Fine structures and transition wavelengths for $1s\,2s\,2p\,{}^4P$ and $1s\,2p\,2p\,{}^4P$ of lithiumlike ions

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Using an *LSJ* coupling scheme and a configuration-interaction wave function, the relativistic energies, fine structures, and transition wavelengths of the $1s\,2p\,2p\,{}^4P$ and $1s\,2s\,2p\,{}^4P$ states are studied. The relativistic correction, Breit-Pauli operator, and mass-polarization correction are calculated for ions from Li I through F VII and for Mg X. Excellent agreement with experimental data is obtained in most cases. For example, the calculated transition wavelengths of Be II, B III, and C IV are 2324.96, 1701.77, and 1344.22 Å, respectively. It is to be compared with the corresponding experimental data of 2324.6, 1701.4, and 1344.2 Å. However, a few questions are raised concerning some part of the experimental data. For the fine structure of Mg X, a 5% error appears in the present calculation. The validity and limitation of the present method is also discussed.

I. INTRODUCTION

In recent years, several high-precision experiments have been carried out to determine the fine structures and transition wavelengths of Li-like $1s\,2p\,2p\,{}^4P$ and $1s\,2s\,2p\,{}^4P$ systems.[1–4] These results have stimulated a considerable amount of theoretical interest.[5–9] For systems with nuclear charge $Z \geq 4$. The theoretical approaches are mostly based on the multiconfiguration Dirac-Fock method (MCDF). Although the recent work of Hata and Grant[6] has improved the agreement between theory and experiment drastically, the remaining deviation for the transition wavelength is still an order of magnitude larger than the experimental uncertainty quoted.[3,4] This is perhaps due to the fact that correlation effects can not easily be calculated to high accuracy in the MCDF approach. In this regard, the nonrelativistic variation method is probably the most effective for this correlation. On the other hand, the relativistic effects can be computed from first-order perturbation theory. For two-electron systems, this method has been used to obtain highly accurate results.[10] The validity of this method, i.e., the neglect of higher-order contributions, and the limitations on its applicability are not entirely clear. Hence, it is important to apply it to three-electron systems where highly accurate experimental data are available.

In this work, the starting point is the nonrelativistic Hamiltonian. It is diagonalized with a multiconfiguration-interaction wave function. This wave function is then used to compute the expectation values of the relativistic perturbation operators. The relativistic effects considered are the following: the mass-correction term, the Darwin term, and the retardation term (orbit-orbit interaction). The mass-polarization effect is also calculated. The contribution of these effects are added to the nonrelativistic energy to give the center-of-gravity energy ($E_{\rm CG}$). For the fine structure, the *LSJ* scheme is used to compute the expectation value of the spin-orbit, spin-other-orbit, and spin-spin operators in the Breit-Pauli approximation. For nuclear charge $Z \geq 6$ the Lamb-shift correction becomes appreciable. To make a meaningful comparison with the experiment, we have also included the radiative correction (QED) calculated by Hata and Grant.[6] These results will be presented in the following sections.

II. THEORY

The Hamiltonian for the Li-like quartet system in atomic units is given by[11]

$$H = H_0 + H_1 + H_2 + H_3 + H_4 + H_{\rm so} + H_{\rm soo} + H_{\rm ss} , \quad (1)$$

where

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

$$H_1 = -\frac{1}{8c^2} \sum_{i=1}^{3} \vec{\rm P}_i^4 \quad (3)$$

$$H_2 = \frac{Z\pi}{2c^2} \sum_{i=1}^{3} \delta(\vec{\rm r}_i) , \quad (4)$$

$$H_3 = -\frac{1}{M} \sum_{\substack{i,j=1 \\ i<j}}^{3} \nabla_i \cdot \nabla_j , \quad (5)$$

and

$$H_4 = -\frac{1}{2c^2} \sum_{\substack{i,j=1 \\ i<j}}^{3} \frac{1}{r_{ij}} \left[\vec{\rm P}_i \cdot \vec{\rm P}_j + \frac{\vec{\rm r}_{ij}(\vec{\rm r}_{ij} \cdot \vec{\rm P}_i) \cdot \vec{\rm P}_j}{r_{ij}^2} \right] , \quad (6)$$

where M is the nuclear mass in a.u. and $c = 137.036$. The spin-orbit, spin-other-orbit, and spin-spin operators are given by

$$H_{\rm so} = \frac{Z}{2c^2} \sum_{i=1}^{3} \frac{\vec{\rm l}_i \cdot \vec{\rm s}_i}{r_i^3} , \quad (7)$$

