

## Theoretical Considerations for Auto-Ionizing States with Microsecond Lifetimes\*

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Employing analytic Hartree-Fock wave functions, model calculations have been performed on the structure and lifetimes of the slowly auto-ionizing states arising from  $(1s, 2s, 2p) \ ^4P$  in  $\text{He}^-$  and  $\text{Li}$ . The effect of mixing with the associated  $^2P$ 's is considered and the phenomenon of differential metastability discussed. A framework is provided to interpret experimental observations.

### I. INTRODUCTION

The decay of an excited atomic state lying above the first ionization potential of that atom to the adjacent continuum may occur with no accompanying radiation; this is the phenomenon of auto-ionization. These auto-ionizing states may be of two types. The first are the kind that interact with the adjacent continuum very strongly through the electrostatic terms in the Hamiltonian and thus have very short lifetimes, typically of the order  $10^{-12}$ – $10^{-14}$  sec. These states have been observed as resonances in scattering<sup>1</sup> and photoabsorption<sup>2</sup> processes, but have essentially no observable effect on atomic spectra because they decay so quickly. The second type are those which interact only weakly with an adjacent continuum through the fine-structure part of the Hamiltonian (spin-orbit, spin-other-orbit, and spin-spin interactions) and, because of the weakness of the interaction, are metastable against auto-ionization, having auto-ionizing lifetimes of the order  $10^{-3}$ – $10^{-7}$  sec. These states live long enough to be initial states of spectroscopic lines; in fact they were first postulated by Beutler<sup>3</sup> in 1933 to explain ultraviolet absorption lines he found in various alkalis. A number of metastable auto-ionizing states have been found experimentally, mostly in the alkalis or alkalilike ions.<sup>4–14</sup> Theoretical calculations have been carried out on the multiplet energies of such states (ignoring fine and hyperfine structure of the levels making up the multiplet) by a number of authors<sup>15–20</sup> and decay lifetime calculations have also been performed.<sup>20–25</sup>

Metastable auto-ionizing states are of interest at present in several connections. First, since their decay lifetimes are long and the levels themselves correspondingly narrow, both can be measured with a high degree of precision, giving a very sensitive test of the theory and the wave functions employed therein. Secondly, within a given multiplet, the fine- and hyperfine-structure levels may have different lifetimes. This differential

metastability would lead to certain of the levels being depopulated much more quickly than others, so that after a certain time the auto-ionized electrons would be polarized. The polarized electrons could then be used in a variety of collisions experiments. Finally, since structure measurements on these narrow states could be, if necessary, extremely accurate, it is possible to obtain a better value of the fine-structure constant, if a calculation could be done with sufficient accuracy.

In an effort to understand the structure and lifetimes of slowly auto-ionizing states, we have performed calculations using analytic Hartree-Fock wave functions. We have confined these calculations to the  $(1s, 2s, 2p)$  configuration in  $\text{Li}$  and  $\text{He}^-$ , since the three-electron system is the simplest in which slowly auto-ionizing states can occur. Although we do not expect that the theoretical results using Hartree-Fock wave functions will give detailed agreement with experiment, it should provide us with a certain amount of insight into the behavior of such states.

The following paper<sup>26</sup> will discuss the results of experiments on the  $(1s, 2s, \text{ and } 2p) \ ^4P$  states in lithium as well as the effect of a magnetic field on such states and give a detailed comparison of the experimental and theoretical results.

### II. THEORY AND DISCUSSION

#### A. Multiplet Structure

In the approximation of  $LS$  coupling, which is generally excellent for low- $z$  atoms and ions, the  $(1s, 2s, 2p)$  configuration consists of a  $^4P$  and two  $^2P$  multiplets.<sup>15</sup> In order to calculate the wave functions and energies, we first consider just the nonrelativistic Hamiltonian

$$H_0 = \sum_{i=1}^3 \left( \frac{P_i^2}{2m} - \frac{Ze^2}{r_i} \right) + \sum_{i < j} \frac{e^2}{r_{ij}}, \quad (1)$$

where  $P_i$  is the momentum of the  $i$ th electron and  $Z$  is the nuclear charge. Since  $H_0$  does not include the fine-structure operator, all values of  $J$  in a

given multiplet level will have the same energy. For the  $^4P$  state, the  $J = \frac{5}{2}$ ,  $M_J = \frac{5}{2}$  is considered, since it simplifies the calculation. We then perform an analytic Hartree-Fock calculation for the  $^4P$  state. The energy is then

