np$ ($n \leq 9$) states for lithium-like systems from Z=11 to 20*

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A new variation method is extended to study the atomic systems with higher nuclear charges and in more highly excited states. The non-relativistic energies of $1s^2np$ ($n \leq 9$) states for the lithium-like systems from Z=11 to 20 are calculated using a full-core-plus-correlation method with multi-configuration interaction wavefunctions. Relativistic and mass-polarization effects on the energy are calculated as the first-order perturbation corrections. The fine structures are determined from the expectation values of spin-orbit and spin-other-orbit interaction operators in the Pauli–Breit approximation. The quantum-electrodynamics correction is also included. Our results are compared with experimental data in the literature.

Keywords: lithium-like system, full-core plus correlation, excitation energy, fine structure
PACC: 3130, 3110, 3270

1. Introduction

Research into the structure and property of highly ionized atomic systems has recently aroused great interest in connection with attempts to achieve amplification of radiation at short wavelengths and efforts to use the spectra of these ions as an important diagnostic tool for plasma.[1−3] In another area, multicharged ions are present in the solar corona and interstellar medium and knowledge of their spectra and collision processes is essential to astrophysics. The experimental data of these ions available in the literature are far from satisfactory now. In many cases, for example, the experimental data of the ionization potentials and excitation energies of the ions are only quoted to about 100cm^{-1} or 1000cm^{-1}, and do not distinguish their fine-structure splittings. Thus reliable theoretical prediction for these important data is obviously of significance.

Theoretically, the lithium-like system has served as a test case for theoretical methods for a long time. At the same time, the precision calculation of the lithium-like systems with a $1s^2$-core presents a formidable challenge. In this respect, an elegant and complete variational approach, namely, the full core plus correlation (FCPC) method, has been developed to calculate the ionization potentials of the lithium-like ground states from Z=3 to 10 with high precision.[4,5] They are predicted to within 1ppm of the experiment. This method has also been applied to the lowly excited states for lithium-like systems from Li I to Ne VIII.[6−8] Most of the calculated excitation energies and fine-structure splittings are in agreement with experimental data up to not more than 1cm^{-1}. The main difference of this method from the usual configuration interaction (CI) method is that the wavefunction of the core is predetermined and frozen as one single term in the three-electron wavefunction. The effect of valence electron is accounted for by multiplying the core wavefunction with a linear combination of single-particle Slater orbitals. The relaxation of the core and the intershell electron–electron correlation are described by another large CI wavefunction. A natural extension is to test this method on systems with higher nuclear charges and in more highly excited states. Not long ago, this method was applied to the lowly excited states $1s^2nl$ (l=s, d, f; $n \leq 5$) of lithium-like systems from Z=11 to 20 [9,10] and the ground states of lithium-like systems from Z=21 to 30.[11] By using this method we have also studied the

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electron density at the nucleus of the ground state for the lithium isoelectronic sequence from Z=3 to 10.[12] In this paper, we extend this method to calculate the excitation energies and fine-structure splittings of $1s^2np$ states ($n \leq 9$) for Na IX to Ca XVIII. The non-relativistic energies of the lithium-like excited states, $1s^2np$, are calculated with the FCPC wavefunction mentioned above using the variation method. The relativistic and mass polarization effects are evaluated with the Pauli–Breit operators as the first-order perturbation corrections. The fine structures are determined by computing the expectation values of the spin-orbit and spin-other-orbit interaction operators in the LSJ coupling scheme. The contribution from quantum-electrodynamics (QED) correction is also included by using the effective nuclear charge.[13]

Computations in the present work are carried out in atomic units (arb. units). The excitation energy of a three-electron system is the energy above the ground state $1s^22s$. In order to make a definitive comparison with the experimental data that are mostly given in cm^{-1}, our excitation energy and fine-structure splitting are converted into cm^{-1} using the reduced Rydberg constants. These constants are the same as in Ref.[5].

