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Radiative transition probabilities of the $1s2p^2\ {}^2P$ and $1s2p^2\ {}^2D$ states of the lithium isoelectronic sequence

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A Z-expansion procedure is used to obtain eigenvalues and eigenfunctions for the $1s^22p\ {}^2P^o$, $1s2p^2\ {}^2P$, and $1s2p^2\ {}^2D$ states of the lithium sequence. Expansions in inverse powers of the nuclear charge Z are obtained also for the dipole-matrix elements and oscillator strengths of the $1s^22p\ {}^2P^o$-$1s2p^2\ {}^2P$ and $1s^22p\ {}^2P^o$-$1s2p^2\ {}^2D$ transitions, valid for $Z > 3$. A separate calculation was performed for lithium. The calculated transition probabilities agree with the Hartree-Fock values of Gabriel for large Z, but there are considerable discrepancies with the experimental data.

I. INTRODUCTION

Recent observations of satellite lines of helium-like ions in the solar corona and in laboratory plasmas have emphasized the need for accurate values of the energies and oscillator strengths of electronic transitions in multiply charged ions. Experimental results from beam-foil spectroscopy and theoretical calculations are available for the wavelengths of several transitions in lithium-like ions,[1-5] but lifetime measurements and calculations are relatively rare.[6-9] Spectra of the satellite groups $1s^22p\ {}^2P^o$-$1s2p^2\ {}^2P$ and $1s^22p\ {}^2P^o$-$1s2p^2\ {}^2D$ were first observed in a vacuum spark by Edlén and Tyrén.[10] More recently, lines belonging to these transitions have been identified in both solar flares[11] and nonflaring solar active regions.[12] In the laboratory, the lines have been observed in high-temperature plasmas, such as θ pinches[4] and laser-produced plasmas,[13,14] and in beam-foil spectra.[15,16] Theoretical calculations have concentrated mainly on obtaining accurate transition wavelengths. Safronova and Kharitonova[17] and Summers[3] have calculated the energies of these states using nonrelativistic second order $1/Z$ expansions. Goldsmith[1] and Vainstein and Safronova[18] have done similar calculations with added terms to account for relativistic effects. Gabriel[9] and Bhalla, Gabriel, and Presnyakov[19] have studied both the wavelengths and intensities of these and several other transitions in an intermediate coupling scheme using Hartree-Fock wave functions.

In this paper, we calculate energies and eigenfunctions of the $1s^22p\ {}^2P^o$, $1s2p^2\ {}^2P$, and $1s2p^2\ {}^2D$ states of the lithium isoelectronic sequence using an approximate high-order $1/Z$ expansion method. The results are used to obtain oscillator strengths of the $1s^22p\ {}^2P^o$-$1s2p^2\ {}^2P$ and $1s^22p\ {}^2P^o$-$1s2p^2\ {}^2D$ transitions.

II. CALCULATIONS

The calculations were done using the nonrelativistic Z-expansion theory of Drake and Dalgarno.[20] The Schrödinger equation is given by

$$(H-E_n)|\psi_n\rangle = 0\ , \tag{1}$$

where H is the nonrelativistic Hamiltonian. The wave functions ψ_n and energies E_n can be found as expansions of the form

$$|\psi_n\rangle = \sum_{s=0}^{\infty} Z^{-s}|\psi_n^{(s)}\rangle$$

and

$$E_n = \sum_{s=0}^{\infty} Z^{-s}E_n^{(s)}\ .$$

The oscillator strength for an electric dipole transition is given in the length formulation by

$$f = \tfrac{2}{3}(E_{n'} - E_n)M\ ,$$

where

$$M = \left|\langle\psi_n|\sum_{Z=1}^{3}\vec{\mathrm{r}}_i|\psi_{n'}\rangle\right|^2\ ,$$

and all quantities are measured in atomic units. We may expand f_l in the form

$$f_l = \sum_{s=0}^{\infty} Z^{-s}f_l^{(s)}\ .$$

The square of the transition matrix element may be similarly expanded:

$$M = \frac{1}{Z^2}\sum_{s=0}^{\infty} Z^{-s}M^{(s)}\ .$$

In this perturbation-variation method, a finite basis set is used to find approximate values for the expansion coefficients. Computational details may be found in Watson and O'Neil.[21]

TABLE I. Atomic orbitals and configurations of the $1s^22p\ ^2P^o$, $1s2p^2\ ^2P$, and $1s2p^2\ ^2D$ states used in the $1/Z$ expansion.

