PHYSICAL REVIEW A VOLUME 42, NUMBER 9 1 NOVEMBER 1990

Radiative decay of triply excited $2p^2np\ ^{4,2}S^\circ$ states to the $1s2pmp\ ^{4,2}P$ states in lithiumlike ions

Brian F. Davis
Department of Physics, University of North Carolina at Wilmington, Wilmington, North Carolina 28403-3297

Kwong T. Chung
Department of Physics, North Carolina State University, Raleigh, North Carolina 27695-8202

(Received 26 April 1990)

The Rayleigh-Ritz variational method is used with a multiconfiguration-interaction function to obtain the nonrelativistic energies and wave functions of the triply excited $2p^2np\ ^4S^\circ$ ($n=2,3,4$) and $2p^23p\ ^2S^\circ$ states and also the doubly excited $1s2pmp\ ^4P$ ($m=2,3,4$), $1s2p^2\ ^2P$, $[(1s2p)^3P,3p]^2P$, and $[(1s2p)^1P,3p]^2P$ states for atomic systems with nuclear charges from $Z=3$ to 10. The relativistic and mass polarization corrections are evaluated via first-order perturbation theory, and the resulting relativistically corrected energies are used to compute transition wavelengths for $2p^2np\ ^{4,2}S^\circ \rightarrow 1s2pmp\ ^{4,2}P$. The fine structure of the $1s2pnp\ ^{4,2}P$ states is also calculated with first-order perturbation theory. The nonrelativistic wave functions are used to compute the electric-dipole transition probabilities for $2p^2np\ ^{4,2}S^\circ \rightarrow 1s2pmp\ ^{4,2}P$; this information is then used to compute the lifetimes for the $2p^2np\ ^{4,2}S^\circ$ states and the branching ratios for the transitions to the $1s2pmp\ ^{4,2}P$ levels. Intermediate-coupling effects for the $2p^3\ ^4S^\circ, ^2D^\circ, ^2P^\circ$ and the $1s2p^2\ ^4P, ^2D, ^2P, ^2S$ states are investigated for the case of $Z=10$ and are shown to be small. Comparisons with experimental wavelength and lifetime measurements are made.

I. INTRODUCTION

The triply excited $2p^2np\ ^{4,2}S^\circ$ states in lithiumlike ions are metastable against autoionization by conservation of parity and orbital angular momentum. This is because they lie energetically below the $2p^2\ ^3P$ bound-state threshold, and in the LS-coupling scheme there does not exist a degenerate $^{4,2}S^\circ$ continuum. These systems, however, undergo electric dipole transitions to the lower triply and doubly excited $^{4,2}P$ states. The lifetimes of these states are essentially determined by the dominant $2p \rightarrow 1s$ transition, i.e., $2p^2np\ ^{4,2}S^\circ \rightarrow 1s2pnp\ ^{4,2}P$. The lowest energy quartet is the $2p^3\ ^4S^\circ$ state, while the Pauli antisymmetry principle requires that the lowest-energy doublet state be $2p^23p\ ^2S^\circ$. The $2p^3\ ^4S^\circ$ state's energy was computed by Chung[1] and subsequently its optical emission to the $1s2p^2\ ^4P$ state was observed in both the lithium atom and the beryllium ion by Agentoft, Anderson, and Chung.[2] The calculated transition wavelengths and experimental data were found to be in close agreement. Very recently, Mannervik *et al.*[3] have remeasured this wavelength in neutral lithium with increased precision and also have determined the $2p^3\ ^4S^\circ$ lifetime. The measured lifetime 13.5±1.5 ps was found to be in good agreement with Chung's calculated value,[2] 12.9 ps. The measured wavelength 145.016±0.006 Å agrees with the previous experimental measurement of Agentoft, Anderson, and Chung,[2] 145.02±0.05 Å, and is close to the theoretical value of Chung.[2] Mannervik *et al.*[3] point out that the improved comparison with the theoretical value 145.019 Å, to be presented in this work, marks a level of accuracy comparable with their experimental measurement in that the experimental uncertainty is roughly of the same order of magnitude as the calculated contribution to the transition wavelength from relativistic effects.

The purpose of the recent work of Mannervik *et al.*[3] was to search for transitions involving more highly excited triply excited states, i.e., $2p^2np\ ^{4,2}S^\circ$ ($n \geq 3$), in addition to the lifetime measurement and the improved wavelength determination discussed above. Likewise, the purpose of this theoretical work is to supply more theoretical predictions for transitions involving the more highly excited triply excited states, and to improve the accuracy of the theoretical transition wavelengths originating from the lowest bound triply excited state $2p^3\ ^4S^\circ$. In this work, we calculate transition probabilities, wavelengths, and branching ratios from $2p^2np\ ^4S^\circ$ ($n=2,3,4$) and $2p^23p\ ^2S^\circ$ to the lower doubly excited bound states $1s2pmp\ ^4P$ ($m=2,3,4$) and $1s2pmp\ ^2P$ ($m=2,3$).

II. ENERGY LEVELS

A. Calculation method for nonrelativistic energy and wave function

The nonrelativistic energies and wave functions for the triply excited $2p^2np\ ^{4,2}S^\circ$ states and the doubly excited $1s2pmp\ ^{4,2}P$ states are computed via the Rayleigh-Ritz variational method in which a secular equation for the energy eigenvalues is obtained by

$$\delta\left[\frac{\langle\Psi_t|\mathcal{H}_0|\Psi_t\rangle}{\langle\Psi_t|\Psi_t\rangle}\right]=0\ , \tag{1}$$

where $\mathcal{H}_0$ is given by

$$\mathcal{H}_0=-\sum_{i=1}^{3}\left[\frac{1}{2}\nabla_i^2+\frac{Z}{r_i}\right]+\sum_{i<j}^{3}\frac{1}{r_{ij}}\ , \tag{2}$$

and Ψ_t is a trial wave function. Atomic units are used in this paper. The fact that these states couple to the continuum only through the spin-dependent interactions allows them to be treated as bound states in the nonrelativistic approximation which satisfy the upper-bound property.

The trial function is chosen to be a multiconfiguration-interaction wave function with variable linear and nonlinear parameters. The number of linear parameters used corresponds to the number of Slater-like orbitals in the basis-set expansion of the trial wave function; the number of nonlinear parameters employed is determined by the number of angular and spin partial waves in this expansion, three for each partial wave, i.e., one for each electron. The Slater-like basis functions used in these calculations are eigenfunctions of L^2, L_z, S^2, and S_z and are of the following form:

$$\phi_{[ls]}^{m,n,k}=\mathcal{R}_{\alpha_l,\beta_l,\gamma_l}^{m,n,k}(r_1,r_2,r_3)\mathcal{Y}_{[(l_1,l_2)L_{12},l_3]}^{L,M_L}(\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2,\hat{\mathbf{r}}_3)\times\chi_{[(s_1,s_2)S_{12},s_3]}^{S,M_S}(1,2,3)\ , \tag{3}$$

where the radial, angular, and spin parts are given, respectively, by

$$\mathcal{R}_{\alpha_l,\beta_l,\gamma_l}^{m,n,k}(r_1,r_2,r_3)=r_1^n r_2^m r_3^k e^{-\alpha_l r_1}e^{-\beta_l r_2}e^{-\gamma_l r_3}\ , \tag{4}$$

$$\mathcal{Y}_{[(l_1,l_2)L_{12},l_3]}^{L,M_L}(\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2,\hat{\mathbf{r}}_3)=\sum_{m_1,m_2,\mu,m_3}\langle l_1 l_2 m_1 m_2|L_{12}\mu\rangle Y_{l_1}^{m_1}(\hat{\mathbf{r}}_1)Y_{l_2}^{m_2}(\hat{\mathbf{r}}_2)Y_{l_3}^{m_3}(\hat{\mathbf{r}}_3)\langle L_{12}l_3\mu m_3|LM_L\rangle\ , \tag{5}$$

$$\chi_{[(s_1,s_2)S_{12},s_3]}^{S,M_S}(1,2,3)=\sum_{m_1,m_2,\mu,m_3}\langle s_1 s_2 m_1 m_2|S_{12}\mu\rangle \xi_{s_1}^{m_1}(1)\xi_{s_2}^{m_2}(2)\xi_{s_3}^{m_3}(3)\langle S_{12}s_3\mu m_3|SM_S\rangle\ . \tag{6}$$

The subscript $[ls]$ on the basis functions ϕ and the subscript l on the nonlinear variation parameters α, β, and γ, refer to the particular angular and spin partial wave

$$[(l_1,l_2)L_{12},l_3] \text{ and } [(s_1,s_2)S_{12},s_3]\ ,$$

that these parameters are associated with. Each partial wave has one such set of nonlinear parameters which are determined by the minimization of the energy. The bracketed notation indicates that the individual orbital angular momenta of electrons 1 and 2, l_1 and l_2, couple to L_{12} which couples to the orbital angular momentum of the third electron l_3 to form total orbital angular momentum L; while the individual spin angular momenta of electrons 1 and 2, s_1 and s_2, couple to S_{12} which couples to the spin angular momentum of the third electron s_3 to form total spin angular momentum S. The net result is the desired ${}^mL$ symmetry of interest, where $m=2S+1$ is the spin multiplicity which, for the three-electron system, is either a 2 for doublets or a 4 for quartets. The same notation is used for the Clebsch-Gordan coefficients in Eqs. (5) and (6).