2. Theory

The total wavefunction of the three-electron system with $1s^2$ core is given by

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

where A is the anti-symmetrization operator. In the first term on the right-hand side of Eq.(1), the factor multiplying Φ_{1s1s} is a linear combination of the Slater orbital for the valence electron. Here Φ_{1s1s} is a predetermined $1s^2$ core wavefunction which is represented in terms of a CI basis set, i.e.

$$\Phi_{1s1s}(1,2) = A\sum_{k,n,l} C_{knl} r_1^k r_2^n \mathrm{e}^{-\beta_l r_1 - \beta_l r_2} \times Y_l(1,2)\chi(1,2). \quad (2)$$

The angular part is

$$Y_l(1,2) = \sum_m \langle l, m, l-m | 0, 0\rangle \times Y_{l,m}(\theta_1,\phi_1)\, Y_{l,-m}(\theta_2,\phi_2). \quad (3)$$

$\chi(1,2)$ is a two-electron singlet spin function given by

$$\chi(1,2) = \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \alpha(2)\beta(1)]. \quad (4)$$

The linear and nonlinear parameters in Eq.(2) are determined by optimizing the energy of the He-like 1s1s system. The second term in the right-hand side of Eq.(1) describes other possible correlation and the core relaxation in the three-electron system. The basis function is chosen as

$$\Phi_{n(i),l(i)}(1,2,3) = \varphi_{n(i)}(R) Y_{l(i)}^{LM}(\widehat{R})\chi_{ss_Z}. \quad (5)$$

Here R represents the radial parts of $\boldsymbol{r}_1$, $\boldsymbol{r}_2$ and $\boldsymbol{r}_3$, $\widehat{R}$ represents their angular parts, and S_Z is the Z-component of the total spin S. The radial and angular basis functions are

$$\varphi_{n(i)}(R) = \prod_{j=1}^{3} r_j^{n_j} \exp(-\alpha_j r_j) \quad (6)$$

and

$$Y_{l(i)}^{LM}(\widehat{R}) = \sum_{m_j} \langle l_1 m_1 l_2 m_2 | l_{12} m_{12}\rangle \langle l_{12} m_{12} l_3 m_3 | LM\rangle \times \prod_{j=1}^{3} Y_{l_j m_j}(\Omega_j), \quad (7)$$

respectively, where $l(i)$ represents the set of l_1, l_2, l_{12}, and l_3. For simplicity, this angular component is denoted by

$$l(i) = [(l_1, l_2) l_{12}, l_3], \quad (8)$$

where l_{12} and l_3 coupling into L is implicitly implied. Similarly, the doublet spin function can be denoted as

$$\chi_{ss_Z} = [(s_1, s_2) S_{12}, s_3]. \quad (9)$$

It has two possible spin doublets:

$$\chi_1 = [(s_1, s_2)\, 0\,, s_3], \quad (10)$$

$$\chi_2 = [(s_1, s_2)\, 1, s_3]. \quad (11)$$

The non-relativistic energies of the $1s^2$-core and $1s^2np$ states are calculated by minimizing the expectation value

$$\delta E_0 = \delta\langle H_0\rangle = \delta\frac{\langle\Psi|H_0|\Psi\rangle}{\langle\Psi|\Psi\rangle}. \quad (12)$$

Here H_0 is the non-relativistic Hamiltonian. For the three-electron system it is (in arb. units)

$$H_0 = \sum_{i=1}^{3}\left[-\frac{1}{2}\nabla_i^2 - \frac{Z}{r_i}\right] + \sum_{\substack{i,j=1\\ i<j}}^{3}\frac{1}{r_{ij}}. \quad (13)$$

The corrections from the relativistic and mass-polarization effects are

$$\Delta E = \langle \Psi | H' | \Psi \rangle. \tag{14}$$

Here the perturbation operator, H', is given by

$$H' = H_1 + H_2 + H_3 + H_4 + H_5, \tag{15}$$

where

$$H_1 = \frac{1}{8c^2}\sum_{i=1}^{3} \boldsymbol{p}_i^4$$
(correction to kinetic energy) (16)

$$H_2 = \frac{Z\pi}{2c^2}\sum_{i=1}^{3} \delta(\boldsymbol{r}_i)$$
(Darwin term) (17)

$$H_3 = -\frac{\pi}{c^2}\sum_{i<j}^{3} [1 + \frac{8}{3}\boldsymbol{s}_i \cdot \boldsymbol{s}_j]\delta(\boldsymbol{r}_{ij})$$
(electron − electron contact term) (18)

$$H_4 = -\frac{1}{M}\sum_{i<j}^{3} \nabla_i \cdot \nabla_j$$
(mass − polarization) (19)

$$H_5 = -\frac{1}{2c^2}\sum_{i<j}^{3} \frac{1}{r_{ij}}\left[\boldsymbol{p}_i \cdot \boldsymbol{p}_j + \frac{\boldsymbol{r}_{ij}(\boldsymbol{r}_{ij} \cdot \boldsymbol{p}_i) \cdot \boldsymbol{p}_j}{r_{ij}^2}\right]$$
(orbit − orbit interaction). (20)