$$H_{\rm soo} = -\frac{1}{2c^2} \sum_{i \neq j}^{3} \left[\frac{1}{r_{ij}^3} (\vec{\rm r}_i - \vec{\rm r}_j) \times \vec{\rm P}_i \right] \cdot (\vec{\rm s}_i + 2\vec{\rm s}_j) , \quad (8)$$

and

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$$H_{ss}=\sum_{\substack{i,j=1\\ i<j}}^{3}\frac{1}{c^2 r_{ij}^3}\left[\vec{s}_i\cdot\vec{s}_j-\frac{3(\vec{s}_i\cdot\vec{r}_{ij})(\vec{s}_j\cdot\vec{r}_{ij})}{r_{ij}^2}\right], \quad (9)$$

where $\vec{l}_i$ and $\vec{s}_i$ are the orbital and spin-angular momentum, respectively. In Eq. (1), H_1, H_2, H_4, H_{so}, H_{soo}, and H_{ss} are the "first-order terms" of the relativistic effect. Hence, if the higher-order contribution cannot be estimated accurately, the validity of this approximation can only be justified by comparing the calculated results with those of a precision experiment. Recently, a method has been suggested to include the higher-order terms for a two-electron system.[12]

To calculate the nonrelativistic energy, the Raleigh-Ritz variation method is used to diagonalize H_0. The basis functions are chosen in the LS coupling scheme. This is similar to that of Chung[13] except that the nonlinear parameters in each partial wave are optimized individually in the present work. The explicit form of these basis functions will not be given here. We refer the interested reader to Ref. 13. Using this wave function, the expectation values for H_1, H_2, H_3, and H_4 are calculated.

To calculate the fine-structure splitting, the LSJ coupling scheme is used. That is, the good quantum number J is formed by

$$|JJ_zLS\rangle=\sum_{S_z,L_z}|LSL_zS_z\rangle\langle LSL_zS_z|JJ_z\rangle \quad (10)$$

where $\langle LSL_zS_z|JJ_z\rangle$ is the Clebsch-Gordan coefficient[14] and $|LSL_zS_z\rangle$ is the angular part of LS-coupling wave function. The wave function in Eq. (10) is used to compute the expectation values of H_{so}, H_{soo}, and H_{ss} for the $J=\frac{5}{2}$ states; the results for $J=\frac{3}{2}$ and $\frac{1}{2}$ are obtained by using the Wigner-Eckart theorem.[14]

III. CENTER-OF-GRAVITY ENERGY

Among the systems of interest in this work, the lithium $1s\,2s\,2p\,{}^4P$ and $1s\,2p\,2p\,{}^4P$ is probably the most extensively studied in theory. The energy has been calculated by Wu and Shen,[15] Holøien and Geltman,[16] Larsson and collaborators,[17] Bunge and Bunge,[18] Weiss,[19] Lunell and Beebe,[20] and Glass.[5] Most of these investigations did not consider relativistic corrections to the center-of-gravity energy. The usual definition of the center of gravity is

$$E_{CG}=\frac{\sum_J(2J+1)E_J}{\sum_J(2J+1)}, \quad (11)$$

where E_J is the energy for the total angular momentum J state. It is easy to show that the perturbations H_{so}, H_{soo}, and H_{ss} do not change the position of E_{CG}. Hence E_{CG} is just the energy given by H_0, H_1, H_2, H_3, and H_4. A comparison of the calculated energy for lithium is given in Table I. In this work, 97 linear parameters are used for the wave function of $^4P^o$ and 81 linear parameters for $^4P^e$. It appears that our result is lower than that of the previous works except for that of Bunge and Bunge.[18] Our result agrees well with the 97-parameter calculation of Larsson and collaborators[17] where the r_{ij} coordinate is explicitly included.

The result of Bunge and Bunge[18] is probably the most

TABLE I. Center-of-gravity energies (E_{CG}) for the $1s\,2s\,2p\,{}^4P$ and $1s\,2p\,2p\,{}^4P$ of the Li atom.