The trial wave function can now be expressed by

$$\Psi_t=\mathcal{A}\sum_{[ls],i}A_{[ls],i}\phi_{[ls]}^{m,n,k}\ , \tag{7}$$

where $\mathcal{A}$ is an antisymmetrization operator. Minimization of the energy-expectation value yielded by this trial function via Eq. (1) fixes values for the linear and nonlinear parameters and consequently yields the nonrelativistic energy E_0 and corresponding wave function Ψ. The results are tabulated in Tables I–III.

The energy-efficient selection process by which specific basis functions were chosen for the expansion of a particular state was carried out via the C IV (for $2p^2np\ {}^4S^\circ$ states) and Ne VIII (for the $2p^23p\ {}^2S^\circ$ and $1s2pnp\ {}^{4,2}P$ states) systems. That is, the angular and spin partial waves, $[ls]$, and the radial powers of r_1, r_2, and r_3 [m, n, and k are collectively designated by i in Eq. (7)] were chosen for a specific system (i.e., $Z=6$ or 10) to yield the lowest energy. The other wave functions corresponding to the same state but with different nuclear charges were then obtained by utilizing the same basis functions with reoptimized linear and nonlinear parameters. We found that the results obtained by this procedure (at least for $Z>4$) can be improved on only very slightly by choosing terms explicitly for the particular ion of interest. For the cases of the Be$^+$ ion and the Li atom, we have found that the electron-correlation effects in these low-Z systems usually require that the basis functions be rechosen specifically for them. If we designate the number of partial waves N_1 and the total number of basis functions used N_2 by (N_1,N_2), then the triply excited $2p^2np\ {}^4S^\circ$ states utilize (8,58), (7,89), and (7,99) for $n=2$, 3, and 4, respectively; while the $2p^23p\ {}^2S^\circ$ doublet system uses (11,77). Notice how fewer angular and spin partial waves are necessary for accounting for the correlations in the quartet systems as the excitation (i.e., n) increases, but how more terms are necessary in order to account for the increasing number of nodes in the wave functions as n increases. The doublet system requires more angular and spin partial waves as a result of the two linearly independent ways in which the angular coupling can be achieved for a given ${}^2L$ symmetry, i.e., $[(l_1l_2)^1L_{12},l_3]^2L$.

The doubly excited $1s2pmp\ {}^4P$ states were constructed using (12,78), (10,82), and (9,94) for $m=2$, 3, and 4, respectively; while the $1s2pmp\ {}^2P$ doublet systems used (16,110), (15,110), and (12,110) for the $1s2p^2\ {}^2P$, $[(1s2p)\ {}^3P,3p]\ {}^2P$, and $[(1s2p)\ {}^1P,3p]\ {}^2P$ states, respectively. Note that the same trends hold for the total number of partial waves and basis functions used for these doubly excited systems as for the triply excited states. The number of partial waves and the total number of terms quoted for these states are strictly correct only for $Z>4$; as explained earlier, these quantities might be slightly different for $Z=3$ and 4 as a result of rechoosing the basis functions, however, in all cases the number of partial waves does not exceed 16 and the total number of terms does not exceed 110. Some of these states have been reported on by us in our earlier works: Refs. 1 and 2 for the $2p^3\,^4S^\circ$ states ($Z<10$), Ref. 4 for $1s2pmp\ ^4P$ ($Z=4$), Ref. 5 for $1s2pmp\ ^{4,2}P$ ($Z=5$), Ref. 6 for $1s2pmp\ ^{4,2}P$ ($Z=8$), Ref. 7 for $1s2p^2\,^4P$ ($Z=3\rightarrow10$), and Ref. 8 for $1s2pmp\ ^2P$ ($Z=4$). Most of these states have been improved on here by obtaining a lower upper bound to the nonrelativistic energy eigenvalue.

The identification of the particular $1s2p3p\ ^2P$ states in the lithium atom from the eigenvalue spectrum yielded by Eq. (1) requires some additional comments. The positive-ion $1s2p3p\ ^2P$ states, $[(1s2p)\,^3P,3p]\,^2P$, and $[(1s2p)\,^1P,3p]\,^2P$, appear as the second- and third-lowest-energy roots, respectively, in the secular equation. This is not the case for lithium due to the larger relative energy separation of the $1s2p\ ^3P$ and $1s2p\ ^1P$ states in this low-Z system. The second root of the lithium secular equation is still identified as the $[(1s2p)\,^3P,3p]\,^2P$ state, however, the third and fourth roots are linear combinations of $[(1s2p)\,^3P,4p]\,^2P$ and $[(1s2p)\,^1P,3p]\,^2P$. The normalization integral of the third root indicates that it is about 60% $[(1s2p)\,^3P,4p]\,^2P$, while that of the fourth root indicates approximately equal admixtures of the two configurations.

B. Relativistic and mass polarization corrections

Accurate transition wavelengths demand relativistically corrected energy eigenvalues; to this end, we have computed relativistic and mass polarization corrections to the energy using first-order perturbation theory. These relativistic and mass polarization corrections are obtained by computing the expectation values of the following operators from the Breit-Pauli approximation:[9] relativistic correction to the kinetic energy

$$\mathcal{H}_1=-\tfrac{1}{8}\alpha^2\sum_{i=1}^{3}p_i^4\ , \tag{8}$$

the Darwin term

$$\mathcal{H}_2=\frac{\pi}{2}\alpha^2 Z\sum_{i=1}^{3}\delta(\mathbf{r}_i)\ , \tag{9}$$

the electron Fermi contact term

$$\mathcal{H}_3=-\pi\alpha^2\sum_{(i<j)=1}^{3}(1+\tfrac{8}{3}\mathbf{s}_i\cdot\mathbf{s}_j)\delta(\mathbf{r}_{ij})\ , \tag{10}$$

the orbit-orbit or retardation term

$$\mathcal{H}_4=-\tfrac{1}{2}\alpha^2\sum_{(i<j)=1}^{3}\frac{1}{r_{ij}}\left[\mathbf{p}_i\cdot\mathbf{p}_j+\frac{\mathbf{r}_{ij}\cdot(\mathbf{r}_{ij}\cdot\mathbf{p}_i)\mathbf{p}_j}{r_{ij}^2}\right]\ , \tag{11}$$

and the mass polarization

$$\mathcal{H}_5=\frac{1}{M}\sum_{(i<j)=1}^{3}\mathbf{p}_i\cdot\mathbf{p}_j\ . \tag{12}$$

Z is the nuclear charge, α is the fine structure constant, and M is the nuclear mass for ^{4}He, ^{7}Li, ^{9}Be, ^{11}B, ^{12}C, ^{14}N, ^{16}O, ^{19}F, and ^{20}Ne. The results of these calculations are given in Tables I–III. The electron-electron contact term is identically zero for the quartet states since the spatial part of these wave functions is antisymmetric. The total energy labeled $E_{\rm tot}$ in Tables I–III is then given by

$$E_{\rm tot}=\langle\mathcal{H}_0\rangle+\langle\mathcal{H}_1+\mathcal{H}_2\rangle+\langle\mathcal{H}_3\rangle+\langle\mathcal{H}_4\rangle+\langle\mathcal{H}_5\rangle\ . \tag{13}$$

C. Fine structure of the lower $1s2pmp\ ^{4,2}P_J$ states

The fine structure accounts for a triplet and a doublet of lines for the quartet, $2p^2np\ ^4S^\circ_{3/2}\rightarrow1s2pmp\ ^4P_J$ and doublet, $2p^23p\ ^2S^\circ_{1/2}\rightarrow1s2pmp\ ^2P_J$ transitions, respectively. If the multiplet of lines is not resolved experimentally, then for comparison purposes the theoretically determined wavelength for the transition should be computed via the "center-of-gravity" energy of the lower state multiplet, i.e.,

$$E_{\rm CG}=\frac{\sum_J E_J}{\sum_J 2J+1}=E_{\rm tot}\ , \tag{14}$$

where $E_{\rm tot}$ is the nonrelativistic energy with spin-independent relativistic and mass polarization corrections. The theoretical fine structures of the lower states are computed in this work for possible future use.