$$\begin{aligned} E_{4p} = & T(1s) + T(2s) + T(2p) + V(1s) + V(2s) + V(2p) \\ & + F^0(1s, 2s) \\ & + F^0(1s, 2p) + F^0(2s, 2p) \\ & \times -G^0(1s, 2s) - \frac{1}{3}G^1(1s, 2p) - \frac{1}{3}G^1(2s, 2p) \end{aligned} \quad (2)$$

where  $T$  refers to the kinetic energy,  $V$  to the nuclear potential energy, and

$$\begin{aligned} F^k(nl, n'l') = & \int \int (r_1^k/r_2^{k+1}) u_{n,l}^*(1) u_{n,l}(1) u_{n,l'}^*(1) \\ & \times (2) u_{n,l'}(2) r_1^2 r_2^2 dr_1 dr_2, \end{aligned} \quad (3a)$$

$$\begin{aligned} G^k(nl, n'l') = & \int \int (r_1^k/r_2^{k+1}) u_{n,l}^*(1) u_{n,l}(1) u_{n,l'}^*(1) \\ & \times (2) u_{n,l'}(2) r_1^2 r_2^2 dr_1 dr_2, \end{aligned} \quad (3b)$$

$u_{n,l}$  being the radial part of the one-electron function with quantum numbers  $(n, l)$ .

To obtain wave functions and energies for the  $^2P$  states we make the simplifying approximation the radial orbitals are the same as for the  $^4P$ . Then, by diagonalizing the  $3 \times 3$  matrix associated with this configuration,<sup>15</sup> we find that the energies of the  $^2P_{\pm}$  levels ( $^2P_+$  referring to the upper one,  $^2P_-$  to the lower) are given by

$$\begin{aligned} E_{2p_{\pm}} = & T(1s) + T(2s) + T(2p) + V(1s) + V(2s) + V(2p) \\ & + F^0(1s, 2s) + F^0(1s, 2p) \\ & + F^0(2s, 2p) \pm K, \end{aligned} \quad (4)$$

$$\begin{aligned} K = & \left( \frac{1}{2} \left[ G^0(1s, 2s) - \frac{1}{3}G^1(1s, 2p) \right]^2 \right. \\ & + \left[ \frac{1}{3}G^1(1s, 2p) - \frac{1}{3}G^1(2s, 2p) \right]^2 \\ & \left. + \left[ \frac{1}{3}G^1(2s, 2p) - G^0(1s, 2s) \right]^2 \right)^{1/2}. \end{aligned} \quad (5)$$

The energies resulting from the calculations are shown in Fig. 1 for Li and Fig. 2 for He<sup>-</sup> along with experimental energies<sup>27</sup> of other relevant levels in these systems.

Since the  $^4P$  arising from the  $(1s, 2s, 2p)$  configuration is the lowest  $^4P$  level in each case, the results of our calculations give upper bounds to their energies; no such claim can be made, however, for the  $^2P$  levels. We can estimate the accuracy of the  $^4P$  wave-function calculations by comparison with experiment<sup>6,28</sup> and with other calculations employing more sophisticated wave functions.<sup>17-19</sup> This comparison is shown in Table I. while our energies are about 0.25 eV higher than those of the more sophisticated calculations, it is expected that the electron densities as given by our wave functions will not be so very different from

those predicted by the better ones. Thus we expect the results using a Hartree-Fock wave function to be fairly realistic. This is borne out by the experimental results of Levitt, Novick, and Feldman.<sup>26</sup>

### B. Fine and Hyperfine Structure

The fine-structure operator is the sum of the spin-orbit plus spin-other-orbit Hamiltonian  $H_{so}$  and the spin-spin Hamiltonian<sup>29</sup>  $H_{ss}$

$$H_{so} = \frac{\alpha^2 Z}{2} \sum_{i=1}^3 \frac{\vec{r}_i \cdot \vec{s}_i}{r_i^3} - \frac{\alpha^2}{2} \sum_{i \neq j} \left( \frac{\vec{r}_{ij}}{r_{ij}^3} \times \vec{p}_i \right) \cdot (\vec{s}_i + 2\vec{s}_j), \quad (6)$$

$$H_{ss} = \alpha^2 \sum_{i < j} \frac{1}{r_{ij}^3} \left( \vec{s}_i \cdot \vec{s}_j - \frac{3(\vec{s}_i \cdot \vec{r}_{ij})(\vec{s}_j \cdot \vec{r}_{ij})}{r_{ij}^2} \right), \quad (7)$$

where  $\alpha$  is the fine-structure constant,  $\vec{r}_{ij} \equiv \vec{r}_i - \vec{r}_j$ .

