

## Magnetic quadrupole decay of the $(1s2s2p)^4P_{5/2}^o - (1s)^22s^2S_{1/2}^e$ transition of the lithium isoelectronic sequence\*

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A  $1/Z$ -expansion method is used to calculate the eigenvalues and eigenfunctions for the  $(1s2s2p)^4P_{5/2}^o$  state of the lithium isoelectronic sequence. The magnetic quadrupole ( $M2$ ) decay rates for the  $(1s2s2p)^4P_{5/2}^o - (1s)^22s^2S_{1/2}^e$  transition are computed for the series from Li I through Ar XVI. It is explicitly demonstrated that, for high values of nuclear charge, the magnetic quadrupole decay channel becomes comparable to that of autoionization in determining the lifetime of the metastable state.

### I. INTRODUCTION

The  $(1s2s2p)^4P_{5/2}^o$  metastable state of the lithium isoelectronic sequence has a lifetime that is primarily determined by two forbidden decay processes: autoionization and magnetic quadrupole ( $M2$ ) radiation. For autoionization, the selection rules of conservation of total angular momentum and parity allow the reaction  $(1s2s2p)^4P_{5/2}^o \rightarrow (1s)^2^1S_0^e + K^2F_{5/2}^o$  to proceed through the tensor part of the spin-spin interaction. Magnetic quadrupole decay gives rise to the x-ray radiative transition  $(1s2s2p)^4P_{5/2}^o \rightarrow (1s)^22s^2S_{1/2}^e$ .

Recent investigations of electron decay-in-flight spectra from autoionizing states of the lithium series<sup>1</sup> and x-ray emission from foil-excited beams<sup>2</sup> have prompted a systematic study of the magnetic quadrupole decay rates for the sequence by means of a nuclear-charge-expansion method. Such a study provides a check on our theoretical understanding of the metastable state. Moreover, a knowledge of the lifetimes and transition probabilities is of astrophysical interest, particularly in solar research, where detailed calculations of metastable states permit the evaluation of such properties as coronal electron temperatures.

### II. THEORY

The probability for the emission of magnetic multipole radiation from a three-electron atom is

$$\langle \gamma' L' S' J' M' | q_m^{(k)}(\nu) | \gamma L S J M \rangle = (-1)^{J' - M'} \begin{pmatrix} J' & k & J \\ -M' & m & M \end{pmatrix} \langle \gamma' L' S' J' || q^{(k)}(\nu) || \gamma L S J \rangle, \quad (5)$$

where the reduced matrix element is given by the following expression:

given, in atomic units, by the expression

$$A_m^{(k)} = \frac{2(k+1)}{k(2k+1)[(2k-1)!!]^2 c^2} \left( \frac{\omega}{c} \right)^{2k+1} |\langle \psi_i | Q_m^{(k)} | \psi_f \rangle|^2. \quad (1)$$

The tensor operator of rank  $k$  in the matrix element is summed over the number of electrons,

$$Q_m^{(k)} = \sum_{\nu=1}^3 q_m^{(k)}(\nu), \quad (2)$$

while  $\omega$  in expression (1) represents the transition energy and  $c = 1/\alpha$ . The particular form for the individual electron operator is

$$q_m^{(k)}(\nu) = \left( \frac{4\pi}{2k+1} \right)^{1/2} [\nabla r_\nu^k Y_k^m(\hat{r}_\nu)] \left( \frac{l_\nu}{k+1} + s_\nu \right), \quad (3)$$

where  $r_\nu$ ,  $l_\nu$ , and  $s_\nu$  are the coordinate, orbital angular momentum, and spin angular momentum of the  $\nu$ th electron and  $Y_k^m(\hat{r}_\nu)$  is the spherical harmonic. Following Drake<sup>3</sup> Eq. (3) may be written in terms of products of irreducible tensor operators with the use of the relation

$$\nabla r^k Y_k^m(\hat{r}) = [k(2k+1)]^{1/2} r^{k-1} Y_{k,k-1,m_k}, \quad (4)$$

where  $Y_{k l m}$  is a vector spherical harmonic.