The fine structure or spin-dependent relativistic corrections are computed via first-order perturbation theory with zeroth-order wave functions formed in the LSJ-coupling scheme. These zeroth-order wave functions of well-defined, J, M_J, L, S, and parity are constructed from the pure LS-coupled wave functions, obtained via Eqs. (1) and (7), by

$$|JM_JLS\rangle=\sum_{M_L,M_S}|LSM_LM_S\rangle\langle LSM_LM_S|JM_J\rangle\ . \tag{15}$$

The fine structure is then computed by evaluating the expectation values of the following operators from the Breit-Pauli approximation

Spin-orbit,

$$\mathcal{H}_{\rm s.o.}=\frac{\alpha^2}{2}Z\sum_{i=1}^{3}\frac{\mathbf{l}_i\cdot\mathbf{s}_i}{r_i^3}\ . \tag{16}$$

Spin-other-orbit,

$$\mathcal{H}_{\rm s.o.o.}=-\frac{\alpha^2}{2}\sum_{(i\neq j)=1}^{3}\left[\frac{\mathbf{r}_{ij}}{r_{ij}^3}\times\mathbf{p}_i\right]\cdot(\mathbf{s}_i+2\mathbf{s}_j)\ . \tag{17}$$

Spin-spin,

$$\mathcal{H}_{\rm s.s.}=\alpha^2\sum_{\substack{i<j\\ i,j=1}}^{3}\frac{1}{r_{ij}^3}\left[\mathbf{s}_i\cdot\mathbf{s}_j-\frac{3(\mathbf{s}_i\cdot\mathbf{r}_{ij})(\mathbf{s}_j\cdot\mathbf{r}_{ij})}{r_{ij}^2}\right]\ . \tag{18}$$

The results of these calculations are given in Tables IV and V for the $1s2pmp\ ^4P_J$ and $1s2pmp\ ^2P_J$ states, respectively. The expectation values $\langle\mathcal{H}_{\rm s.o.}\rangle$, $\langle\mathcal{H}_{\rm s.o.o.}\rangle$, and $\langle\mathcal{H}_{\rm s.s.}\rangle$ for the state of highest J, and the splittings between the J levels in cm^{-1} are quoted. The energy of the other J levels can then be obtained by utilizing the conversion between atomic energy units and cm^{-1} or by using the following relationships:

$$\langle \mathcal{H}_{\text{s.o.}} \rangle = 2C_{\text{s.o.}}\mathbf{L}\cdot\mathbf{S}, \quad \langle \mathcal{H}_{\text{s.o.o}} \rangle = 2C_{\text{s.o.o.}}\mathbf{L}\cdot\mathbf{S} , \tag{19}$$

and

$$\langle \mathcal{H}_{\text{s.s.}} \rangle = C_{\text{s.s.}}[\tfrac{3}{2}\mathbf{L}\cdot\mathbf{S} + 3(\mathbf{L}\cdot\mathbf{S})^2 - L(L+1)S(S+1)] , \tag{20}$$

where

$$2\mathbf{L}\cdot\mathbf{S} = J(J+1) - L(L+1) - S(S+1) , \tag{21}$$

and the C's are reduced matrix elements.[10]

The fine-structure splittings are given by the differences $[E_{J(\max)} - E_{J(\max)-1}]$ and $[E_{J(\max)-1} - E_{J(\max)-2}]$. An inversion is indicated by a negative splitting. Table IV shows that there are some inverted splittings for the low-Z quartets. The ordering of the $1s2p^2\,{}^4P_J$ levels in terms of decreasing energy is $\frac{3}{2}$, $\frac{1}{2}$, and $\frac{5}{2}$ for $Z=3$ and $\frac{3}{2}$, $\frac{5}{2}$, and $\frac{1}{2}$ for $Z=4$; for $Z>4$ the normal ordering $\frac{5}{2}$, $\frac{3}{2}$, and $\frac{1}{2}$ is found. The only other quartet inversions occur for the $1s2p3p\,{}^4P_J$ and $1s2p4p\,{}^4P_J$ levels of lithium where the $J=\frac{5}{2}$ and $\frac{3}{2}$ levels are inverted. The only ${}^2P$ state which displays inversion is the $[(1s2p)\,{}^3P,3p]\,{}^2P$ for $Z=3$ to 7. The reason for these inverted splittings is the larger combined magnitudes of the spin-other-orbit and spin-spin interactions as compared to the spin-orbit interaction. This is possible for low Z, however, as Z increases the spin-orbit interaction dominates and the normal ordering of the J levels is obtained.

TABLE I. Nonrelativistic energy, relativistic corrections, and lifetime for the $2p^2np\,{}^{4,2}S^\circ$ states of lithiumlike ions. $\langle H_1+H_2 \rangle$, $\langle H_4 \rangle$, and $\langle H_5 \rangle$ are the expectation values of the relativistic operators corresponding to the kinetic energy correction plus Darwin term, orbit-orbit or retardation, and the nonrelativistic mass polarization effect, respectively. E_{tot} is the sum of the nonrelativistic energy E_0 plus the aforementioned corrections. Energy results are quoted in atomic units, and lifetimes are quoted in seconds (the number in brackets is the power of ten to which the number is raised).

	Z	E_0	$\langle H_1+H_2 \rangle$ $\times 10^{-4}$	$\langle H_4 \rangle$ $\times 10^{-4}$	$\langle H_5 \rangle$ $\times 10^{-4}$	E_{tot}	τ
$2p^3\,{}^4S^\circ$	2	−0.722 952	−0.170	0.007	0.115	−0.722 957	1.248[−8]
	3	−2.103 588	−1.158	0.053	0.152	−2.103 684	1.227[−11]
	4	−4.236 334	−4.353	0.182	0.184	−4.236 732	3.244[−12]
	5	−7.119 242	−11.824	0.438	0.204	−7.120 360	1.206[−12]
	6	−10.752 153	−26.334	0.864	0.237	−10.754 671	5.463[−13]
	7	−15.135 050	−51.379	1.503	0.245	−15.140 013	2.823[−13]
	8	−20.267 932	−91.100	2.400	0.252	−20.276 976	1.603[−13]
	9	−26.150 803	−150.376	3.598	0.243	−26.165 457	9.772[−14]
	10	−32.783 664	−234.771	5.141	0.261	−32.806 601	6.288[−14]
$2p^23p\,{}^4S^\circ$	3	−1.873 415	−1.113	0.032	0.074	−1.873 516	1.358[−11]
	4	−3.653 153	−3.934	0.108	0.093	−3.653 526	3.817[−12]
	5	−6.044 909	−10.350	0.264	0.105	−6.045 907	1.457[−12]
	6	−9.048 247	−22.630	0.526	0.123	−9.050 492	6.716[−13]
	7	−12.662 966	−43.610	0.922	0.128	−12.667 222	3.513[−13]
	8	−16.888 963	−76.692	1.481	0.132	−16.896 471	2.011[−13]
	9	−21.726 179	−125.840	2.229	0.128	−21.738 527	1.233[−13]
	10	−27.174 580	−195.581	3.196	0.137	−27.193 805	7.976[−14]
$2p^24p\,{}^4S^\circ$	3	−1.835 481	−1.109	0.029	0.066	−1.835 583	1.378[−11]
	4	−3.526 068	−3.865	0.093	0.078	−3.526 438	3.896[−12]
	5	−5.780 138	−10.054	0.217	0.086	−5.781 113	1.503[−12]
	6	−8.597 218	−21.793	0.420	0.099	−8.599 346	6.979[−13]
	7	−11.977 075	−41.713	0.723	0.102	−11.981 234	3.668[−13]
	8	−15.919 592	−72.957	1.145	0.104	−15.926 763	2.108[−13]
	9	−20.424 712	−119.182	1.706	0.100	−20.436 449	1.296[−13]
	10	−25.492 404	−184.556	2.426	0.107	−25.510 606	8.398[−14]
$2p^23p\,{}^2S^\circ$	3	−1.890 076	−1.131	0.030	0.768	−1.890 179	1.358[−11]
	4	−3.692 762	−4.032	0.093	0.929	−3.693 157	3.837[−12]
	5	−6.107 885	−10.632	0.215	1.035	−6.108 917	1.457[−12]
	6	−9.134 547	−23.237	0.413	1.201	−9.136 817	6.701[−13]
	7	−12.772 508	−44.718	0.706	1.245	−12.776 896	3.500[−13]
	8	−17.021 678	−78.511	1.114	1.279	−17.029 405	2.003[−13]
	9	−21.882 017	−128.616	1.655	1.236	−21.894 701	1.228[−13]
	10	−27.353 503	−199.598	2.348	1.326	−27.373 215	7.940[−14]

The $1s2p^2\,{}^4P$ fine structures for $Z=3$, 6, 7, 8, and 9 have been calculated in an earlier work[11] and were found to agree with experimental data.[12] The fine-structure results in this work improve the agreement with experiment slightly as compared to Ref. 11. For $Z=10$, the experimental results of Livingston *et al.*[13] are 746±15 and 856±15 cm^{-1}, while the measurements of Knystautas and Druetta[14] are 816±60 cm^{-1} and 832±60 cm^{-1}; our theoretical results are 803 and 831 cm^{-1} for the $E_{3/2}$-$E_{1/2}$ and $E_{5/2}$-$E_{3/2}$ splittings, respectively.