Here, M is the nuclear mass in arb. units and c=137.036. The total energy including the corrections is

$$E_{\rm tot} = E_0 + \Delta E. \tag{21}$$

To obtain a more accurate energy for a system with larger Z, the correction from the QED effect should be also included. It is assumed that the QED effects of the $1s^2$-core cancel out in the ionization potential (IP) of the system. Thus, this correction can be evaluated for the valence np electron by using the hydrogenize formula [13] with an effective nuclear charge, $Z_{\rm eff}$,

$$\Delta E_{\rm QDT} = \frac{4Z_{\rm eff}^4}{n^3}\frac{\alpha^3}{3\pi}\left[\frac{1}{8}C_{1J} - \ln K_0(n,1)\right] = \Delta E_{\rm QDT}^J(n{\rm p}) + \Delta E_{\rm QDT}^{\rm g}(n{\rm p}), \tag{22}$$

where

$$C_{1J} = \begin{cases} \frac{1}{2} & \text{for } J = 3/2, \\ -1 & \text{for } J = 1/2. \end{cases} \tag{23}$$

The first term in the right-hand side of Eq.(22) contributes to the splitting of the ^{2}P system. The second term causes a shift of the centre of gravity of the LS-term energy. Here n is the principal quantum number of the valence electron, and α is the fine-structure constant. In this work, the $Z_{\rm eff}$ is defined by

$$E_{\text{non-rel}}(1s^2 n{\rm p}) - E_{\text{non-rel}}(1s^2) = -\frac{Z_{\rm eff}^2}{2n^2}. \tag{24}$$

The values of the Bethe logarithms, $K_0(n,1)$, are taken from Ref.[14]. The centre of gravity IP of the $1s^2n$p states becomes

$${\rm IP}(1s^2 n{\rm p}) = E_{\rm tot}(1s^2\,{}^1{\rm S}) - E_{\rm tot}(1s^2 n{\rm p}^2{\rm P}) - \Delta E_{\rm QED}^{\rm g}(n{\rm p}). \tag{25}$$

The excitation energy of the excited states $1s^2n$p is the energy above the ground state $1s^22s$. That is,

$$\text{Excitation energy}(1s^2 n{\rm p}) = {\rm IP}(1s^2 2{\rm s}) - {\rm IP}(1s^2 n{\rm p}). \tag{26}$$

For the $1s^2n$p states, most of the fine-structure splitting comes from the spin-orbit and the spin-other-orbit interactions. These operators are

$$H_{\rm so} = \frac{Z}{2c^2}\sum_{i=1}^{3} \frac{\boldsymbol{l}_i \cdot \boldsymbol{s}_i}{r_i^3}, \tag{27}$$

$$H_{\rm soo} = -\frac{1}{2c^2}\sum_{i\neq j}^{3}\left[\frac{1}{r_{ij}^3}(\boldsymbol{r}_i - \boldsymbol{r}_j) \times \boldsymbol{p}_i\right] \cdot (\boldsymbol{s}_i + 2\boldsymbol{s}_j). \tag{28}$$

In calculation of the fine structure, the LSJ coupling scheme is used. The wavefunction with a total angular momentum J is formed by

$$|LSJM_J\rangle = \sum_{M_L, M_S} |LSM_LM_S\rangle\langle LSM_LM_S|JM_J\rangle, \tag{29}$$

where $|LSM_LM_S\rangle$ is the angular part of the LS-coupling wavefunction and $\langle LSM_LM_S|JM_J\rangle$ is the Clebsch–Gordan coefficient. The energy for the fine-structure is obtained by computing the expectation values of $H_{\rm so}$ and $H_{\rm soo}$,

$$\Delta E_{\rm fs}^J = \langle LSJM_J|H_{\rm so} + H_{\rm soo}|LSJM_J\rangle + \Delta E_{\rm QED}^J(n{\rm p}). \tag{30}$$