Application of the Wigner-Eckart theorem eliminates the dependency of matrix elements of spherical tensors on the magnetic quantum numbers so that for  $LS$ -coupled states

$$\begin{aligned}
(\gamma' L' S' J' || Q^{(k)}(\nu) || \gamma L S J) &= (4\pi k)^{1/2} [(2J'+1)(2J+1)(2k+1)]^{1/2} \\
&\times \left[ \frac{\delta(S', S)}{(k+1)} (-1)^{2L'+S'+L+J+2k} \left\{ \begin{matrix} J' & k & J \\ L & S' & L' \end{matrix} \right\} \sum_{L'', \gamma''} \left\{ \begin{matrix} 1 & k & k-1 \\ L' & L'' & L \end{matrix} \right\} \right. \\
&\times (\gamma' L' || \gamma_\nu^{k-1} Y_{k-1}(\nu) || \gamma'' L'') (\gamma'' L'' || L_\nu || \gamma L) + \left. \left\{ \begin{matrix} L' & L & k-1 \\ S' & S & 1 \\ J' & J & k \end{matrix} \right\} \right. \\
&\times \left. \sum_{\gamma''} (\gamma' L' || \gamma_\nu^{k-1} Y_{k-1}(\nu) || \gamma'' L) (\gamma'' S' || s_\nu || \gamma S) \right]. \quad (6)
\end{aligned}$$

The  ${}^4P_{5/2}^o - {}^2S_{1/2}^o$  transition of interest has a  $\Delta S = \pm 1$ , so that the matrix element involving the first sum in Eq. (6) vanishes for  $\Delta S \neq 0$ . Furthermore, the triangular conditions imposed on the rows and columns in the  $9j$  symbol determine the selection rules. As shown by Mizushima and Koide,<sup>4</sup> the magnetic quadrupole moment ( $K=2$ ) is the lowest moment which has finite matrix elements between states with different total spin, leading to the following selection rules:

$$\Delta S = \pm 1 \begin{cases} \Delta L = 0, & \pm 1 (0 \leftrightarrow 0) \\ \Delta J = 0, & \pm 1, \pm 2 (0 \leftrightarrow 0, 0 \leftrightarrow \frac{1}{2}, \frac{1}{2} \leftrightarrow \frac{1}{2}). \end{cases} \quad (7)$$

A complete theoretical discussion of the development of variational and perturbed eigenfunctions for the lithium sequence has been presented previously.<sup>5</sup> The computation of the magnetic quadrupole decay rate may easily be extended for the entire isoelectronic sequence. The substitution of perturbed wave functions given by Eq. (4) of Onello *et al.*<sup>5</sup> into expression (1) for the initial and final states allows the square of the matrix element to be expressed as a nuclear-charge series expansion, that is,

$$|\langle \psi_i | Q_m^{(k)} | \psi_f \rangle|^2 = \sum_{s=0}^{\infty} Z^{-s} Q_{km}^{(s)}. \quad (8)$$

### III. CALCULATIONS AND RESULTS

In the method of configuration interaction, each configuration consists of a sum of determinantal wave functions chosen to be eigenfunctions of  $\bar{L}^2$  and  $\bar{S}^2$ . The single-electron wave function (spin orbital) is a product of a Slater-type orbital  $\chi$  and an  $\alpha$  or  $\beta$  spin function. The  $\chi$  function is normalized but nonorthogonal and is defined by

$$\chi_{nlm} = \frac{(2\xi)^{n+1/2}}{[(2n)!]^{1/2}} r^{n-1} e^{-\xi r} Y_{l,m}(\theta, \phi). \quad (9)$$

$\xi$  is a nonlinear screening parameter and  $Y_{l,m}(\theta, \phi)$

is the ordinary spherical harmonic selected with the phase convention that  $\bar{Y}_{l,m} = Y_{l,-m}$ . The  $\alpha$  and  $\beta$  spin functions represent the two components of spin. The matrix elements of the spin-dependent operator  $Q_m^{(k)}$  over the three-electron Slater determinants constructed from nonorthogonal spin orbitals were evaluated using the cofactor methods of Prosser and Hagstrom.<sup>6</sup>

As a check on our variational and  $Z$ -expansion computer codes, we calculated the magnetic quadrupole decay rate for the  $(1s)^2 {}^1S_0^o - (1s2p) {}^3P_2^o$  transition of helium. Weiss's<sup>7</sup> 20-term configuration interaction with five screening parameters and a  $(1s)^2$  hydrogenic configuration substituted for the  $(4f)^2$  was selected to represent the helium ground state. A 26-term configuration-interaction wave function with seven screening parameters optimized

TABLE I. Configurations and screening parameters  $\xi$  for the  $(1s2s2p) {}^4P_{5/2}^o$  state of  $O_{VI}$  ( $Z=8$ ).