	Slater orbital					
Atomic orbital	n	l	Scaled orbital exponent	Configurations		
				$1s^22p\ ^2P^o$		
$1s$	1	0	1.0	$1s^22p$	$2p\ 2p''^2(2)$	
$1s'$	1	0	1.225	$1s1s'2p(2)$	$2p\ 3p^2(3)$	
$1s''$	1	0	0.8125	$1s1s''2p(2)$	$2p\ 3p'^2$	
$2s$	2	0	0.5	$1s2s2p(2)$	$2p\ 2p''3p(5)$	
				$1s2s'2p$	$2p\ 2p''3p'(4)$	
				$1s'^22p$		
$2s'$	2	0	1.0	$1s''^22p$	$2p\ 3p\ 3p'(5)$	
$3s$	3	0	1.25	$1s^22p'$	$2p2p'^2(2)$	
				$1s^22p''$	$2p2p'2p''(4)$	
$2p$	2	1	0.5	$1s^23p$	$2p\ 2p'3p(5)$	
$2p'$	2	1	0.4125	$1s^23p'$	$2p\ 2p'3p'(3)$	
$2p''$	2	1	0.3325	$1s1s'2p'(2)$		
$3p$	3	1	0.6875	$1s1s''2p'(2)$		
$3p'$	3	1	0.4375	$1s'3s2p(2)$		
				$1s''2s2p$		
				$1s2p3d(2)$		
$3d$	3	2	0.4375	$1s2p3d'(2)$		
$3d'$	3	2	0.6875	$1s2p4d$		
$4d$	4	2	0.4375			
				$1s2p^2\ ^2P$		
$1s$	1	0	1.0	$1s2p^2$	$1s'2p2p'''$	$1s3d3d'$
$1s'$	1	0	1.225	$1s2p'^2$	$1s''2p^2$	$1s3d4d(2)$
$1s''$	1	0	0.8125	$1s2p''^2$	$1s''2p2p'(2)$	$1s3d'^2$
$2p$	2	1	0.5	$1s2p'''^2$	$1s''2p2p''(2)$	$1s3d'4d(2)$
$2p'$	2	1	0.4125	$1s2p2p'(2)$	$1s'2p'^2$	$1s4d^2$
$2p''$	2	1	0.33125	$1s2p2p''(2)$	$1s'2p'2p''(2)$	$1s'3d^2$
$2p'''$	2	1	0.19375	$1s2p2p'''(2)$	$1s'2p''2p'''(2)$	$1s''2p'2p'''(2)$
$3p$	3	1	0.57	$1s2p'2p''(2)$	$1s'2p''^2$	$1s2p3p(2)$
$3p'$	3	1	0.20	$1s2p'2p'''(2)$	$1s'2p''2p'''$	$1s2p3p'(2)$
$4p$	4	1	0.57	$1s2p''2p'''(2)$	$1s''2p'^2$	$1s2p4p(2)$
$3d$	3	2	0.2925	$1s'2p^2$	$1s''2p'2p''(2)$	$1s2p'3p$
$3d'$	3	2	0.21625	$1s'2p2p'(2)$	$1s''2p''^2$	$1s2p'3p'(2)$
$4d$	4	2	0.30	$1s'2p2p''(2)$	$1s3d^2$	$1s4p^2$
				$1s2p^2\ ^2D$		
$1s$	1	0	1.0	$1s2p^2$	$1s'2p^2$	$1s2p''3p'$
$1s'$	1	0	1.225	$1s2p2p'(2)$	$1s'2p2p'(2)$	$1s'2p3p'$
$2s$	2	0	1.25	$1s2p2p''(2)$	$1s'2p2p''(2)$	$1s'2p'^2$
$2p$	2	1	0.5	$1s2p2p'''(2)$	$1s'2p2p'''(2)$	$1s2p'''3p$
$2p'$	2	1	0.30625	$1s2p3p(2)$	$2s2p^2$	$1s3p'^2$
$2p''$	2	1	0.170	$1s2p3p'(2)$	$2s2p2p'(2)$	$1s'2p'2p''(2)$
						$1s'2p'2p'''$
$2p'''$	2	1	0.57	$1s2p4p(2)$	$2s2p2p''$	$1s'2p'3p'$
$3p$	3	1	0.20	$1s2p'^2$	$2s2p2p'''$	$1s'2p''2p'''$
$3p'$	3	1	0.57	$1s2p'2p''(2)$	$1s3d^2$	$2s2p'^2$
$4p$	4	1	0.20	$1s2p'2p'''(2)$	$1s3d'^2$	$1s'3d^2$
$3d$	3	2	0.2925	$1s2p'3p(2)$	$1s4d^2$	
$3d'$	3	2	0.21625	$1s2p'3p'(2)$	$1s3d3d'(2)$	
				$1s2p'4p$		
$4d$	4	2	0.30	$1s2p''^2$	$1s3d4d$	
					$1s3d'4d(2)$	
				$1s2p''2p'''(2)$	$1s2p''3p$	
				$1s2p'''^2$		