The QED correction to the fine structure splitting is estimated from Eqs.(22) and (23),

$$\Delta E_{\rm QED}^{\rm fs}(n{\rm p}) = \Delta E_{\rm QED}^{3/2} - \Delta E_{\rm QED}^{1/2} = \frac{Z_{\rm eff}^4\,\alpha^3}{4\pi\, n^3}. \tag{31}$$

3. Results and discussion

For the $1s^2$-core states of the lithium-like systems, the wavefunction, Eq.(2), with 222-terms in seven l components is used. For the $1s^22s$ energy, we used

nine d_i terms and 560 terms of $\Phi_{n(i)l(i)}$ with 10 partial waves in Eq.(1). And eight d_i terms and 559 terms of $\Phi_{n(i)l(i)}$ with 13 partial waves are used in calculating the $1s^2np$ energy. The energy convergence pattern for $1s^2np$ states is very similar for all n in this isoelectronic sequence. In this work the highest orbital angular momentum l used in the angular component (0, l, $l+1$) of our wavefunction is 6. The non-relativistic energies of the $1s^2$-core and $1s^2np$ states for each system are obtained by solving the corresponding secular equation. In this process, the FCPC wavefunctions are also determined. The results of non-relativistic energies for $1s^2np$ states are listed in the column marked by 'Non-rel.' of Table 1.

Table 1. Non-relativistic energies, relativistic and mass-polarization effects on the energy of lithium-like $1s^2np$ states from Z=11 to 20 (in arb. units).

	Non-rel.	$<H_1+H_2>$	$<H_3>$	$<H_4>$	$<H_5>$
Z=11					
$1s^22p$	−124.63162068	−0.1781785	0.0076100	−0.0001175	0.0006145
$1s^23p$	−118.84793238	−0.1744466	0.0075353	−0.0000035	−0.0001717
$1s^24p$	−116.84076283	−0.1729985	0.0075142	0.0000183	−0.0003411
$1s^25p$	−115.91588423	−0.1723791	0.0075068	0.0000254	−0.0003987
$1s^26p$	−115.41487422	−0.1720802	0.0075035	0.0000284	−0.0004235
$1s^27p$	−115.11335277	−0.1719193	0.0075017	0.0000299	−0.0004359
$1s^28p$	−114.91793184	−0.1718257	0.0075007	0.0000307	−0.0004428
$1s^29p$	−114.78407653	−0.1717664	0.0075002	0.0000312	−0.0004470
Z=12					
$1s^22p$	−149.41242767	−0.2556557	0.0100342	−0.0001436	0.0009043
$1s^23p$	−142.28747867	−0.2499229	0.0099267	−0.0000082	−0.0001642
$1s^24p$	−139.81330691	−0.2476993	0.0098970	0.0000175	−0.0003935
$1s^25p$	−138.67284939	−0.2467658	0.0098860	0.0000259	−0.0004713
$1s^26p$	−138.05492270	−0.2463161	0.0098812	0.0000294	−0.0005048
$1s^27p$	−137.68298162	−0.2460736	0.0098786	0.0000311	−0.0005216
$1s^28p$	−137.44188655	−0.2459303	0.0098774	0.0000321	−0.0005309
$1s^29p$	−137.27660284	−0.2458131	0.0098788	0.0000326	−0.0005349
Z=13					
$1s^22p$	−176.44331518	−0.3560375	0.0129263	−0.0001584	0.0012666
$1s^23p$	−167.83813386	−0.3475930	0.0127780	−0.0000123	−0.0001441
$1s^24p$	−164.84478531	−0.3447156	0.0127273	0.0000157	−0.0004549
$1s^25p$	−163.46508815	−0.3431468	0.0127141	0.0000243	−0.0005526
$1s^26p$	−162.71890447	−0.3422841	0.0127282	0.0000272	−0.0005785
$1s^27p$	−162.27002783	−0.3421212	0.0126987	0.0000303	−0.0006238
$1s^28p$	−161.98145959	−0.3417729	0.0127100	0.0000309	−0.0006267
$1s^29p$	−161.78159403	−0.3416428	0.0127094	0.0000315	−0.0006337
Z=14					
$1s^22p$	−205.72431902	−0.4833890	0.0163283	−0.0001855	0.00170951
$1s^23p$	−195.49992490	−0.4714886	0.0161296	−0.0000175	−0.0001094
$1s^24p$	−191.94590180	−0.4669037	0.0160751	0.0000142	−0.0004977
$1s^25p$	−190.30632979	−0.4650326	0.0160511	0.0000246	−0.0006326
$1s^26p$	−189.41774208	−0.4640379	0.0160517	0.0000285	−0.0006799
$1s^27p$	−188.88240615	−0.4636153	0.0160364	0.0000311	−0.0007189
$1s^28p$	−188.53664570	−0.4632471	0.0160393	0.0000321	−0.0007300
$1s^29p$	−188.29907269	−0.4630611	0.0160375	0.0000328	−0.0007394
Z=15					
$1s^22p$	−237.25538002	−0.6422455	0.0202791	−0.0001999	0.00224077
$1s^23p$	−225.27283961	−0.6258697	0.0200202	−0.0000214	−0.0000584
$1s^24p$	−221.10546477	−0.6197878	0.0199481	0.0000122	−0.0005507
$1s^25p$	−219.18371912	−0.6169342	0.0199236	0.0000229	−0.0007137
$1s^26p$	−218.14169606	−0.6156548	0.0199123	0.0000275	−0.0007849
$1s^27p$	−217.51428387	−0.6149620	0.0199064	0.0000297	−0.0008207
$1s^28p$	−217.10749379	−0.6145570	0.0199037	0.0000309	−0.0008400
$1s^29p$	−216.82885014	−0.6143082	0.0199009	0.0000317	−0.0008527