To calculate the fine structure we note that within the framework of  $LS$  coupling,  $H_{so}$  is proportional to  $\vec{L} \cdot \vec{S}$  and  $H_{ss}$  to  $\frac{3}{2}(\vec{L} \cdot \vec{S}) + 3(\vec{L} \cdot \vec{S})^2 - L(L+1)S(S+1)$ ,  $L$  and  $S$  being, respectively, the total orbital and spin angular momenta of the atom. We can, thus write

$$H_{so} = C_{so} \vec{L} \cdot \vec{S}, \quad (8a)$$

$$H_{ss} = C_{ss} \left[ \frac{3}{2}(\vec{L} \cdot \vec{S}) + 3(\vec{L} \cdot \vec{S})^2 - L(L+1)S(S+1) \right]. \quad (8b)$$

The  $(1s, 2s, 2p)$   $^4P$  level has angular momentum components  $J = \frac{5}{2}, \frac{3}{2}, \frac{1}{2}$ . We calculate directly the energy of the  $J = \frac{5}{2}$  state, and using Eqs. (8), the en-

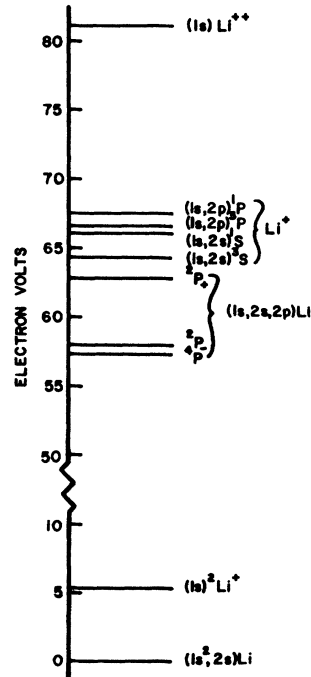


FIG. 1. Calculated  $(1s, 2s, 2p)$  multiplet energies in Li along with experimental energies of other relevant levels.

TABLE I. Energy, in eV, of the  $(1s, 2s, 2p)^4P$  level in Li and He.

	Expt		Theory	
	This work	(Ref. 6)	(Ref. 19)	(Ref. 17)
Li	57.68	$57.3 \pm 0.3$	57.44	57.47
He <sup>-</sup>	19.978	19.741	19.749	19.785

ergies of the lower  $J$  states.

The hyperfine Hamiltonian can be written as the sum of three terms: the Fermi contact term,<sup>30</sup>  $H_c$ ; the magnetic dipole interaction,<sup>30</sup>  $H_{md}$ ; and the quadrupole term  $H_q$ :

$$H_c = \frac{4\pi}{3} \frac{\alpha^2 g_n}{M} \sum_{i=1}^3 \vec{I} \cdot \vec{s}_i \delta^3(\vec{r}_i), \quad (9)$$

$$H_{md} = \frac{\alpha^2 g_n}{M} \sum_{i=1}^3 \left( \frac{\vec{I} \cdot \vec{r}_i}{r_i^3} - \frac{\vec{I} \cdot \vec{s}_i}{r_i^3} + \frac{3(I \cdot r_i)(s_i \cdot r_i)}{r_i^5} \right), \quad (10)$$

where  $I$  is the nuclear spin,  $g_n$  the nuclear  $g$  factor,  $M$  the nuclear mass, and  $\alpha$  the fine-structure constant. Since we are assuming  $LS$  coupling, we can then write

$$H_c = a_c \vec{I} \cdot \vec{S}, \quad (11a)$$

$$H_{md} = C_{md} \left\{ \vec{I} \cdot \vec{L} + \frac{2}{15} [(\vec{I} \cdot \vec{S})L(L+1) - \frac{3}{2}(\vec{I} \cdot \vec{L})(\vec{L} \cdot \vec{S}) - \frac{3}{2}(\vec{L} \cdot \vec{S})(\vec{I} \cdot \vec{L})] \right\}. \quad (11b)$$

Since the quadrupole contribution is much smaller than  $H_{hf}$  or  $H_{md}$ , we consider only diagonal (in  $J$ ) matrix elements and can write  $H_q$  as<sup>31</sup>

$$H_q = [Qq_J/2I(2I-1)J(2J-1)] [3(\vec{I} \cdot \vec{J})^2 + \frac{3}{2}\vec{I} \cdot \vec{J} - I(I+1)J(J+1)]. \quad (12)$$

Here  $Q$  is the nuclear quadrupole moment and

$$q_J = -\langle J, M_J = J | (3 \cos^2 \theta_{2p} - 1/r_{2p}^3) | J, M_J = J \rangle = \langle (1/r_{2p}^3) \rangle f_J,$$

$$C_q = Q \langle (1/r_{2p}^3) \rangle \text{ independent of } J.$$

The calculations are carried out directly for the highest  $F$  state ( $\vec{F} = \vec{I} + \vec{J}$ ) in each case, and Eqs. (11) and (12) are then used to find the contributions for the lower  $F$  states.