	E (a.u.)	This work	Bunge and Bunge		Other theory	Expt
$1s\,2s\,2p$	$\langle H_0\rangle$	−5.367 8371	−5.367 948[a]	−5.367 992(37)[b]	−5.367 80[c]	
	$\langle H_1+H_2\rangle$	−0.000 6045			−5.366 7[d]	
	$\langle H_3\rangle$	−0.000 0154			−5.367 24[e]	
	$\langle H_4\rangle$	0.000 0092			−5.367 439[f]	
	Total	−5.368 4478	−5.368 559[g]	−5.368 603(37)[g]		
$1s\,2p\,2p$	$\langle H_0\rangle$	−5.245 2624	−5.245 308[a]	−5.245 351(37)[b]	−5.243 26[d]	
	$\langle H_1+H_2\rangle$	−0.000 5519			−5.244 93[e]	
	$\langle H_3\rangle$	−0.000 0274			−5.244 717[f]	
	$\langle H_4\rangle$	−0.000 0183				
	Total	−5.245 8234	−5.245 869[g]	−5.245 912(37)[g]		
	λ_{CG} (cm^{-1})[h]	26 911	26 925	26 925		26 915.16±0.06[i]

[a]Reference 18 C I calculation.
[b]Reference 18 suggested value.
[c]Ahlenius and Larsson (Ref. 17).
[d]Lunell and Beebe (Ref. 20).
[e]A. W. Weiss, quoted in Ref. 17.
[f]Glass (Ref. 5).
[g]Results if the relativistic contributions from this work are included.
[h]Conversion factor 1 a.u. = 219 457 cm^{-1}.
[i]Levitt *et al.* (Ref. 2).

TABLE II. Nonrelativistic energies for the $1s\,2s\,2p\ ^4P$ and $1s\,2p\,2p\ ^4P$ states of the lithiumlike ion (in a.u.).

	Z / $-E$	4	5	6	7	8	9
$1s\,2s\,2p\ ^4P$	This work	10.066 454	16.267 391	23.969 309	33.171 751	43.874 513	56.077 431
	Larsson and collaborators[a]	10.066 41	16.267 30	23.969 19	33.171 60	43.874 31	56.077 21
	Lunell and Beebe[b]	10.064 92	16.256 32	23.966 63	33.168 29	43.870 07	56.071 82
	Junker and Bardsley[c]					43.830	56.022
$1s\,2p\,2p\ ^4P$	This work	9.870 676	16.000 221	23.631 579	32.763 917	43.396 832	55.530 143
	Lunell and Beebe[b]	9.868 36	15.997 58	23.628 43	32.759 94	43.391 77	55.523 83
	Junker and Bardsley[c]					43.384	55.517

[a]Reference 17.
[b]Reference 20.
[c]Reference 22.

accurate theoretical value in the literature. In this reference, not only the full CI-calculation result is given, but the extrapolated results are also suggested for the ^4P states. The relativistic effects are not calculated but an uncertainty of 0.000 037 a.u. due to the relativistic contribution is quoted. Our calculated relativistic corrections for ^{7}Li are $-0.000\,611$ and $-0.000\,571$ a.u. for the $^4P^o$ and $^4P^e$ states, respectively. They are an order of magnitude larger than those given in Ref. 18. To make a meaningful comparison between theory and experiment, we add the relativistic correction in Table I to the result of Bunge and Bunge. The transition wavelength (λ_{CG}) becomes 26 925 cm^{-1} rather than the 26 914 cm^{-1} given before.[18] The experimental value is 26 915.16±0.06 cm^{-1} (Ref. 2). The QED contribution to this λ_{CG} is of the order of 1 cm^{-1}. Hence, the discrepancy between theory and experiment would be about 9 cm^{-1}. Since the maximum fine-structure splitting of $^4P^o$ is 2.7 cm^{-1} and that of $^4P^e$ is 1.8 cm^{-1} (Refs. 1 and 2), this discrepancy is very difficult to understand. The λ_{CG} in the present work is 26 911 cm^{-1} which is off by 4 cm^{-1}. It should be noted that another experiment[21] has quoted λ_{CG} to be 3714.3 Å or 26 923 cm^{-1}. It is of interest to know which experimental datum is more reliable. A better comparison can be obtained if the transition wavelengths between the different J states ($\lambda_{JJ'}$) can also be reported (with the hyperfine structure) in the experiment.

For ions of nuclear charge $Z=4$ to 9 and $Z=12$, some of the ^4P states have been studied by Holøien and Geltman,[16] Larsson and collaborators,[17] Junker and Bardsley,[22] and Lunell and Beebe.[20] All these are without relativistic correction. The calculated energies are upper bounds to the nonrelativistic eigenvalue. Since the energies in this work are lower than these results in the literature, it is probably more accurate. A comparison of the theoretical results is given in Table II. In Table III, the calculated corrections to E_{CG} for the ^4P states are given. It is interesting to note that while the mass-polarization effect and retardation effect are about equal and opposite in sign for Be$^+$, the retardation effect becomes much more important as Z increases. In the case of Mg X, it is an order of magnitude larger than the mass-polarization effect.