41-term configuration-interaction wave function $\xi$ 's		
$\xi s = 8.27$	$\xi p = 3.54$	
$\xi s' = 3.44$	$\xi p'' = 6.80$	
$\xi s'' = 4.15$	$\xi d = 3.83$	
configurations		
$(1s2s2p)_{\text{hydrogenic}}$	$1s3s'2p$	$2s'3s''2p$
$1s2s2p$	$1s3s''2p$	$2s''3s''2p$
$1s2s'2p$	$1s'3s'2p$	$2s3s2p''$
$1s2s''2p$	$1s'3s''2p$	$2s3s'2p''$
$1s'2s'2p$	$1s''3s''2p$	$2s3s''2p''$
$1s'2s''2p$	$1s3s2p''$	$2s'3s'2p''$
$1s''2s''2p$	$1s3s'2p''$	$2s'3s''2p''$
$1s2s2p''$	$1s3s''2p''$	$(2p3p) {}^3S2p''$
$1s2s'2p''$	$1s'3s'2p''$	$(2p) {}^2{}^3P2p''$
$1s2s''2p''$	$1s'3s''2p'$	$(1s2p) {}^3P3d$
$1s'2s'2p''$	$2s3s2p$	$(2s3p) {}^3P3d$
$1s2s''2p''$	$2s3s'2p$	$1s2s3p$
$1s''2s''2p''$	$2s3s''2p$	$1s2s'3p$
$1s3s2p$	$2s'3s'2p$	

TABLE II. Energy-expansion coefficients  $E_n^{(s)}$  (a.u.).

Order $s$	$(1s2s2p)^4P_{5/2}^o$
0	-7.500 000 00(0)
1	5.464 689 58(-1)
2	-2.364 652 61(-1)
3	-5.033 435 17(-2)

in the standard variational minimization of the total energy was developed for the  $(1s2p)^3P_2^o$  state. The calculated value for the magnetic quadrupole decay rate of  $3.19 \times 10^{-1} \text{ sec}^{-1}$  agrees quite well with Drake's<sup>3</sup> value of  $3.27 \times 10^{-1} \text{ sec}^{-1}$  obtained with correlated variational functions. Our values for the zero- and first-order expansion coefficients, 1.664 79 and 0.8104, are in good agreement with Drake's<sup>3</sup> values of 1.664 80 and 0.8162. The magnetic quadrupole decay rates for He I through Ar XVII derived with the  $Z$ -expansion procedure are in close agreement with those obtained by Drake.<sup>3</sup>

Since the  $Z$ -expansion method is expected to converge more rapidly for higher values of the nuclear charge, the 58-term  $(1s)^22s^2S_{1/2}^o$  wave function for O VI developed previously<sup>5</sup> was used to represent the ground state. The  $(1s2s2p)^4P_{5/2}^o$  state for O VI consists of 41 configurations with six optimized screening parameters obtained in the variational minimization of the energy. The values of the screening parameters together with the list of con-

TABLE III.  $1/Z$ -expansion eigenvalues (in a.u.) for the lithium isoelectronic sequence.

$Z$	This work	$-E[(1s2s2p)^4P_{5/2}^o]$ Holóien and Geltman <sup>a</sup>
3	5.363 84	5.365 89
4	10.063 17	10.062 8
5	16.264 19	16.263 0
6	23.966 04	23.964 3
7	33.168 37	33.166 4
8	43.871 01	43.868 8
9	56.073 84	56.071 4
10	69.776 81	69.774 5
11	84.979 88	
12	101.683 03	
13	119.886 24	
14	139.589 50	
15	160.792 79	
16	183.496 11	
17	207.699 45	
18	233.402 82	

<sup>a</sup>Reference 9.TABLE IV. Magnetic quadrupole  $Q_{km}^{(s)}$  expansion coefficients.

$s$	$Q_{km}^{(s)}$
0	1.664 786 89(0)
1	5.775 083 12(-1)
2	-3.188 524 26(0)
3	-2.078 260 39(1)

figurations used to represent the  $^4P_{5/2}^o$  state are shown in Table I.

The energy expansion coefficients given by Eq. (12) of Onello *et al.*<sup>5</sup> are shown through third order in Table II. Table III lists the expansion eigenvalues of the lithium sequence from Li I through Ar XVI and compares them to the variational estimates of Holóien and Geltman.<sup>8</sup> For O VI the energy from the  $Z$  expansion differs from the variational energy obtained with the 41-term configuration-interaction wave function by only  $1.3 \times 10^{-4}$  a.u. Estimates of the relativistic contribution to the energies of these states is available from the work of Snyder.<sup>9</sup> Our calculation of 553.9 eV for the x-ray emission of the  $(1s2s2p)^4P_{5/2}^o - (1s)^22s^2S_{1/2}^o$  transition for O VI agrees with the experimental value<sup>10</sup> of 554.2 eV. The  $1/Z$ -expansion energies for the two states of F VII involved in the same transition yield an emission energy of 714.4 eV compared with the observed value<sup>11</sup> of 715.1 eV. When an estimated relativistic correction<sup>9</sup> of 17 eV is included in the calculation of the binding energy of the  $^4P_{5/2}^o$  state

TABLE V. Nonrelativistic  $1/Z$ -expansion magnetic quadrupole decay rates ( $\text{sec}^{-1}$ ) for the  $(1s2s2p)^4P_{5/2}^o - (1s)^22s^2S_{1/2}^o$  transition of the lithium isoelectronic sequence.