III. RADIATIVE TRANSITIONS

A. Theory

The $2p^2np\ {}^{4,2}S^\circ$ lifetimes are determined mostly by radiation. The electric dipole selection rules only allow them to decay to the even-parity P states of the same multiplicity. The lifetimes are found by computing the reciprocal sum of the transition rates from the initial state, $2p^2np\ {}^{4,2}S^\circ(n=2,3,4)$ to the final $1s2pmp\ {}^{4,2}P(m=2,3,4)$ states.

$$\tau_i=\frac{1}{\sum_f W_{fi}} \tag{22}$$

τ_i is the lifetime of the initial state, and W_{fi} is the transition rate from the initial state to a particular final state. If we sum over the final magnetic substates $\Psi_f(L_f,S_f,J_f,M_f)$ and average over the initial magnetic substates $\Psi_i(L_i,S_i,J_i,M_i)$ then we obtain the following transition rate:

$$W_{fi}=2\alpha^3(\Delta E_{fi})^2 f_{fi}\ . \tag{23}$$

The oscillator strength f_{fi} is given by

$$f_{fi}=\tfrac{2}{3}(\Delta E_{fi})S_{fi}/(2J_i+1)\ . \tag{24}$$

The energy difference

$$\Delta E_{fi}=E_f-E_i\ , \tag{25}$$

is computed with nonrelativistic energy eigenvalues, and the line strength[15]

$$\mathrm{S}_{fi}=|\langle\Psi_f(L_f,S_f,J_f)\|\mathbf{r}\|\Psi_i(L_i,S_i,J_i)\rangle|^2\ , \tag{26}$$

is computed via the LS-coupled nonrelativistic wave functions with the dipole length form. In the context of the LS-coupling scheme this line strength can be expressed with the aid of 6-J symbols as follows:[15]

$$\mathrm{S}_{fi}=\left|(-1)^{L_f+S_f+J_i+1}\delta_{S_fS_i}\sqrt{(2J_i+1)(2J_f+1)}\right.\\ \left.\times\begin{Bmatrix}J_f & 1 & J_i\\ L_i & S_f & L_f\end{Bmatrix}\langle\psi_f(L_f)\|\mathbf{r}\|\psi_i(L_i)\rangle\right|^2\ . \tag{27}$$

The reduced dipole matrix elements are computed with

TABLE II. Nonrelativistic energy and relativistic corrections for the $(1s2pnp)\,{}^4P$ states of lithiumlike ions (in a.u., for notation see Table I).

	Z	E_0	$\langle H_1+H_2\rangle$ $\times10^{-4}$	$\langle H_4\rangle$ $\times10^{-4}$	$\langle H_5\rangle$ $\times10^{-4}$	E_{tot}
$1s2p^2\,{}^4P$	3	−5.245 281	−5.513	0.183	−0.273	−5.245 841
	4	−9.870 743	−18.040	0.689	−0.605	−9.872 539
	5	−16.000 276	−45.341	1.707	−0.976	−16.004 737
	6	−23.631 651	−96.108	3.403	−1.479	−23.641 069
	7	−32.764 003	−181.160	5.950	−1.891	−32.781 713
	8	−43.396 935	−313.359	9.518	−2.306	−43.427 550
	9	−55.530 240	−507.623	14.276	−2.580	−55.579 833
	10	−69.163 798	−780.959	20.395	−3.143	−69.240 169
$1s2p3p\,{}^4P$	3	−5.096 709	−5.540	0.147	−0.243	−5.097 273
	4	−9.428 687	−17.933	0.494	−0.461	−9.430 477
	5	−15.124 266	−44.612	1.167	−0.697	−15.128 681
	6	−22.182 094	−93.911	2.270	−1.020	−22.191 360
	7	−30.601 634	−176.113	3.906	−1.275	−30.618 982
	8	−40.382 632	−303.325	6.182	−1.532	−40.412 500
	9	−51.524 964	−489.718	9.200	−1.695	−51.573 185
	10	−64.028 555	−751.255	13.067	−2.048	−64.102 579
$1s2p4p\,{}^4P$	3	−5.063 938	−5.522	0.142	−0.240	−5.064 500
	4	−9.312 399	−17.889	0.461	−0.441	−9.314 186
	5	−14.875 266	−44.435	1.064	−0.654	−14.879 668
	6	−21.751 442	−93.352	2.041	−0.945	−21.760 668
	7	−29.940 538	−174.639	3.479	−1.173	−29.957 771
	8	−39.442 375	−300.202	5.466	−1.401	−39.471 988
	9	−50.256 863	−483.827	8.092	−1.545	−50.304 591
	10	−62.383 951	−741.228	11.446	−1.860	−62.457 115

$$\langle \psi_f(L_f)\|\mathbf{r}\|\psi_i(L_i)\rangle = (-1)^{M_f-L_f}\langle \psi_f(L_f,M_f)|r_q|\psi_i(L_i,M_i)\rangle \bigg/ \begin{pmatrix} L_f & 1 & L_i \\ -M_f & q & M_i \end{pmatrix}, \tag{28}$$

In these equations the position vector operator $\mathbf{r}$ and its spherical components r_q are understood to be the sums of these quantities for all three electrons. The quantity in parentheses is a 3-J symbol.

The line strengths can be summed over to obtain[15]

$$\sum_{J_f=|L_f-S_f|}^{|L_f+S_f|} S_{fi} = \frac{2J_i+1}{2L_i+1}|\langle \psi_f(L_f)\|\mathbf{r}\|\psi_i(L_i)\rangle|^2 . \tag{29}$$

The summed oscillator strength, as a result of Eq. (29), is

$$f_{fi} = \tfrac{2}{3}(\Delta E_{fi})|\langle \psi_f(L_f)\|\mathbf{r}\|\psi_i(L_i)\rangle|^2/(2L_i+1) . \tag{30}$$

This procedure approximates ΔE_{fi} as J independent. This is the approximation of LS coupling with the nonrelativistic Hamiltonian, Eq. (2). The accuracy of this approximation is easily judged by noting the magnitude of the fine-structure splitting of the lower states given in Tables IV and V. Substitution of the above expression for the oscillator strength into Eq. (23) yields the desired result for the transition rate.

B. Transition results: $2p^2np\ ^4S^\circ \rightarrow 1s2pmp\ ^4P$

The results of the radiative transition calculations for the $2p^2np\ ^4S^\circ$ states are given in Table VI. For each transition three quantities are tabulated: the relativistic transition wavelength, the transition rate, and the branching ratio. The transition wavelength in Å is obtained from the energies in a.u. by,

$$\lambda = \left[\frac{hc}{2R_\infty}\right]\left[\frac{M+m}{M}\right]\left[\frac{1}{\Delta E_{if}}\right] . \tag{31}$$

The constants in the first set of parentheses yield a value of 455.633 53 Å a.u. (Ref. 16). M and m are the nuclear and electron masses, respectively. The transition rate is computed with Eq. (23). The branching ratio $\mathfrak{R}$ (in percent) for an initial state's transition to a final state is defined by

TABLE III. Nonrelativistic energy and relativistic corrections for the $(1s2pnp)\,^2P$ states of lithiumlike ions (in a.u., for notation see Table I).