For the systems considered in Tables I and III, the retardation effect of the $1s\,2p\,2p\ ^4P^e$ state is roughly twice as much as the corresponding $1s\,2s\,2p\ ^4P$ state. This is because most of these effects are coming from the $2p$ electrons in the $1s$-$2p$ interaction. The $2p$ electrons are also found to be the most important contributors in the spin-orbit interaction.

The theoretical results quoted in Table II do not include those from the MCDF approach. This is because the E_{CG}'s have not been given in Refs. 6–8.

TABLE III. Center-of-gravity energies for the $1s\,2s\,2p\ ^4P^o$ and $1s\,2p\,2p\ ^4P^e$ of Li-like ions (in a.u.).

	Z	4	5	6	7	8	9	12
$^4P^o$	$\langle H_0\rangle$	−10.066 454	−16.267 391	−23.969 309	−33.171 751	−43.874 513	−56.077 431	−101.686 887
	$\langle H_1+H_2\rangle$	−0.002 009	−0.005 086	−0.010 821	−0.020 439	−0.035 371	−0.057 353	−0.185 664
	$\langle H_3\rangle$	−0.000 032	−0.000 051	−0.000 076	−0.000 097	−0.000 117	−0.000 131	−0.000 194
	$\langle H_4\rangle$	0.000 035	0.000 085	0.000 169	0.000 296	0.000 473	0.000 710	0.001 863
	Total	−10.068 460	−16.272 443	−23.980 037	−33.191 991	−43.909 529	−56.134 205	−101.870 882
$^4P^e$	$\langle H_0\rangle$	−9.870 676	−16.000 221	−23.631 579	−32.763 917	−43.396 832	−55.530 143	−100.931 309
	$\langle H_1+H_2\rangle$	−0.001 806	−0.004 540	−0.009 619	−0.018 131	−0.031 365	−0.050 803	−0.164 302
	$\langle H_3\rangle$	−0.000 061	−0.000 098	−0.000 148	−0.000 189	−0.000 231	−0.000 258	−0.000 384
	$\langle H_4\rangle$	0.000 069	0.000 171	0.000 341	0.000 596	0.000 954	0.001 433	0.003 765
	Total	−9.872 474	−16.004 688	−23.641 006	−32.781 641	−43.427 473	−55.579 772	−101.092 229

TABLE IV. Comparison between theory and experiment on the fine-structure splittings for the $1s\,2p\,2p\ ^4P^e$ and $1s\,2s\,2p\ ^4P^o$ states of the lithiumlike ions. Column A, this work. Column B, this work with the QED contribution from Hata and Grant (in cm^{-1}).

		$1s\,2s\,2p\ ^4P^o$				$1s\,2p\,2p\ ^4P^e$			
Z		A	B	Expt.	Other theory	A	B	Expt.	Other theory
3	Δ_{53}	0.9507	0.9567	0.997 34(33)[a]	1.291[b] 0.956[d]	−1.917	−1.917	−1.83(3)[c]	−1.449[b] −1.935[e]
	Δ_{51}	−1.824	−1.821	−1.724 70(27)[a]	−0.673[b] −1.760[d]	−0.003	0.003	0.01(3)[c]	0.434[b] 0.018[e]
6	Δ_{53}	94.27	94.56	100(5)[f]	96.807[b] 90[g] 94.4[h]	39.91	40.06	41(5)[f]	32.864[b] 31[g] 39.5[h]
	Δ_{31}	3.78	3.814	0(7)[f]	8.523[b] 0.9[g] 4.4[h]	76.01	76.23	83.0(7)[f]	75.97[b] 74[g] 74.6[h]
7	Δ_{53}	208.1	208.7	212(3)[f]	212.34[b] 203[g] 208.5[h]	112.9	113.3	115(3)[f]	114.32[b] 102[g] 111.9[h]
	Δ_{31}	34.3	34.5	35(4)[f]	40.708[b] 29[g] 35.1[h]	157.9	158.3	160(4)[f]	158.2[b] 156[g] 158.0[h]
8	Δ_{53}	401.7	402.8	418(4)[f]	409.13[b] 396[g] 404[h]	249.5	250.3	252(4)[f]	250.04[b] 232[g] 248[h]
	Δ_{31}	98.05	98.40	102(5)	105.93[b] 90[g] 101[h]	293.0	293.8	295(5)[f]	294.26[b] 292[g] 296[h]
9	Δ_{53}	706.6	708.5	716(10)[i]	718.83[b]	477.5	478.9	487(5)[i]	475.37[b]
	Δ_{31}	211.6	212.3	220(5)[i]	219.49[b]	500.6	501.9	523(10)[i]	504.15[b]
12	Δ_{53}	2669	2676	2708(20)[j]	2731.29[b] 2670[g]	2066	2071	1955(25)[j]	2018.13[b] 1960[g]
	Δ_{31}	1055	1058	1010(20)[j]	1038.56[b] 980[g]	1796	1801	1824(35)[j]	1835.75[b] 1820[g]