Table 1. (*Continued*)

	Non-rel.	$<H_1+H_2>$	$<H_3>$	$<H_4>$	$<H_5>$
Z=16					
$1s^22p$	–271.03649187	–0.8374701	0.0248217	–0.0002277	0.0028679
$1s^23p$	–257.15687239	–0.8154585	0.0244916	–0.0000268	0.0001145
$1s^24p$	–252.32849691	–0.8069978	0.0244020	0.0000108	–0.0005958
$1s^25p$	–250.10066836	–0.8034385	0.0243691	0.0000229	–0.0008013
$1s^26p$	–248.89283098	–0.8017219	0.0243545	0.0000280	–0.0008898
$1s^27p$	–248.16550685	–0.8007979	0.0243471	0.0000305	–0.0009343
$1s^28p$	–247.69401388	–0.8001532	0.0243468	0.0000318	–0.0009559
$1s^29p$	–247.37099522	–0.7998605	0.0243425	0.0000327	–0.0009725
Z=17					
$1s^22p$	–307.06764936	–1.0742385	0.0299975	–0.0002418	0.0035991
$1s^23p$	–291.15202265	–1.0451755	0.0295846	–0.0000306	0.0001016
$1s^24p$	–285.61354304	–1.0340506	0.0294729	0.0000087	–0.0006406
$1s^25p$	–283.05761427	–1.0293687	0.0294319	0.0000214	–0.0008917
$1s^26p$	–281.67174354	–1.0271106	0.0294140	0.0000268	–0.0009996
$1s^27p$	–280.83714910	–1.0258921	0.0294045	0.0000295	–0.0010541
$1s^28p$	–280.29599071	–1.0251758	0.0293989	0.0000309	–0.0010846
$1s^29p$	–279.92496835	–1.0247495	0.0293958	0.0000318	–0.0011022
Z=18					
$1s^22p$	–345.34884016	–1.3579896	0.0358471	–0.000243	0.00444180
$1s^23p$	–327.25828858	–1.320363	0.0353387	–0.000033	0.00021441
$1s^24p$	–320.96108806	–1.3059861	0.0352016	0.0000065	–0.0006813
$1s^25p$	–318.05455714	–1.2999307	0.0351512	0.0000191	–0.0009844
$1s^26p$	–316.47842376	–1.2970121	0.0351290	0.0000245	–0.0011148
$1s^27p$	–315.52918668	–1.2954372	0.0351170	0.0000271	–0.0011809
$1s^28p$	–314.91367822	–1.2945095	0.0351112	0.0000285	–0.0012166
$1s^29p$	–314. 4917209	–1.2938643	0.0351116	0.0000293	–0.0012353
Z=19					
$1s^22p$	–385.88005757	–1.6943827	0.0424132	–0.0002838	0.0054039
$1s^23p$	–365.47566876	–1.6466413	0.0417953	–0.0000399	0.0003518
$1s^24p$	–358.36217900	–1.6285281	0.0415834	0.0000057	–0.0007405
$1s^25p$	–355.07797249	–1.6206495	0.0415681	0.0000199	–0.0010791
$1s^26p$	–353.30337004	–1.6169335	0.0415411	0.0000261	–0.0012347
$1s^27p$	–352.22921406	–1.6152775	0.0415172	0.0000289	–0.0013127
$1s^28p$	–351.54333851	–1.6138948	0.0415209	0.0000306	–0.0013508
$1s^29p$	–351.06992891	–1.6129977	0.0415135	0.0000319	–0.0013843
Z=20					
$1s^22p$	–428.66130118	–2.0901729	0.0497362	–0.0003126	0.00649329
$1s^23p$	–405.80416238	–2.0300165	0.0489945	–0.0000457	0.00051564
$1s^24p$	–397.82386047	–2.0072978	0.0487136	0.0000042	–0.0007865
$1s^25p$	–394.12298649	–1.9991672	0.0486997	0.0000192	–0.0011814
$1s^26p$	–392.17511061	–1.9927229	0.0486900	0.0000263	–0.0013591
$1s^27p$	–390.97447985	–1.9902020	0.0486732	0.0000296	–0.0014516
$1s^28p$	–390.19592059	–1.9887310	0.0486647	0.0000315	–0.0015020
$1s^29p$	–389.66223674	–1.9878027	0.0486584	0.0000326	–0.0015335