	Z	E_0	$\langle H_1+H_2\rangle$ $\times 10^{-4}$	$\langle H_3\rangle$ $\times 10^{-4}$	$\langle H_4\rangle$ $\times 10^{-4}$	$\langle H_5\rangle$ $\times 10^{-4}$	E_{tot}
$[1s2p\ ^3P,2p]\,^2P$	3	−5.213 536	−5.579	0.017	−0.032	0.119	−5.214 083
	4	−9.799 471	−18.147	0.082	−0.177	0.286	−9.801 266
	5	−15.884 394	−45.460	0.235	−0.501	0.477	−15.888 919
	6	−23.468 728	−96.204	0.515	−1.069	0.733	−23.478 331
	7	−32.552 735	−181.161	0.963	−1.947	0.946	−32.570 855
	8	−43.136 539	−313.158	1.617	−3.198	1.159	−43.167 897
	9	−55.220 214	−507.103	2.517	−4.886	1.300	−55.271 031
	10	−68.803 799	−779.953	3.703	−7.073	1.587	−68.881 972
$[1s2p\ ^3P,3p]\,^2P$	3	−5.104 253	−5.533	0.003	0.115	−0.187	−5.104 813
	4	−9.445 590	−17.948	0.014	0.363	−0.337	−9.447 381
	5	−15.149 693	−44.689	0.039	0.831	−0.500	−15.154 125
	6	−22.215 617	−94.088	0.084	1.585	−0.725	−22.224 931
	7	−30.643 024	−176.402	0.155	2.696	−0.903	−30.660 470
	8	−40.431 765	−303.794	0.257	4.232	−1.082	−40.461 804
	9	−51.581 759	−490.399	0.397	6.261	−1.196	−51.630 253
	10	−64.092 960	−752.238	0.580	8.852	−1.444	−64.167 385
$[1s2p\ ^1P,3p]\,^2P$	3[a]	−5.070 025	−5.545	0.008	0.052	−0.077	−5.070 581
	3[a]	−5.062 006	−5.548	0.010	0.022	−0.021	−5.062 560
	4	−9.370 126	−17.968	0.070	−0.223	0.266	−9.371 912
	5	−15.033 708	−44.709	0.194	−0.598	0.447	−15.038 174
	6	−22.058 359	−94.022	0.414	−1.217	0.678	−22.067 773
	7	−30.444 036	−176.116	0.761	−2.146	0.864	−30.461 700
	8	−40.190 764	−303.315	1.261	−3.447	1.050	−40.221 210
	9	−51.298 560	−489.495	1.944	−5.182	1.171	−51.347 716
	10	−63.767 436	−750.721	2.839	−7.412	1.421	−63.842 824

[a] These energy levels correspond to the third- and fourth-lowest energy roots of the lithium ^2P secular equation (see text). They are both linear combinations of $[(1s2p)\,^1P,3p]\,^2P$ and $[(1s2p)\,^3P,4p]\,^2P$.

TABLE IV. Spin-dependent perturbations and fine-structure splittings for the $1s2pnp\ {}^4P$ states in lithium-like ions. For each $1s2pnp\ {}^4P$ state the following is listed: first column, the expectation values $\langle H_{\text{s.o.}} \rangle$, $\langle H_{\text{s.o.o}} \rangle$, and $\langle H_{\text{s.s.}} \rangle$ for the $J=\frac{5}{2}$ state in 10^{-4} atomic units; and second column, the splittings $E_{3/2}-E_{1/2}$ and $E_{5/2}-E_{3/2}$ in cm^{-1}.

	$1s2p^2\ {}^4P$		$1s2p3p\ {}^4P$		$1s2p4p\ {}^4P$	
3	0.1236	1.91	0.1006	1.61	0.0976	1.57
	−0.1411		−0.1046		−0.0998	
	−0.0116	−1.92	−0.0086	−1.09	−0.0082	−0.98
4	0.5927	9.78	0.4362	7.40	0.4109	7.05
	−0.0416		−0.3508		−0.3205	
	−0.5218	−1.98	−0.0280	0.058	−0.0256	0.50
5	1.7903	31.06	1.2647	22.42	1.1701	20.99
	−1.2794		−0.8280		−0.7369	
	−0.1005	7.66	−0.0650	8.84	−0.0582	9.46
6	4.2265	76.03	2.9215	53.51	2.6717	49.49
	−2.5390		−1.6115		−1.4104	
	−0.1974	40.06	−0.1254	34.16	−0.1104	34.02
7	8.5461	157.96	5.8298	109.42	5.2881	100.28
	−4.4268		−2.7764		−2.4026	
	−0.3420	113.14	−0.2147	88.13	−0.1871	85.02
8	15.5306	293.08	10.5021	200.84	9.4677	182.77
	−7.0691		−4.3991		−3.7753	
	−0.5436	249.85	−0.3387	186.07	−0.2928	176.08
9	26.0986	500.66	17.5407	340.45	15.7384	308.11
	−10.5935		−6.5562		−5.5913	
	−0.8119	478.05	−0.5031	346.58	−0.4324	323.70
10	41.3092	803.01	27.6397	542.94	24.7082	489.21
	−15.1280		−9.3247		−7.9139	
	−1.1564	830.76	−0.7138	591.60	−0.6107	547.29

TABLE V. Spin-dependent perturbations and fine-structure splittings for the $1s2pnp\ {}^2P$ states in lithiumlike ions. For each $1s2pnp\ {}^2P$ state the following is listed: first column, the expectation values $\langle H_{\text{s.o.}} \rangle$ and $\langle H_{\text{s.o.o}} \rangle$ for the $J=\frac{3}{2}$ state in 10^{-4} atomic units; and second column, the splitting $E_{3/2}-E_{1/2}$ in cm^{-1}.

	$[(1s2p)\,{}^3P,2p]\,{}^2P$		$[(1s2p)\,{}^3P,3p]\,{}^2P$		$[(1s2p)\,{}^1P,3p]\,{}^2P$	
3[a]	0.0756	3.59	0.0385	−1.75	0.0380	0.26
	−0.0211		−0.0651		−0.0341	
					0.0488	0.53
					−0.0408	
4	0.3608	18.66	0.1383	−4.88	0.1632	8.66
	−0.0774		−0.2124		−0.0317	
5	1.1021	59.82	0.3638	−8.48	0.4923	27.83
	−0.1936		−0.4926		−0.0696	
6	2.6288	147.32	0.7899	−10.38	1.1743	68.17
	−0.3913		−0.9476		−0.1390	
7	5.3598	307.29	1.5092	−7.25	2.3985	141.67
	−0.6926		−1.6194		−0.2468	
8	9.8060	571.91	2.6318	5.36	4.3957	262.99
	−1.1195		−2.5504		−0.4012	
9	16.5696	979.40	4.2848	33.01	7.4407	449.69
	−1.6942		−3.7834		−0.6107	
10	26.3462	1574.05	6.5728	81.62	11.8520	722.15
	−2.4391		−5.3331		−0.8838	

[a] The first and second sets of results quoted for Li $[(1s2p)\,{}^1P,3p]\,{}^2P$ correspond to the fourth and third-lowest-energy roots of the secular equation, respectively (see text).

TABLE VI. $2p^2np\ ^4S^\circ \rightarrow 1s2pmp\ ^4P$ transition results. λ is the transition wavelength in Å [see Eq. (31)]. W is the transition rate in s^{-1} [see Eq. (23)]. $\mathfrak{R}$ is the branching ratio [see Eq. (32)]. (The number in brackets is the power of ten to which the number is raised.)

$2p^2np\ ^4S^\circ$		$1s2p^2\ ^4P$			$1s2p3p\ ^4P$			$1s2p4p\ ^4P$		
Z	n	λ	W	$\mathfrak{R}$	λ	W	$\mathfrak{R}$	λ	W	$\mathfrak{R}$
	2	145.019	7.90[10]	96.90	152.215	1.93[9]	2.37	153.900	6.02[8]	0.74
3	3	135.121	9.01[8]	1.22	141.347	7.16[10]	97.24	142.799	1.13[9]	1.54
	4	133.618	1.02[8]	0.14	139.704	1.29[9]	1.78	141.121	7.12[10]	98.08
	2	80.852	3.03[11]	98.24	87.733	4.32[9]	1.40	89.742	1.11[9]	0.36
4	3	73.270	1.83[8]	0.07	78.876	2.60[11]	99.29	80.496	1.68[9]	0.64
	4	71.803	4.94[8]	0.19	77.178	1.27[9]	0.49	78.729	2.55[11]	99.31
	2	51.288	8.21[11]	98.97	56.898	6.86[9]	0.83	58.724	1.66[9]	0.20
5	3	45.754	7.19[9]	1.05	50.167	6.77[11]	98.61	51.581	2.36[9]	0.34
	4	44.569	5.52[9]	0.83	48.746	1.30[9]	0.20	50.080	6.58[11]	98.98
	2	35.359	1.82[12]	99.34	39.841	9.77[9]	0.53	41.401	2.28[9]	0.12
6	3	31.229	3.35[10]	2.25	34.675	1.45[12]	97.54	35.850	3.19[9]	0.21
	4	30.293	2.09[10]	1.46	33.524	1.48[9]	0.10	34.621	1.41[12]	98.44
	2	25.828	3.53[12]	99.55	29.437	1.31[10]	0.37	30.750	2.98[9]	0.08
7	3	22.653	9.42[10]	3.31	25.382	2.75[12]	96.54	26.353	4.19[9]	0.15
	4	21.906	5.32[10]	1.95	24.448	1.75[9]	0.06	25.347	2.67[12]	97.99
	2	19.682	6.22[12]	99.67	22.629	1.69[10]	0.27	23.738	3.70[9]	0.06
8	3	17.174	2.11[11]	4.23	19.376	4.76[12]	95.66	20.183	5.38[9]	0.11
	4	16.569	1.11[11]	2.34	18.609	2.06[9]	0.04	19.352	4.63[12]	97.62
	2	15.491	1.02[13]	99.75	17.933	2.11[10]	0.21	18.876	4.52[9]	0.04
9	3	13.464	4.06[11]	5.00	15.272	7.70[12]	94.92	15.951	6.69[9]	0.08
	4	12.965	2.06[11]	2.67	14.634	2.46[9]	0.03	15.255	7.51[12]	97.30
	2	12.506	1.59[13]	99.80	14.559	2.57[10]	0.16	15.367	5.36[9]	0.03
10	3	10.837	7.05[11]	5.62	12.345	1.18[13]	94.31	12.921	8.17[9]	0.07
	4	10.420	3.48[11]	2.93	11.807	2.90[9]	0.02	12.333	1.16[13]	97.05

$$\mathfrak{R}(i \rightarrow f) = \left| \frac{W_{fi}}{\sum_{f'=1}^{3} W_{f'i}} \right| \times 100 \ . \qquad (32)$$