[a]Feldman *et al.* (Ref. 1).
[b]Hata and Grant (Ref. 6).
[c]Levitt and Feldman (Ref. 2).
[d]These numbers are taken from the table of Ref. 5. The number given in the abstract is 0.926 and -1.797 cm^{-1}. The number given in the text is 0.950 and -1.760 cm^{-1}.
[e]Glass (Ref. 5).
[f]Livingston and Berry (Ref. 3).
[g]Cheng *et al.* (Ref. 7).
[h]Chen *et al.* (Ref. 8).
[i]Martinson *et al.* (Ref. 28).
[j]Träbert *et al.* (Ref. 4).

IV. TRANSITION WAVELENGTHS AND FINE STRUCTURE

The calculated fine structure of Li $1s\,2p\,2p\ ^4P$ for $\Delta_{53}=E_{5/3}-E_{3/2}$ is -1.917 cm^{-1} and for $\Delta_{51}=E_{5/2}-E_{1/2}$ it is -0.003 cm^{-1} in this work. This agrees with the -1.87 ± 0.05- and 0.07 ± 0.11-cm^{-1} results given in Ref. 1. However, a refined result in Ref. 2 gives $-1.83(3)$ cm^{-1} and 0.01(3) cm^{-1}. This makes the calculated Δ_{53} differ from that of the experiment by about three times the uncertainty quoted. In the case of $1s\,2s\,2p\ ^4P$, the calculated Δ_{53} and Δ_{51} differ from experimental values by about 5% (see Table IV) while Δ_{31} differs by about 2%. Since higher-order relativistic effects for lithium are negligible, the source of this discrepancy is difficult to pin down. Energywise, the result of the present work is significantly more accurate than that of Glass,[5] but the disagreement with experiment in the fine structure is

about the same (see footnote g in Table IV). Compared with the experimental result of Gaupp *et al.*[23] on $^4P^e$, our Δ_{53} lies within their quoted uncertainty. The MCDF method is not considered to be suitable for low-Z systems because of the correlation effect. A comparison of the present work with that of Hata and Grant[6] seems to support this assertion.

For Be II and B III, there are no fine-structure experimental data available for the ^4P states. For C IV, N V and O VI the experimental data are given by Livingston and Berry[3] and for Mg X by Träbert *et al.* Before making any comparison with these results, it is perhaps more convenient to discuss the comparison for λ_{CG} and $\lambda_{JJ'}$.

For Be II, the experimental data for λ_{CG} is 2324.60±0.03 Å (Ref. 24) and 2324.6±0.3 Å (Ref. 25). In this work, the calculated λ_{CG} is 2324.96 Å and $\lambda_{JJ'}$ ranges from 2324.52 to 2325.35 Å. The Lamb shift is very small for this system. Hence, the agreement between theory and experiment should be considered as satisfactory. For B III, the calculated $\lambda_{JJ'}$ ranges from 1700.98 to 1702.28 Å and λ_{CG} is 1701.77 Å. This also agrees with the experimental result of 1701.4 Å (Ref. 26) and 1701±1 Å (Ref. 27). The wave function of Be II has 87 linear parameters for $^4P^o$ and 74 linear parameters for $^4P^e$. The corresponding wave functions for B III, C IV, N V, O VI, and F VII have 80 and 78 linear parameters, respectively. All results presented here are the actual converged data. No extrapolation procedure has been taken.

For C IV, N V, O VI, F VII, and Mg X, highly accurate experimental data are available for $\lambda_{JJ'}$. Hence, an unambiguous comparison can be made between theory and experiment. For these systems, the Lamb-shift contributions become more appreciable. This radiative (QED) correction to the ^4P states has been calculated using a screened Coulomb potential by Hata and Grant.[6] To make a meaningful comparison between theory and experiment, we shall include their numbers in the theoretical wavelengths. The radiative correction calculated by Hata and Grant[6] for $Z=6$, 7, 8, and 12 is given in Table V. It can be seen from this table that for systems with $Z=5$ or less, the corresponding QED contributions to the transition wavelength are very small.