TABLE II. Atomic orbitals and configurations of the lithium states $1s^22p\ ^2P^o$, $1s2p^2\ ^2P$, and $1s2p^2\ ^2D$.

	Slater orbital					
Atomic orbital	n	l	Orbital exponent	Configurations		
				$1s^22p\ ^2P^o$		
				$1s^22p$	$2p3d^2(3)$	
$1s$	1	0	4.69873	$1s^22p'$	$2p2p'3p'(5)$	
	1	0	2.47673	$1s^23p$	$2p3p'^2(2)$	
	2	0	1.632		$1s1s'2p'(2)$	
	2	0	1.07	$1s1s'2p(2)$	$1s2s'2p'(2)$	
	2	0	0.66055	$1s2s2p(2)$	$1s1s'3p(2)$	
$1s'$	1	0	3.0	$1s2s'2p(2)$	$2p^22p'(3)$	
$2s$	2	0	2.52	$1s3s2p(2)$	$1s2s2p'(2)$	
$2s'$	2	0	5.75	$1s'^22p$		
$3s$	3	0	5.75	$1s'2s2p(2)$		
$2p$	2	1	2.80	$1s'2s'2p(2)$		
	2	1	1.632	$1s'3s2p(2)$		
	2	1	1.07	$2s^22p$		
	2	1	0.66	$2s2s'2p(2)$		
	2	1	0.38	$2s3s2p(2)$		
				$2s'^22p$		
$2p'$	2	1	4.45	$2s'3s2p(2)$		
$3p$	3	1	4.45	$3s^22p$		
$3p'$	3	1	8.9	$2p2p'^2(3)$		
$3d$	3	2	2.7	$2p2p'3p(6)$		
$3d'$	3	2	7.2	$2p3p^2(3)$		
				$1s2p^2\ ^2P$		
$1s$	1	0	2.90	$1s2p^2$	$1s'2p2p''(2)$	$2s2p''^2$
$1s'$	1	0	4.35	$1s2p'^2$	$1s'2p3p$	$1s3d^2$
$2s$	2	0	3.0	$1s3p^2$	$2s2p^2$	$1s3d3d'(2)$
						$1s3d4d(2)$
$2p$	2	1	1.5	$1s3p'^2$	$2s2p2p'(2)$	$1s3d'^2$
$2p'$	2	1	0.92	$1s2p2p'(2)$	$2s2p2p''(2)$	$1s3d'4d(2)$
$2p''$	2	1	0.51	$1s2p2p''(2)$	$1s'2p'^2$	
$3p$	3	1	1.71		$1s'2p'2p''(2)$	$1s4d^2$
$3p'$	3	1	0.60	$1s2p3p(2)$	$1s'2p'3p(2)$	$1s'3d'^2$
$4p$	4	1	0.25	$1s2p'2p''(2)$	$1s'2p''^2$	$2s2p'3p(2)$
$4p'$	4	1	0.50	$1s2p'3p(2)$	$1s'2p''3p$	$1s2p3p'(2)$
				$1s2p''3p(2)$		
$3d$	3	2	0.88	$1s'2p^2$	$2s2p'^2$	$1s2p4p(2)$
$3d'$	3	2	0.65	$1s'2p2p'(2)$	$2s2p'2p''(2)$	$1s2p4p'(2)$
$4d$	4	2	0.90			$1s2p'3p'$
						$1s2p'4p(2)$
				$1s2p^2\ ^2D$		
$1s$	1	0	2.9	Same as Z-exp basis		
$1s'$	1	0	3.75			
$2s$	2	0	3.75			
$2p$	2	1	1.5			
$2p'$	2	1	0.92			
$2p''$	2	1	0.50			
$2p'''$	2	1	1.71			
$3p$	3	1	0.60			
$3p'$	3	1	1.71			
$4p$	4	1	0.60			
$3d$	3	2	0.88			
$3d'$	3	2	0.65			
$4d$	4	2	0.90			