Examination of Table VI shows that the $2p \rightarrow 1s$ transition is by far the dominant $2p^2np\ ^4S^\circ \rightarrow 1s2pmp\ ^4P$ transition. The branching ratio for this transition decreases slightly as a function of Z for the cases of $2p^23p\ ^4S^\circ$ and $2p^24p\ ^4S^\circ$. The $2p^23p\ ^4S^\circ \rightarrow 1s2p3p\ ^4P$ branching ratio decreases from 97% for $Z=3$ to 94% for $Z=10$; while the rate of decrease for $2p^24p\ ^4S^\circ \rightarrow 1s2p4p\ ^4P$ is three times slower, i.e., decreasing from 98% for $Z=3$ to 97% for $Z=10$. This implies that the $3p \rightarrow 1s$ branching ratio for $2p^33p\ ^4S^\circ$ increases more with Z than the $4p \rightarrow 1s$ branching ratio for $2p^24p\ ^4S^\circ$. This can be understood by analyzing the transition rates in terms of oscillator strength and energy difference squared as given in Eq. (23). An analysis of these quantities based on three-electron wave functions that are formed by products of hydrogenic wave functions reveals[17] that the oscillator strength is independent of Z, while the energy difference is proportional to Z^2, thereby yielding a transition rate which is proportional to Z^4. The results of this work show that the oscillator strengths for the $2p \rightarrow 1s$ transitions do converge quite rapidly with respect to Z. This oscillator strength for the $2p^3\ ^4S^\circ$, $2p^23p\ ^4S^\circ$, and $2p^24p\ ^4S^\circ$ states rises from 0.249, 0.215, and 0.213, respectively, for $Z=3$, to 0.373, 0.271, and 0.264, respectively, for $Z=10$. (Intermediate results for $2p^3\ ^4S^\circ$ are 0.324, 0.353, and 0.368 for $Z=5$, 7, and 9.) Rapid convergence for the $3p \rightarrow 1s$ and $4p \rightarrow 1s$ oscillator strengths from the $2p^23p\ ^4S^\circ \rightarrow 1s2p^2\ ^4P$ and $2p^24p\ ^4S^\circ \rightarrow 1s2p^2\ ^4P$ transitions is not observed; these oscillator strengths undergo the following changes from the results for $Z=3$ to those for $Z=10$: $0.0025 \rightarrow 0.0124$ for $3p \rightarrow 1s$ and $0.000\,27 \rightarrow 0.005\,69$ for $4p \rightarrow 1s$. Therefore the larger $3p \rightarrow 1s$ branching ratio as compared to $4p \rightarrow 1s$ is entirely due to the larger $3p \rightarrow 1s$ oscillator strength while the ΔE_{fi}^2 factor acts, albeit weakly, in the opposite sense.

In order to obtain a meaningful result for the branching ratio and a reliable lifetime we must include in our analysis all lower ^4P states with nontrivial transition rates. Therefore we consider the consequences of omitting from our analysis the transitions to the $1s2pmp\ ^4P(m \geq 5)$ and $2s2pmp\ ^4P$ states. Transitions to the omitted doubly excited states $2p^2np\ ^4S^\circ \rightarrow 1s2pmp\ ^4P(m \geq 5)$ involve two electrons and therefore the oscillator strengths and consequently the transition rates should be small. This was checked for the case of the carbon ion, where we included the transitions to the $1s2pmp\ ^4P(m=5$ and 6) states in the analysis. The $2p^24p\ ^4S^\circ \rightarrow 1s2p5p\ ^4P$ transition was found to have the largest rate among these, 2.87×10^9 sec^{-1}; it was from 3 to 8 times larger than the other rates. The branching ratios for $2p^24p\ ^4S^{\circ} \rightarrow 1s2p^2\ ^4P$, $1s2p3p\ ^4P$, and $1s2p4p\ ^4P$ changed from the values given in Table VI to 1.45, 0.10, and 98.20, respectively—a very small change.

Transitions to the triply excited states $2s2pnp\ ^4P$ were considered by including only the $2s2p^2\ ^4P$ state in the analyses for the beryllium and neon ions. Transitions to these triply excited states include many one-electron transitions where the oscillator strength may be large, but the small energy difference in Eq. (23) acts to make the transition rate small. It is interesting to note, however, that even though the one-electron transition $2p^3\ ^4S^{\circ} \rightarrow 2s2p^2\ ^4P$ has a larger oscillator strength than $2p^23p\ ^4S^{\circ} \rightarrow 2s2p^2\ ^4P$, the latter has a larger transition probability due to the larger energy-difference factor. This transition rate is 4.93×10^8 and 1.10×10^{11} sec^{-1} for the beryllium and neon ions, respectively. The corresponding branching ratios are 0.19 and 0.87, respectively, which have a very minimal effect on changing the branching ratios quoted in Table VI. The triply excited $2s2p^2\ ^4P$ states are autoionizing levels, which therefore have large level widths due to their interaction via the Coulomb potential with the energy-degenerate continua. The wave functions used to compute the transition rates were generated by the saddle-point method as in Ref. 18. This method computes only the innershell-vacancy part or closed-channel component of the resonance wave function. The oscillator strength computed with this square-integrable function is in actuality spread out over an energy interval on the order of the width of this resonance,[19] where there are interference effects resulting from the contributions to the transition matrix element from the open-channel components of the resonance wave function (the dominant component being $[1s2p\ ^3P^{\circ},\epsilon p]\ ^4P$). This smearing out of the oscillator strength over a wavelength interval corresponding to the width of the state would make these transitions even more difficult to observe. The wavelengths resulting from the transitions $2p^2np\ ^4S^{\circ}(n=2,\ 3,\ \text{and}\ 4) \rightarrow 2s2p^2\ ^4P$ are 2290, 582.5, and 501.1 Å for the beryllium ion and 776.4 Å, 73.5, and 57.8 Å for the neon ion.

The $2p^3\ ^4S^{\circ} \rightarrow 2s2p^2\ ^4P$ decay is of greater importance for the He^- lifetime since the He^- $1s2p^2\ ^4P$ bound state does not exist. The lifetime quoted in Table I for the He^- $2p^3\ ^4S^{\circ}$ state is based only on its decay to this $2s2p^2\ ^4P$ resonance. This lifetime must therefore only be considered as an upper bound to the true lifetime. This is because there has been a ^4P shape resonance observed near the He^- $1s2p\ ^3P$ threshold,[20] to which the $2p^3\ ^4S^{\circ}$ state could decay.

Two-electron one-photon transitions from a particular initial state are usually expected to have a smaller transition probability as compared to one-electron one-photon decays from the same initial state. Exceptions to this rule are present in Table VI. The two-electron one-photon transitions $2p^23p \rightarrow 1s2p4p$ and $2p^24p \rightarrow 1s2p3p$ are more probable than the decays, $2p^23p \rightarrow 1s2p^2$ and $2p^24p \rightarrow 1s2p^2$ for the cases of the lithium atom and the positive beryllium ion. The one-electron one-photon transition rates for the other positive ions $(Z>4)$ are larger than the two-electron one-photon rates as is usually the case. An anomalously high two-electron one-photon transition rate usually results from a large transition energy factor ΔE_{fi} in the equation for the transition rate, Eq. (23). This, however, is not the case for the Li and Be^+ transitions under scrutiny here; the oscillator strengths for these two-electron one-photon transitions are actually larger than those for the one-electron transitions. In fact, the transition-energy factor is not the source of the larger oscillator strengths either, see Eq. (30); but instead these two-electron transitions have larger "reduced dipole matrix elements" as compared to the one-electron transitions.