Using the wavefunctions obtained above, the expectation values of the relativistic and mass-polarization operators are calculated. The results are also given in Table 1. It is seen that the mass-polarization correction to the energy is comparatively small, and the relativistic corrections, especially the correction to kinetic energy and the Darwin term, obviously increase with increasing value of nuclear charge Z from this table. The IP values are obtained by subtracting the $1s^2np$ energies from the $1s^2$-core energies. The QED correction to the IP is estimated using Eq.(22). The excitation energies of the $1s^2np$ states ($n \leq 9$) from Na IX to Ca XVIII are evaluated with Eq.(26) and they are given in Table 2. The experimental data and other theoretical results available in the literature are also listed in this table. The results of the $1s^2np$ states ($n \leq 5$) for the lithium-like systems from Z=3 to 42 were obtained by using the perturbation method with power series in $1/Z$ and αZ.[15]

Table 2. Excitation energy of $1s^2np$ states for lithium-like systems from Na IX to Ca XVIII (in cm^{-1}).

	Z	11	12	13	14	15
	This work	145815	162664	179872	197515	215682
$1s^22p$	Kelly[16]	145805	162665	179877	197513	215690
	Other expt.	145813[a]	162665[b]	179878[c]	197513[d]	215688[e]
	V & S[15]	145854	162710	179927	197568	215727
	This work	1415825	1727316	2069872	2443482	2848182
$1s^23p$	Kelly[16]	1415876	1727394	2069937	2443593	2848300
	Other expt.	1415877[a]	1727393[b]	2069937[c]	2443533[d]	2848300[e]
	V&S[15]	1415903	1727497	2070088	2443776	2848671
	This work	1856677	2270731	2726747	3224245	3763948
$1s^24p$	Kelly[16]	1856665	2270148	2726700	3224200	3758300
	Other expt.	1856660	2270150[b]	2726700[c]	3224183[d]	764040[e]
	V & S[15]	1856682	2270905	2726857	3224646	3764390
	This work	2059642	2521206	3029719	3584497	4186186
$1s^25p$	Kelly[16]	2059605	2520900	3029700		
	Other expt.	2059600[a]	2520900[b]	3029700[c]	3584483[d]	
	V & S[15]	2059783	2521392	3024689	3584761	4186811
	This work	2169660	2656911	3193620	3779716	4415129
$1s^26p$	Kelly[16]	2169668	2656500	3193600	3779300	
	Other expt.	2169670[a]	2656500[b]	3193600[c]	3779700[d]	
	This work	2235867	2738589	3292124	3897283	4552964
$1s^27p$	Kelly[16]	2235886	2738400	3292100	3897900	
	Other expt.	2235890[a]	2738400[b]	3292100[c]	3897283[d]	
	This work	2278776	2791531	3356555	3973185	4642323
$1s^28p$	Kelly[16]		2791200	3356500		
	Other expt.		2791200[b]	3356500[c]		
	This work	2308145	2827817	3399529	4025363	4703557
$1s^29p$	Kelly[16]		2827600	3399500		
	Other expt.		2827600 [b]	3399500[c]		