TABLE III. Eigenvalue expansion coefficients $E^{(s)}$.

s	$1s^22p\ ^2P^o$	$1s2p^2\ ^2P$	$1s2p^2\ ^2D$
0	−1.125 000(0)	−7.500 000(−1)	−7.500 000(−1)
1	1.093 526(0)	6.667 298(−1)	6.536 824(−1)
2	−5.024 103(−1)	−4.536 265(−1)	−3.818 746(−1)
3	−1.258 319(−1)	−4.903 188(−2)	−9.109 562(−2)
4	1.433 014(−1)	7.817 505(−2)	−1.648 713(−2)
5	−1.834 173(−1)	3.654 516(−3)	−2.455 665(−3)
6	−1.408 782(−1)	4.172 207(−1)	9.324 469(−2)
7	4.051 577(0)	−4.040 002(−1)	3.034 963(−1)
8	1.141 479(1)	−3.653 172(0)	−3.366 886(−1)
9	5.583 699(0)	7.734 046(−1)	−3.126 990(0)
10	−1.956 390(1)	2.116 235(+1)	−3.367 930(0)

The basis sets and configurations used in the $1/Z$ expansions are shown in Table I. In each state, hydrogenic orbitals are used for the $1s$ and $2p$ atomic orbitals. This ensures exact values for the zero- and first-order coefficients in the $1/Z$ expansions, and therefore correct values for the series limits at high Z, but it results in some loss of accuracy at low Z. The other exponents were chosen as physically reasonable, but no optimization was performed.

The series did not converge for $Z < 4$ and a separate variational calculation was carried out using a different basis set to obtain the energies and oscillator strengths at $Z = 3$. In the lithium $1s^22p\ ^2P$ basis set, the $1s$ and $2p$ orbitals were selected to be Hartree-Fock orbitals. The nine other orbitals had exponents similar to those used by Weiss[22] in his 45-configuration wave function. The $1s2p^2\ ^2P$ and $1s2p^2\ ^2D$ basis sets each consist of 13 Slater-type orbitals with arbitrary exponents. The basis sets and configurations are shown in Table II. Each wave function is made up of a total of 60 configurations.

TABLE IV. Eigenvalues for the Li isoelectronic sequence (a.u.).