The reason for this seemingly contradictory result of a larger overlap for $\langle 1s2p4p\|\mathbf{r}\|2p^23p\rangle$ and $\langle 1s2p3p\|\mathbf{r}\|2p^24p\rangle$ as compared to $\langle 1s2p^2\|\mathbf{r}\|2p^23p\rangle$ and $\langle 1s2p^2\|\mathbf{r}\|2p^24p\rangle$, respectively, lies in recognizing that the $2p$ orbital in the initial state is quite different from the $2p$ orbital in the final state. The $2p$ orbital in the initial state experiences an essentially unscreened nuclear charge Z; while the $2p$ orbital in the final state sees a nuclear charge that is screened almost fully by the $1s$ electron, i.e., charge $Z-1$. For small-Z systems these effective nuclear charges are quite different with the result that the $2p$-electron orbitals in the initial and final states are very different with correspondingly different electron-probability distributions. The independent-electron picture of atomic states is good when identifying the upper states among themselves by $2p^3$, $2p^23p$, and $2p^24p$, and when separately describing the lower states with $1s2p^2$, $1s2p3p$, and $1s2p4p$; however, paradoxes may arise when phrases such as one-electron and two-electron transitions are used which by their nature juxtapose two different atomic states with their approximate independent-electron labels. The one-electron transitions $2p^23p \rightarrow 1s2p^2$ and $2p^24p \rightarrow 1s2p^2$ for small-Z systems actually involve more than one electron when the differences in the $2p$ orbitals of the initial and final states are taken into account.

C. Transition results: $2p^23p\ ^2S^{\circ} \rightarrow 1s2pmp\ ^2P$

The calculated relativistic transition wavelengths, transition rates, and branching ratios for the dipole decays from the $2p^23p\ ^2S^{\circ}$ level to the $[(1s2p)\ ^3P,2p]\ ^2P$, $[(1s2p)\ ^3P,3p]\ ^2P$, and $[(1s2p)\ ^1P,3p]\ ^2P$ states are given in Table VII.

A comparison of the $2p^23p\ ^4S^{\circ} \rightarrow 1s2p3p\ ^4P$ data in Table VI with the doublet transitions of Table VII shows similar transition wavelengths and rates for the $2p^23p\ ^2S^{\circ} \rightarrow [(1s2p)\ ^3P,3p]\ ^2P$ transitions. The branching ratios to the lower states are, however, quite different. The branching ratios for the doublet system yield more $3p \rightarrow 1s$ radiative decays; the branching ratio for $2p^23p \rightarrow 1s2p^2$ decreases from 22.5% for $Z=3$ to 14.7% for $Z=10$ for the doublet system, while for the quartet system it increases from only 1.2% for $Z=3$ to just 5.6% for $Z=10$.

The branching ratio for $2p \rightarrow 1s$ transitions decreases as a function of Z for the quartet $2p^23p$ system, while they increase for the doublet system. The $2p \rightarrow 1s$ transitions in the doublet system lead to either the

TABLE VII. $2p^23p\ ^2S^\circ \rightarrow 1s2pmp\ ^2P$ transition results. For notation and units, see Table VI.

	$[(1s2p)\,^3P,2p]\,^2P$			$[(1s2p)\,^3P,3p]\,^2P$			$[(1s2p)\,^1P,3p]\,^2P$		
Z	λ	W	$\Re$	λ	W	$\Re$	λ	W	$\Re$
3[a]	137.089	1.66[10]	22.47	141.748	5.57[10]	75.68	143.636	1.04[9]	1.42
3[a]							143.274	3.18[8]	0.43
4	74.599	5.19[10]	19.91	79.187	2.06[11]	78.95	80.240	2.98[9]	1.14
5	46.591	1.25[11]	18.15	50.375	5.46[11]	79.59	51.030	1.55[10]	2.26
6	31.772	2.53[11]	16.96	34.814	1.19[12]	80.06	35.237	4.44[10]	2.98
7	23.020	4.61[11]	16.14	25.479	2.30[12]	80.39	25.765	9.92[10]	3.47
8	17.432	7.75[11]	15.52	19.445	4.03[12]	80.66	19.647	1.91[11]	3.82
9	13.652	1.23[12]	15.05	15.323	6.59[12]	80.86	15.470	3.32[11]	4.08
10	10.977	1.85[12]	14.70	12.384	1.02[13]	81.02	12.494	5.39[11]	4.28

[a] The lower states correspond to the third- and fourth-lowest-energy roots of the lithium ^2P secular equation (see text). They are both linear combinations of $[(1s2p)\,^1P,3p]\,^2P$ and $[(1s2p)\,^3P,4p]\,^2P$. Numbers in brackets denote powers of ten.

$[(1s2p)\,^3P,3p]\,^2P$ or the $[(1s2p)\,^1P,3p]\,^2P$ state, the former being preferred by a factor of 54 for $Z=3$, with this factor decreasing to 19 for $Z=10$. The reason for this preference lies in the angular and spin couplings of the states involved. The $1s2p3p$ configuration can form two linearly independent couplings for the doublet system; we have designated these $[(1s2p)\,^3P,3p]\,^2P$ and $[(1s2p)\,^1P,3p]\,^2P$. Designating the upper state as $[(2p^2)\,^3P,3p]\,^2S^\circ$ it is easy to see why the transition to the lower energy $[(1s2p)\,^3P,3p]\,^2P$ state is preferred as a result of conservation of spin in the electric dipole interaction.

D. Intermediate coupling of the $2p^3$ and $1s2p^2$ configurations

The spin-dependent operators ($\mathcal{H}_{\text{s.o.}}$, $\mathcal{H}_{\text{s.o.o.}}$, and $\mathcal{H}_{\text{s.s.}}$) couple the $2p^3\,^4S^\circ$, $^2D^\circ$, and $^2P^\circ$ terms. The $^4S^\circ$ energy is shifted by this interaction, which grows rapidly with Z. We investigate whether this coupling affects the results of this work by carrying out an intermediate-coupling calculation for Ne VIII.

The $2p^3\,^2D^\circ$ and $^2P^\circ$ autoionizing states are calculated with the saddle-point method.[18] Wave functions composed of 16 partial waves with 110 and 123 terms yield $-32.540\,415$ and $-32.183\,087$ a.u., for the nonrelativistic energies of these states. The spin-independent relativistic and mass polarization corrections for these states are $-0.023\,249$ and $-0.024\,639$ a.u. First-order perturbation theory yields 0.000 467 and 0.000 482 a.u. for the $J=\frac{3}{2}$ spin-dependent corrections for these states; the corresponding correction for $^4S^\circ$ is zero.

The off-diagonal matrix elements for $J=\frac{3}{2}$ are

$$\langle ^2D^\circ | \mathcal{H}_{\text{s.o.}} + \mathcal{H}_{\text{s.o.o.}} | ^2P^\circ \rangle = 0.009\,61\ ,$$

$$\langle ^2P^\circ | \mathcal{H}_{\text{s.o.}} + \mathcal{H}_{\text{s.o.o.}} | ^4S^\circ \rangle = -0.008\,57\ ,$$

$$\langle ^2D^\circ | \mathcal{H}_{\text{s.s.}} | ^4S^\circ \rangle = 0.000\,126 a.u.$$

These results yield for the second-order correction to the energy $-0.000\,122$, $-0.000\,258$, and 0.000 380 a.u. for the $^4S^\circ$, $^2D^\circ$, and $^2P^\circ$ levels. The $^4S^\circ_{3/2}$ wave function is corrected in the first order via the coupling coefficients $-0.000\,518$ and 0.0143 for the $^2D^\circ_{3/2}$ and $^2P^\circ_{3/2}$ functions. The second-order shift in the energy of the $^4S^\circ$ state due to these intermediate-coupling effects does not affect the quoted transition wavelengths of Table VI.

The lower $1s2pmp\,^4P$ states are shifted due to these effects also. For an example, consider $1s2p^2\,^4P_J$. The first-order spin-dependent correction to the energy (from Table IV) is 0.002 503, $-0.001\,283$, and $-0.004\,942$ a.u. for the $J=\frac{5}{2}$, $\frac{3}{2}$, and $\frac{1}{2}$ components. The $1s2p^2\,^4P_J$ state is coupled[7] to $1s2p^2\,^2D_J$, ^2P_J, and ^2S_J with resulting second-order energy corrections of $-0.000\,099$, $-0.000\,038$, and $-0.000\,092$ a.u. for the $J=\frac{5}{2}$, $\frac{3}{2}$, and $\frac{1}{2}$ components. Including all the effects discussed above, the triplet of lines resulting from $2p^3\,^4S^\circ_{3/2} \rightarrow 1s2p^2\,^4P_J$ are 12.5071, 12.5058, and 12.5045 Å. These are shifted very slightly from the 12.506 Å quoted in Table VI; the source of this shift is coming almost entirely from the first-order fine structure of the lower ^4P state. Based on this analysis we ignore the intermediate coupling effects on the wavelengths quoted in this work.