System	$Z$ expansion
Li I	$1.02 \times 10^1$
Be II	$3.41 \times 10^2$
B III	$3.39 \times 10^3$
C IV	$1.96 \times 10^4$
N V	$8.17 \times 10^4$
O VI	$2.73 \times 10^5$
F VII	$7.77 \times 10^5$
Ne VIII	$1.96 \times 10^6$
Na IX	$4.47 \times 10^6$
Mg X	$9.45 \times 10^6$
Al XI	$1.87 \times 10^7$
Si XII	$3.52 \times 10^7$
P XIII	$6.31 \times 10^7$
S XIV	$1.09 \times 10^8$
Cl XV	$1.81 \times 10^8$
Ar XVI	$2.92 \times 10^8$

TABLE VI. Experimental (Ref. 12; the experimental rates include contributions from both autoionization and  $M2$  decay) and calculated  $M2$  decay rates of the  $(1s2s2p)^4P_{5/2}^o$  state for some members of the lithium sequence.

System	$Z$	$\tau$ (nsec) Expt.	$A$ (sec $^{-1}$ ) Expt.	$A_{M2}$ (sec $^{-1}$ ) $Z$ expansion	Magnetic quadrupole branching ratio
OVI	8	25 $\pm$ 3	4(+0.6, -0.4) $\times 10^7$	2.73 $\times 10^5$	0.00
FVII	9	15 $\pm$ 1	(6.7 $\pm$ 0.4) $\times 10^7$	7.77 $\times 10^5$	0.01
ALXI	13	2.9 $\pm$ 0.2	3.5(+0.2, -0.3) $\times 10^8$	1.87 $\times 10^7$	0.05
SIXII	14	2.1 $\pm$ 0.1	(4.8 $\pm$ 0.2) $\times 10^8$	3.52 $\times 10^7$	0.07
SXIV	16	1.1 $\pm$ 0.1	9.1(+0.9, -0.8) $\times 10^8$	1.09 $\times 10^8$	0.12
CLXV	17	0.91 $\pm$ 0.04	(1.10 $\pm$ 0.05) $\times 10^9$	1.81 $\times 10^8$	0.16
ARXVI	18	0.66 $\pm$ 0.04	(1.52 $\pm$ 0.09) $\times 10^9$	2.92 $\times 10^8$	0.19

of Cl XV, we obtain a value of 5668.4 eV, which agrees with the measured value<sup>2</sup> of 5669.5 $\pm$ 3 eV.

Table IV lists through third order the magnetic-quadrupole-expansion coefficients of Eq. (8). The magnetic quadrupole decay rates for the  $^4P_{5/2}^o \rightarrow ^2S_{1/2}^e$  transition developed from the  $Z$ -expansion method are listed in Table V for the lithium isoelectronic sequence from Li I through Ar XVI. Theoretically calculated nonrelativistic energies derived for both states with the  $Z$ -expansion technique were used in the calculation of the decay rates. For OVI the variational decay rate of  $2.77 \times 10^5$  sec $^{-1}$  is within 1.5% of the  $Z$ -expansion value. It has been suggested<sup>2</sup> that the  $M2$  matrix element which connects the  $(1s2p)^3P_2$  and  $(1s)^2^1S_0^e$  states will be nearly equal that connecting the  $(1s2s2p)^4P_{5/2}^o$  and  $(1s)^2s^2S_1^e$  states. For  $Z$  between 10 and 18 the present lithium sequence decay rates are 8 to 10% smaller than the corresponding  $M2$  helium-sequence rates.<sup>3</sup>

Table VI gives a comparison between recently

determined experimental decay rates<sup>12</sup> of the  $(1s2s2p)^4P_{5/2}^o$  state for some members of the lithium sequence with the  $M2$  decay rates calculated in this paper. We note that the  $M2$  decay channel becomes increasingly important as one goes to higher  $Z$  values, since  $M2$  decay scales as  $Z^8$ . Approximately 19% of the decay of the  $(1s2s2p)^4P_{5/2}^o$  state of Ar XVI goes by  $M2$  x-ray emission, while the remainder proceeds through the spin-spin-induced autoionization decay channel. Extrapolation of both the experimental<sup>12</sup> and theoretical results suggests that the magnetic quadrupole decay of the  $^4P_{5/2}^o$  state may become comparable to that of autoionization decay at  $Z \cong 24$ .

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