Z	$1s^22p\ ^2P^o$	$1s2p^2\ ^2P$	$1s2p^2\ ^2D$
4	−14.148	−9.793	−9.791
5	−23.179	−15.876	−15.882
6	−34.458	−23.459	−23.475
7	−47.988	−32.542	−32.569
8	−63.768	−43.125	−43.164
9	−81.798	−55.207	−55.259
10	−102.078	−68.790	−68.854
11	−124.609	−83.873	−83.950
12	−149.390	−100.456	−100.545
13	−176.420	−118.539	−118.641
14	−205.701	−138.123	−138.237
15	−237.232	−159.206	−159.333
16	−271.013	−181.789	−181.929
20	−428.638	−287.110	−287.313
26	−732.575	−490.120	−490.390
28	−851.888	−569.787	−570.082

Using these basis sets, we calculated wave functions and energies of the lithium isoelectronic sequence. The energy expansion coefficients for each state through tenth order are shown in Table III, and the resulting eigenvalues for several values of Z are presented in Table IV. The energies are less accurate than those obtained by calculations in which the exponents are optimized.[2,8,22] The $1s^22p\ ^2P^o$ wave functions of Weiss[22] are much more compact and yield better energies; our more diffuse wave functions, however, should yield accurate values for the transition matrix elements. The expansion coefficients for the square of the matrix element and the oscillator strengths using calculated energies are shown in Table V.

In Table VI, our calculated transition wavelengths are compared to the values given by Gabriel.[9,23] Gabriel calculated the energy dif-

TABLE V. Expansion coefficients $M^{(s)}$ and $f^{(s)}$ for the $1s^22p\ ^2P^o$–$1s2p^2\ ^2P$ and $1s^22p\ ^2P^o$–$1s2p^2\ ^2D$ transition.

s	$1s^22p\ ^2P^o$–$1s2p^2\ ^2P$ $M^{(s)}$	$1s^22p\ ^2P^o$–$1s2p^2\ ^2P$ $f^{(s)}$	$1s^22p\ ^2P^o$–$1s2p^2\ ^2D$ $M^{(s)}$	$1s^22p\ ^2P^o$–$1s2p^2\ ^2D$ $f^{(s)}$
0	1.664 787(0)	4.161 967(−1)	9.248 817(−1)	2.312 204(−1)
1	−9.046 128(−1)	−6.998 365(−1)	−8.923 248(−1)	−4.942 835(−1)
2	−4.448 304(0)	−8.005 427(−1)	−2.398 158(0)	−2.635 631(−1)
3	−3.731 572(0)	3.886 038(−1)	−1.482 011(0)	2.824 206(−1)
4	1.239 326(+1)	3.896 796(0)	3.778 872(0)	1.067 390(0)
5	1.445 865(+1)	−1.381 711(−2)	−2.661 458(−1)	−1.142 603(0)
6	−1.111 834(+2)	−3.099 805(+1)	−2.275 432(+1)	−5.049 027(0)
7	−2.811 860(+2)	−4.323 103(+1)	2.519 757(+1)	1.045 600(+1)
8	3.986 962(+2)	1.601 097(+2)	2.667 313(+2)	5.148 775(+1)
9	3.099 112(+3)	6.629 902(+2)	5.354 305(+2)	6.500 718(+1)
10	6.874 226(+3)	9.504 449(+2)	1.072 063(+3)	1.736 700(+2)

TABLE VI. $1s^22p\ ^2P^o$-$1s2p^2\ ^2P$.

Z	System	Wavelength (Å) Calculated	Empirical	Radiative lifetime (10^{-12} s) This paper	Gabriel	Experimental[a]
4	Be	104.6	• • •	7.96[b]	• • •	
5	B	62.41	• • •	2.34[b]	• • •	3.9
6	C	41.44	41.38	0.91	0.79	1.4
7	N	29.51	29.47	0.43	0.38	≤2.2
8	O	22.07	22.05	0.23	0.216	≤2.1
9	F	17.14	17.12	0.13	0.12	
10	Ne	13.69	13.67	0.082	0.076	
11	Na	11.19	11.17	0.054	0.050	
12	Mg	9.31	9.30	0.037	0.034	
13	Al	7.87	7.86	0.026	0.024	
14	Si	6.74	6.73	0.019	0.017	
15	P	5.84	5.82	0.014	0.013	
16	S	5.11	5.09	0.011	0.098	
20	Ca	3.23	3.20	0.0040	0.0038	
26	Fe	1.88	1.86	0.0013	0.0013	
28	Ni	1.62	1.60	0.00098	0.00099	