[a] Ref.[17], [b]Ref.]18], [c]Ref.[19], [d]Ref.[20], [e]Ref.[21].

Table 2. (*Continued*)

	Z	16	17	18	19	20
	This work	234404	253835	274074	295181	317287
$1s^22p$	Kelly[16]	234417	253850	274027	295173	317275
	Other expt.	234408[f]				320705[g]
	V & S[15]	234474	253916	274130	296564	317325
	This work	3284205	3751639	4250617	4781367	5343614
$1s^23p$	Kelly[16]	3285547	3750293		4782403	5345313
	Other expt.					5347000[g]
	V & S[15]	3284890	3752563	4251825	4782824	5345720
	This work	4345419	4969272	5635397	6345857	7101055
$1s^24p$	Kelly[16]	4341800	4967700		6345850	7097403
	Other expt.				6345850[g]	7101000[g]
	V & S[15]	4346220	4970285	5636736	6345726	7097448
	This work	4835045	5531122	6274458	7067956	7914015
$1s^25p$	Kelly[16]		5515700		7068640	7914900
	Other expt.					7914000[g]
	V & S[15]	4835905	5532217	6275904	7067141	7906105
	This work	5100465	5835720	6620943	7458422	8341908
$1s^26p$	Kelly[16]		5797100		7458800	8341000
	Other expt.					8341000[g]
	This work	5260272	6019129	6829582	7694437	8605908
$1s^27p$	Kelly[16]				7694680	8605100
	Other expt.					8605100[g]
	This work	5363883	6138039	7057591	7846725	8777071
$1s^28p$	Kelly[16]				7846830	8776600
	Other expt.					8776600[g]
$1s^29p$	This work	5434833	6219553	7241519	7951512	8894384
	Kelly[16]				7951650	8894400

[f] Ref.[21], [g] Ref.[22].

It appears that our values of excitation energies of $1s^2np$ states ($n \leq 9$) for Na IX are in excellent agreement with experimental data available in the literature,[16,18–23] and our results are much better than the theoretical predictions of Vainshtein and Safronova.[15] Our results of $1s^22p$ states for other lithium-like systems also agree closely with the experimental data.[16,17–21,23] Considering the fact that the experimental uncertainties are several tens of cm^{-1} for $1s^23p$ and $1s^24p$ states, and several hundreds of cm^{-1}, or even more, for $1s^2np$ states ($5 \leq n \leq 9$) in Refs.[16], [17–21] and [23], we find that the agreement of our results with available experimental data [16,17] is satisfactory for these states. So far as we know, no experimental data are available for some cases up to now. We hope that our predictions will be useful in making higher precision experimental measurements.

As we know, the fine structure for a given configuration is caused mainly by the spin-orbit and spin-other-orbit interactions in an atomic system. The fine-structure splitting of $1s^2np$ states obtained from Eq.(30) are given in Table 3. The experimental data and other theoretical results are also listed in this table for comparison. In Fig.1 we plot the calculated fine-structure splitting from Z=11 to 20. The splittings follow a well behaved isoelectronic curve. The comparison with experiment is also shown in this figure. We find that our results agree closely with the results derived from experimental data in most cases. The only exception is for Cl XV $1s^23p$ for which our theoretical result is $5783cm^{-1}$, whereas it is $1940cm^{-1}$ in Kelly.[16] In this case the value of Kelly's is probably too small, because it obviously deviates from the isoelectronic regularity of fine-structure splitting, as shown in Fig.1. In many cases considered there are no experimental data available in the literature to compare with. We hope that more precise experimental measurements can be carried out to allow a more critical comparison between theory and experiment.