In the published result of Livingston and Berry,[3] only one digit is quoted after the decimal. For the sake of discussion, we assume the next digit to be a zero with the understanding that round-off errors might have occurred at this digit.

In comparing theory with experiment, we note that the best agreement occurs in C IV (see Table VI). In this case, the deviation between theory and experiment ranges from 0.01 to −0.08 Å. The deviation for λ_{CG} is 0.02 Å. Considering that the quoted experimental uncertainty is ±0.3 Å, this agreement is quite remarkable. If the theoretical result presented in this work is correct, one can reduce the quoted uncertainty in the experiment by a factor of 3.

For N V, the deviation between theory and experiment for $\lambda_{JJ'}$ ranges from 0.3 to 0.15 Å with an average of about 0.07 Å. This is within the quoted uncertainty ±0.1 Å in the results of Livingston and Berry.[3] However, the calculated $\lambda_{CG}=1110.71$ Å deviates from that of the experiment by −0.39 Å. It is four times the quoted uncertainty. Since H_{so}, H_{soo}, and H_{ss} do not shift the position of E_{CG}, the deviation of λ_{CG} should be comparable to that of $\lambda_{JJ'}$. The reason for this discrepancy between theory and experiment is difficult to understand.

This situation becomes worse for O VI. Here the deviation between theory and experiment ranges from −0.20 to −0.43 Å for $\lambda_{JJ'}$. But the λ_{CG} deviation is −1.19 Å which is almost 12 times the quoted uncertainty in the experiment.

Recently, the $\lambda_{JJ'}$ for the F VII ^4P states have been measured and found to range from 818.09 to 823.42 Å by Martinson *et al.*[28] The difference between their result and the present calculation is −0.09 Å at 818.09 Å and increases with the wavelength to −0.26 Å at 823.42 Å. The calculated $\lambda_{CG}=822.30$ Å differs from that of the experiment by −0.17 Å. In view of the deviation in $\lambda_{JJ'}$, this is very reasonable. Here we do not have the kind of discrepancy as that in N V and O VI. Our λ_{CG} differ significantly from the 814 Å reported by Knystautas and Drouin.[29]

For Mg X, the calculated $\lambda_{JJ'}$ deviates from that of

TABLE V. Contribution of radiative corrections to the $1s\,2p^2\,^4P-1s\,2s\,2p\,^4P$ transition calculated by Hata and Grant (Ref. 6) in cm^{-1}.

$1s\,2s\,2p\,^4P_J$	$1s\,2p^2\,^4P_{J'}$	$Z=6$	7	8	12
$\frac{3}{2}$	$\frac{5}{2}$	−12.7	−24.7	−43.2	−215
$\frac{1}{2}$	$\frac{3}{2}$	−12.8	−24.9	−43.6	−217
$\frac{3}{2}$	$\frac{3}{2}$	−12.9	−25.2	−44.2	−221
$\frac{5}{2}$	$\frac{5}{2}$	−13.2	−25.2	−44.2	−221
$\frac{1}{2}$	$\frac{1}{2}$	−12.9	−25.2	−44.2	−221
$\frac{3}{2}$	$\frac{1}{2}$	−13.1	−25.5	−44.7	−226
$\frac{5}{2}$	$\frac{3}{2}$	−12.9	−25.7	−45.1	−227

TABLE VI. $1s\,2p\,2p\ ^4P^e$ to $1s\,2s\,2p\ ^4P^o$ transition-wavelength comparison between theory and experiment. Row A, this work; row B, this work plus the radiative correction of Hata and Grant (Ref. 6); row C, experiment; row D, $\Delta\lambda$ equals row B minus row C (in Å).