The $^2D^\circ$ and $^2P^\circ$ states couple to an infinite number of open channels; we investigate the transition rates to some of the most favored continua with the saddle-point complex-rotation method.[21] The $^2D^\circ$ autoionizes to the $[(1s2p)\,^3P,\epsilon d]^2D^\circ$ and $[(1s2p)\,^1P,\epsilon d]\,^2D^\circ$ continua with transition rates of 2.9×10^{14} and 9.8×10^{13} s^{-1}. The $^2P^\circ$ autoionizes to the $[(1s2p)\,^3P,\epsilon d]\,^2P^\circ$, $[(1s2p)\,^1P,\epsilon d]\,^2P^\circ$, $[(1s2p)\,^3P,\epsilon s]\,^2P^\circ$, $[(1s2s)\,^1S,\epsilon p]\,^2P^\circ$, $[(1s2p)\,^1P,\epsilon s]\,^2P^\circ$, and $[(1s2s)\,^3S,\epsilon p]\,^2P^\circ$ continua with rates of 1.5×10^{14}, 4.8×10^{13}, 1.2×10^{13}, 6.6×10^{12}, 4.0×10^{12}, and 3.0×10^{12} s^{-1}. An estimate of the effect of these results on the lifetime of the $^4S^\circ$ may be obtained by multiplying these rates by the squares of the spin-induced coupling constants. This procedure implies rates of 8×10^7 and 3×10^{10} s^{-1} to the $[(1s2p)\,^3P,\epsilon d]\,^2D^\circ_{3/2}$ and $^2P^\circ_{3/2}$ continua. This rough estimate ignores the other continua these doublets can couple to and also the interference effects. The largest error arises, however, as a result of the $^4S^\circ$ direct coupling to these and other continua. (The rates that result from the direct coupling to the continua will be of the same order of magnitude as those from the coupling to the doublets since this direct coupling is generated by the spin-dependent operators also.[21]) Recognizing that the magnitude of this spin-induced autoionization is still much smaller than the 1.6×10^{13} s^{-1} decay rate to the radiatively preferred $1s2p^2\,^4P$ state, it is evident that the lifetime of the $2p^3\,^4S^\circ$

state could only be changed by at most 1% over the result quoted in Table I. The autoionization branching ratio may be as large as those to the radiatively unpreferred $1s2pmp\ ^4P$ states, but the only branching ratios in Table VI that might be affected would be those to the preferred states and the change would only be about one percent. Since these spin-induced transition rates grow like Z^6, Z^4, and Z^4 for coupling via spin-orbit, spin-other-orbit, and spin-spin we ignore their contribution in this work.

IV. COMPARISON WITH EXPERIMENT AND CONCLUSIONS

The purpose of this work is to compare theoretical calculations with existing experiments and to provide transition wavelengths, branching ratios, and lifetime data for triply excited three-electron systems for future experiments. With the advance of high resolution experimental techniques, these interesting transitions will undoubtedly be seen in future experiments.

In a very recent work, Mannervik *et al.*[3] made an improved measurement on the triply excited states of lithium. They found the $2p^3\ ^4S^\circ \rightarrow 1s2p^2\ ^4P$ transition wavelength to be 145.016±0.006 Å. This gives a very significant improvement over the earlier experimental result of Agentoft, Anderson, and Chung,[2] 145.02±0.05 Å. The earlier theoretical result 145.009 Å lies just outside the experimental uncertainty. The result of the present work 145.019 Å agrees well with the new experiment. We note that if we replace our $1s2p^2\ ^4P$ nonrelativistic energy with that of Bunge and Bunge,[22] $-5.245\,308$ a.u., then the transition wavelength would be 145.017 Å. This result also agrees well with the experiment. The same transition for the Be II system is calculated to be 80.852 Å in this work. This agrees with the experimental result of 80.85±0.03 Å by Agentoft, Anderson, and Chung.[2]

The lifetime of the lithium $2p^3\ ^4S^\circ$ state was originally estimated to be less than 50 ps in the experiment of Agentoft, Anderson, and Chung.[2] The theoretical result was quoted to be 12.9 ps. This lifetime has more recently been measured to be 13.5±1.5 ps in the improved experiment of Mannervik *et al.*[3] The result of this work, 12.3 ps, agrees with the experiment. The slightly shorter lifetime obtained here is largely due to the inclusion of the $1s2p3p\ ^4P$ and $1s2p4p\ ^4P$ decay channels (see Table VI).

Mannervik *et al.*[3] made an effort to search for the $2p^2np\ ^4S^\circ \rightarrow 1s2pmp\ ^4P$ and $2p^2np\ ^2S^\circ \rightarrow 1s2pmp\ ^2P$ transitions for $n > 2$. Very weak lines were reported at 142.2 and 143.5 Å. Unfortunately Tables VI and VII do not reveal any good candidates for these two spectral lines. Mannervik *et al.*[3] observed an unresolved transition at the long-wavelength end of the strong $2p^2\ ^3P \rightarrow 1s2p\ ^3P^\circ$ transition line at 141 Å. When they assumed that this feature was due to one spectral line, their fitting procedure gave a wavelength of 141.6 Å. Our results predict that the main decay mode for $2p^23p\ ^4S^\circ$ is to $1s2p3p\ ^4P$ at 141.347 Å and for $2p^23p\ ^2S^\circ$ is to $1s2p3p\ ^2P$ at 141.748 Å. If our predictions are correct, then the 141.6 Å feature could be a blend of these two transitions. The resolution in the experiment does not allow such detailed study at this time.

In conclusion, we have calculated the transition wavelengths of the $2p^2np\ ^{4,2}S^\circ$ states of the lithiumlike ions. These transition wavelengths together with the branching ratios and lifetimes should help in making unambiguous identifications in future experiments.

ACKNOWLEDGMENTS

We appreciate the stimulating correspondence and encouragement of Dr. S. Mannervik, who has motivated us to undertake this research. This work is supported by the National Science Foundation, Grant No. 87-15238.

---

[1] K. T. Chung, Phys. Rev. A **20**, 724 (1979).

[2] M. Agentoft, T. Anderson, and K. T. Chung, J. Phys. B **17**, 1433 (1984).

[3] S. Mannervik, R. T. Short, D. Sonnek, E. Träbert, G. Möller, V. Lodwig, P. H. Heckman, J. H. Blanke, and K. Brand, Phys. Rev. A **39**, 3969 (1989).

[4] K. T. Chung and B. F. Davis, Phys. Rev. A **29**, 1871 (1984).

[5] K. T. Chung, R. Bruch, E. Träbert, and P. H. Heckmann, Phys. Scr. **29**, 108 (1984).

[6] R. Bruch, N. Stolterfoht, S. Datz, P. D. Miller, P. L. Pepmiller, Y. Yamazaki, H. F. Krause, J. K. Swenson, K. T. Chung, and B. F. Davis, Phys. Rev. A **35**, 4114 (1987).

[7] B. F. Davis and K. T. Chung, Phys. Rev. A **37**, 111 (1988).

[8] B. F. Davis and K. T. Chung, Phys. Rev. A **29**, 2586 (1984).

[9] H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Plenum, New York, 1977), p. 181.

[10] A. Messiah, *Quantum Mechanics* (Wiley, New York, 1966), Vol. II.

[11] K. T. Chung, Phys. Rev. A **29**, 682 (1984).

[12] M. Levitt and P. Feldman, Phys. Rev. **180**, 48 (1969); A. E. Livingston and H. G. Berry, Phys. Rev. A **17**, 1966 (1978); E. Träbert, H. Hellman, P. H. Heckman, S. Bashkin, H. A. Klein, and J. D. Silver, Phys. Lett. **93A**, 76 (1982); I. Martinson, B. Denne, J. O. Ekberg, L. Engström, S. Huldt, C. Jupén, U. Litzén, S. Mannervik, and A. Trigueiros, Phys. Scr. **27**, 201 (1983).

[13] A. E. Livingston, J. E. Hardis, L. J. Curtis, R. L. Brooks, and H. G. Berry, Phys. Rev. A **30**, 2089 (1984).

[14] E. J. Knystautas and M. Druetta, Phys. Rev. A **31**, 2279 (1985).

[15] M. Weissbluth, *Atoms and Molecules* (Academic, New York, 1978).

[16] E. R. Cohen and B. N. Taylor, *The 1986 Adjustment of the Fundamental Physical Constants,* report of the Codata Bulletin No. 63 (Pergamon, Elmsford, NY, 1986).

[17] R. D. Cowen, *The Theory of Atomic Structure* (University of California Press, Berkeley, 1981), p. 402.

[18] B. F. Davis and K. T. Chung, J. Phys. B **15**, 3113 (1982).

[19] U. Fano and J. W. Cooper, Rev. Mod. Phys. **40**, 441 (1968).

[20] R. V. Hodges, M. J. Coggiola, and J. R. Peterson, Phys. Rev. A **23**, 59 (1981).

[21] B. F. Davis and K. T. Chung, Phys. Rev. A **39**, 3942 (1989).

[22] C. F. Bunge and A. V. Bunge, Phys. Rev. A **17**, 822 (1978).