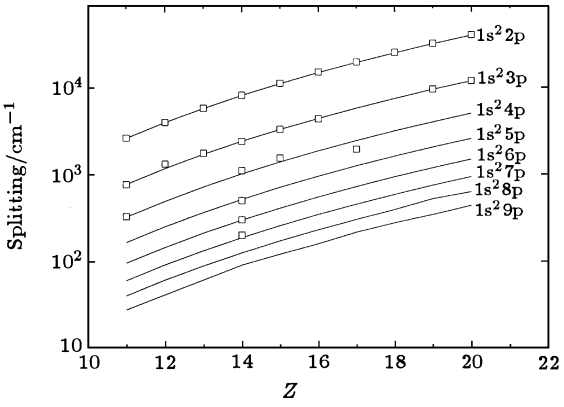


Fig.1. Fine-structure splitting of $1s^2np$ states for the lithium-like systems from Z=11 to 20. (–, this work; □, experiment).

Table 3. Fine-structure splitting ($\Delta E = E_{3/2}-E_{1/2}$) for $1s^2np$ ^2P states of lithium-like systems (in cm^{-1}).

	Z	11	12	13	14	15
$1s^22p$	This work	2625	3977	5793	8174	11199
	Kelly [16]	2650	3978	5800	8180	11310
	Other expt.	2626[a]	3975[b]	5789[c]	8176[d]	11226[e]
	V & S[15]	2680	4046	5878	8273	11340
$1s^23p$	This work	770	1166	1702	2394	3285
	Kelly [16]	762	1313	1750	2390	3300
	Other expt.	760[a]	1310[b]	1750[c]	2390[d]	3330[e]
	V&S[15]	789	1192	1733	2439	3344
$1s^24p$	This work	325	492	716	1010	1386
	Expt.	330[a]			1100[d]	1530[e]
	V & S[15]	333	503	731	1029	1410
$1s^25p$	This work	166	251	366	516	708
	Other expt.				500[d]	
	V & S[15]	170	258	374	527	722
$1s^26p$	This work	96	145	212	298	409
	Expt.				300[d]	
$1s^27p$	This work	60	91	133	188	258
	Expt.				200[d]	
$1s^28p$	This work	40	61	89	126	172
$1s^29p$	This work	28	41	61	91	121

Table 3. (*Continued*)

	Z	16	17	18	19	20
$1s^2 2p$	This work	15063	19770	25572	32520	40837
	Kelly [16]	15130	19770	25570	32538	40843
	Other expt.					40860[f]
	V&S[15]	15180	19940	25730	34710	41030
$1s^2 3p$	This work	4402	5783	7464	9510	11924
	Kelly [16]	4360	1940		9590	11990
	Other expt.					12000[f]
	V&S[15]	4479	5884	7596	9659	12120
$1s^2 4p$	This work	1856	2440	3150	4005	5022
	Kelly [16]				4020	5540
	Other expt.					
	V & S[15]	1890	2482	3204	4074	5112
$1s^2 5p$	This work	950	1248	1611	2048	2568
	Other expt.					
	V & S[15]	968	1271	1641	2086	2617
$1s^2 6p$	This work	549	721	9317	1184	1485
$1s^2 7p$	This work	345	454	586	745	935
$1s^2 8p$	This work	230	304	393	523	626
$1s^2 9p$	This work	159	216	278	345	438

[a] Ref.[17], [b]Ref.[18], [c]Ref.[19], [d]Ref.[20], [e]Ref.[21], [f]Ref.[23].

4. Summary

In this work, we aim at examining whether accurate prediction of excitation energy and fine structure are possible for the lithium-like systems with higher nuclear charge and in the higher energy region of these systems. The results indicate that our calculated excitation energy and fine structure splitting of the $1s^2np$ states ($n \leq 9$) for the systems from Z=11 to 20 agree well with the experimental data available in the literature. It has been pointed out that the value of fine-structure splitting for Cl XV $1s^2 3p$ given by Kelly [16] deviates drastically from the isoelectronic behaviour. We expect that accurate prediction should be also possible in highly excited energy region of these systems by combining this method with quantum defect theory (QDT).

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