Z	$J\rightarrow J'$	$\frac{1}{2}\rightarrow\frac{1}{2}$	$\frac{1}{2}\rightarrow\frac{3}{2}$	$\frac{3}{2}\rightarrow\frac{1}{2}$	$\frac{3}{2}\rightarrow\frac{3}{2}$	$\frac{3}{2}\rightarrow\frac{5}{2}$	$\frac{5}{2}\rightarrow\frac{3}{2}$	$\frac{5}{2}\rightarrow\frac{5}{2}$	λ_{CG}
3	A	3716.32	3715.68	3715.94	3715.68	3715.94	3715.81	3716.07	3715.95
	C[a]								3715.38±0.1
4	A	2325.39	2325.05	2324.86	2324.52	2325.01	2324.63	2325.12	2324.96
	C[b,c]								2324.6
5	A	1702.28	1702.09	1701.38	1701.20	1702.20	1700.98	1701.98	1701.77
	C[d]								1701.4
6	A	1344.59	1344.66	1343.22	1343.28	1344.99	1342.57	1344.27	1343.99
	B	1344.82	1344.90	1343.45	1343.51	1345.22	1342.80	1344.51	1344.22
	C[e]		1344.9	1343.5		1345.3	1342.8	1344.5	1344.2±0.3
	D		0.0	−0.05		−0.08	0.0	0.01	0.02
7	A	1111.09	1111.51	1109.14	1109.56	1112.13	1108.17	1110.73	1110.40
	B	1111.40	1111.83	1109.45	1109.87	1112.45	1108.47	1111.04	1110.71
	C[e]		1111.8	1109.3	1109.8	1112.4	1108.4	1111.0	1111.1±.1
	D		0.03	0.15	0.07	0.05	0.07	0.04	−0.39
8	A	946.00	946.87	943.38	944.25	947.85	942.03	945.61	945.22
	B	946.40	947.27	943.77	944.64	948.26	942.41	946.00	945.61
	C[e]	946.6	947.6	944.0	945.0	948.7	942.7	946.4	946.8±.1
	D	−0.20	−0.33	−0.23	−0.36	−0.43	−0.29	−0.40	−1.19
9	A	822.68	824.12	819.31	820.73	825.52	817.53	822.28	821.83
	B	823.16	824.61	819.78	821.21	826.02	818.00	822.77	822.31
	C[f]	823.42		819.89	821.37		818.09	822.91	822.47
	D	−0.26		−0.11	−0.16		−0.09	−0.14	−0.16
12	A	586.25	589.91	580.13	583.71	592.98	576.75	585.79	585.17
	B	587.01	590.69	580.86	584.47	593.78	577.46	586.55	585.93
	C[g]	587.10	590.70	580.93	584.35	593.75	577.62	586.80	586.04±.05
	D	−0.09	−0.01	−0.07	0.12	0.03	−0.16	−0.25	−0.11

[a]Levitt and Feldman (Ref. 2).
[b]Mannervik *et al.* (Ref. 24).
[c]Bentzen *et al.* (Ref. 25).
[d]Martinson *et al.* (Ref. 26).
[e]Livingston and Berry (Ref. 3).
[f]Martinson *et al.* (Ref. 28).
[g]Träbert *et al.* (Ref. 4).

experiment[4] by −0.25 to 0.12 Å. This suggests that the calculated fine structure is somewhat different from that of experiment.[4] The calculated $\lambda_{CG}=585.93$ Å differs from the experimental 586.04±0.05 Å by −0.11 Å. This is reasonable in view of the difference in $\lambda_{JJ'}$. There is no discrepancy in Mg X similar to that of N V and O VI.

For the fine structure of C IV, our $\Delta_{53}=94.27$ cm^{-1} seems to lie outside the experimental result of 100±5 cm^{-1}. This could be misleading since $\lambda_{JJ'}$ lies well within the relative uncertainty ±0.1 Å quoted in the experiment.[3] For N V, again Δ_{53} of $^4P^o$ is the only datum that deviates slightly from that of the experiment. This deviation increases substantially from N V (1.8%) to O VI (3.9%) with all other splittings of the two systems lying well within the experimental accuracy.

For the fine structure of F VII, only the Δ_{53} of $^4P^o$ fall within the reported experimental uncertainty while other splittings deviate from the reported value by about 2—4 % (see Table IV). This disagreement is also difficult to understand in view of the agreement of $\lambda_{JJ'}$. The $\Delta\lambda_{JJ'}$ between theory and experiment ranges from −0.09 to −0.26 Å. Hence, the maximum relative deviation is only 0.17 Å, very close to the quoted uncertainty ±0.08 Å in the experiment. By contrast, the fine structure of the $^4P^o$ state calculated by Hata and Grant[6] agrees excellently with the reported value in the experiment. Their $\Delta\lambda_{JJ'}$

ranges from 0.91 to 1.22 Å with a maximum relative deviation of 0.31 Å.

For the fine structure of Mg X, only the calculated Δ_{31} for $^4P^e$ lies within the experimental uncertainty whereas Δ_{53} deviates 5.7% from that of experiment[4] (see Table IV). For Δ_{53} and Δ_{31} of $^4P^o$, the deviations are 1.4 and 4.5 %, respectively.