[a] The experimental value includes a contribution from autoionization.
[b] These values were calculated using the theoretical wavelengths.

ferences between the resonance line and the satellite line and then adjusted the results to agree with some accurately known satellite energies. His results agree well with other published results.[3,10-12] Because of the relative inaccuracy of our energies, we used the empirical wavelengths[9] to calculate the lifetimes shown in Tables VI and VII. The uncertainty in the lifetimes then arises from the calculated value of the dipole matrix element. The calculated lifetimes of Gabriel[9] and the experimental values of Knystautas and Drouin[15] are listed in the tables. The differences between our lifetime results and the Hartree-Fock values of Gabriel[9] are due primarily to the effect of core polarization, which is ignored in Hartree-Fock calculations.

The measured lifetimes of Knystautas and Drouin[16] for the $1s2p^2\ ^2P$ state are considerably longer than the theoretical values for B III and C IV. The upper limits measured for the N V and O VI lifetimes are consistent with the calculated values. Our calculated lifetimes are slightly

TABLE VII. $1s^22p\ ^2P^o$-$1s2p^2\ ^2D$.

Z	System	Wavelength (Å) Calculated	Empirical	Radiative lifetimes (10^{-12} s) This paper	Gabriel
4	Be	104.6	• • •	25.0	
5	B	62.46	62.21[a]	6.94	
6	C	41.50	41.55	2.72	2.40
7	N	29.56	29.57	1.26	1.16
8	O	22.12	22.11	0.66	0.62
9	F	17.17	17.17	0.39	0.37
10	Ne	13.72	13.71	0.24	0.26
11	Na	11.21	11.20	0.15	0.15
12	Mg	9.33	9.32	0.10	0.11
13	Al	7.89	7.88	0.073	0.071
14	Si	6.76	6.74	0.053	0.051
15	P	5.85	5.84	0.039	0.038
16	S	5.12	5.10	0.029	0.029
20	Ca	3.23	3.21	0.011	0.011
26	Fe	1.88	1.87	0.0037	0.0037
28	Ni	1.61	1.60	0.0027	0.0027

[a] Measured value from Ref. 16.
[b] Calculated using the theoretical wavelength.

TABLE VIII. Lithium energies and oscillator strengths.

	$1s^22p\ ^2P^o$	$1s2p^2\ ^2P$	$1s2p^2\ ^2D$
Energy (a.u.)	−7.4046	−5.2097	−5.2022
Transition	$1s^22p\ ^2P^o$–$1s2p^2\ ^2P$		$1s^22p\ ^2P^o$–$1s2p^2\ ^2D$
Matrix element M	0.0824		0.0372
Oscillator strength f	0.1207		0.0545
Radiative lifetime (10^{-12} s)	54		177

longer than the Hartree-Fock values of Gabriel,[9] but they come into agreement as the nuclear charge increases.

The energies and oscillator strengths of the transitions in lithium are shown in Table VIII. Buchet *et al.*[15] have observed the $1s^22p\ ^2P^o$-$1s2p^2\ ^2P$ transition in beam-foil spectra and report a wavelength of 207.5 ± 0.5 Å, in harmony with our calculated value of 207.6 Å. They obtain an upper limit of 0.015 ± .01 ns for the lifetime compared to our value of 0.054 ns. Although our lifetime is appropriate to purely radiative decay, the contribution from autoionization of the $1s2p^2\ ^2P^o$ state is surely small for Li and there is a substantial discrepancy between theory and experiment.

Note added in proof: H. Nussbaumer [J. Phys. B 9, 1757 (1976)] has calculated transition probabilities for Fe XXIV and Ni XXVI using a small set of configurations but including spin-orbit interactions. His probabilities for individual transitions are significantly different from those of Gabriel,[9] who took account of spin-orbit interactions empirically. Our average lifetimes agree more closely with the results of Gabriel.

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