Compared with the other theoretical fine-structure results in the literature, the present calculation seems to give a similar degree of accuracy to those of Hata and Grant[6] and Chen *et al.*[8] for C IV, N V, and O VI. However, it gives inferior fine-structure data for Mg X even though λ_{CG} calculated in this work is far more accurate. In Cheng *et al.*[30] $\Delta\lambda_{CG}=-5.7$ Å and in the work of Hata and Grant it is about -0.58 Å.

V. SUMMARY AND DISCUSSION

The purpose of this work was to carry out a reasonably accurate calculation to test the validity of the relativistic perturbation theory for a three-electron system. That is, to compute the relativistic effects using the H_1, H_2, H_3, H_4, H_{so}, H_{soo}, and H_{ss} in Eqs. (2)—(9) as perturbation operators in the first-order perturbation method. It should be pointed out that the higher-order relativistic effects neglected in Eq. (1) are not always small even for median-Z systems, especially the higher-order expansion terms coming from the mass correction in the kinetic energy operator. On the other hand, the higher-order contribution of H_1 is also not small for median and large Z. This can be seen from the recent work of Bruch *et al.*[31] in the case of boron. This contribution grows quickly as Z increases. Fortunately, these two kinds of higher-order contributions are opposite in sign and substantial cancellation occurs. But whether this cancellation is complete is always a matter of speculation. The method of the present work has been used to obtain highly accurate results for two-electron systems in the past.[10] Since there are precise experimental data available on the $^4P^e$-$^4P^o$ transitions, they provide excellent conditions to test this relativistic perturbation theory for three-electron systems.

From the λ_{CG} calculations carried out in this work, it appears that for Be II, B III, and C IV the theory and experiment agree very well. For N V, the theoretical and experimental λ_{CG} differ slightly, but judging from the agreement in $\lambda_{JJ'}$, this disagreement is probably fictitious. We do not know if the alignment in the beam-foil experiment or the possible nonstatistical population distribution of the upper J states may have affected the experimental data. This is particularly serious in O VI where $\Delta\lambda_{CG}$ is almost 12 times the uncertainty quoted in the experiment.[3]

The $\Delta\lambda_{JJ'}$ for O VI ranges from -0.20 to -0.43 Å suggesting that the probable $\Delta\lambda_{CG}$ should be around -0.3 Å. This deviation could be interpreted as an indication that our method is beginning to break down. However, for larger Z, namely, Mg X, $\Delta\lambda_{CG}=-0.11$ Å is only twice the quoted experimental uncertainty.[4] One must be cautious in drawing any conclusion from this result. For this system, the radiative correction given by Hata and Grant[6] contributes 0.76 Å to λ_{CG}. Judging from the approximation used in computing this correction, it is not impossible to have an error of 10%. A change of 0.07 Å could bring our result into total agreement with experiment or further away from it. But, in any case, the breakdown of our method does not seem to have increased from $Z=8$ to $Z=12$ as far as λ_{CG} is concerned.

In the fine-structure calculation, it is found that for C IV, N V, and O VI, the agreement with experiment is similar to that of recent MCDF calculations.[6,8] However, for Mg X, the present result seems to be poorer. It is not clear whether this breakdown is due to higher-order effects or the inadequacy of the *LSJ* coupling scheme. More theoretical study is needed in this area. For lithium, the present approach is clearly superior to the MCDF method. But here we also have a 5% deviation in the $^4P^o$ Δ_{53} and Δ_{51} results in comparing with experiment. The source of this discrepancy is even harder to understand. For lithium, the higher-order effects are too small to be significant. Our nonrelativistic energy is much lower than that of Glass,[5] but the fine-structure result in this work does not give appreciable improvement. It would be of interest to see whether a better result may be obtained if a different type of wave function such as that of Larsson and collaborators[17] is used.

In conclusion, we find that for λ_{CG} the present method seems to work well for the systems investigated. No obvious breakdown is found. As for the fine structure, the present method seems to give an inferior result in Mg X in comparing with MCDF method. It would be of interest to study the trend of this breakdown from $Z=8$ to 12. To accomplish this, we need more precise experiment data, especially for the quartet states of nuclear charge $Z=10$ and 11.

It is worthwhile to mention that for higher excited states of the three-electron systems the present method can generate results of accuracy equal to the ones presented in this work. There seems to be a severe lack of experimental data of fine structures for these higher excited states. We hope that the measurement of these fine structures can be carried out to compare with the vast amount of theoretical data available.[32]

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