Since the configuration we are considering has two unpaired  $s$  electrons, the Fermi contact contribution is so large that the hyperfine splittings are of the same order of magnitude as the fine-structure separations. Thus it cannot be considered a small perturbation, and we must diagonalize the fine-plus-hyperfine energy matrix to obtain the energy levels. The results are shown in Fig. 3 for Li and Fig. 4 for He<sup>-</sup>, and the parameters  $C_{so}$ ,  $C_{ss}$ ,  $a_c$ ,  $C_{md}$ , and  $C_q$  are shown in Table II.

The accuracy of these calculations is determined by how well the parameters  $C_{so}$ ,  $C_{ss}$ ,  $a_c$ ,  $C_{md}$ , and  $C_q$  are known. We estimate that our values of  $a_c$

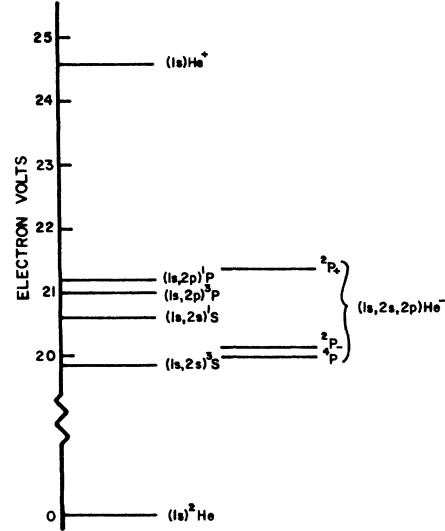


FIG. 2. Calculated  $(1s, 2s, 2p)$  multiplet energies in He<sup>-</sup> along with experimental energies of other relevant levels.

are good to 2%;  $C_{md}$ ,  $C_{ss}$ , and  $C_q$  5% in Li, 10% in He<sup>-</sup>; but, for both cases,  $C_{so}$  is a problem. It arises because the two contributions to  $C_{so}$ , the spin-orbit effect and the spin-other-orbit effect,

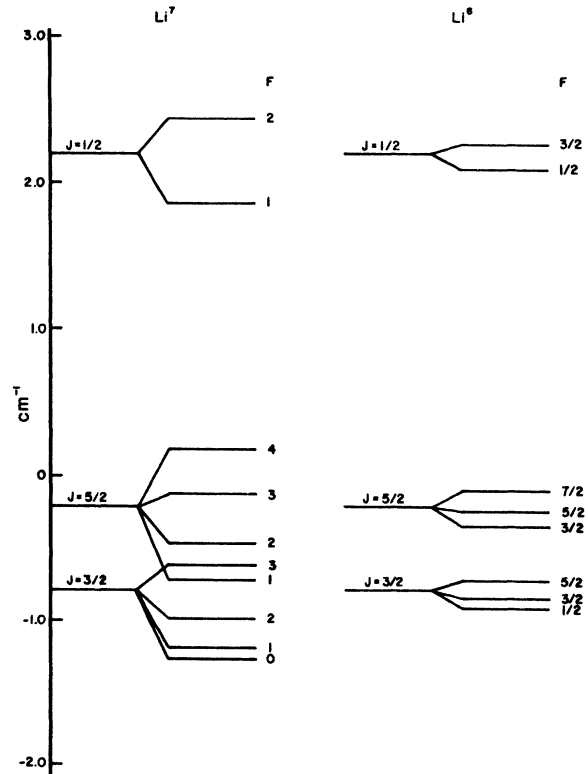


FIG. 3. Calculated fine and hyperfine structure of  $(1s, 2s, 2p)^4P$  in Li<sup>6</sup> and Li<sup>7</sup>.

are nearly equal in magnitude and opposite in sign. Thus we would put the maximum error of  $C_{so}$  at 50–100%.

It is important to note, however, that, although the values of the constants determined using our Hartree-Fock wave function have inaccuracies as pointed out above, the parametrization that we have written out for the fine and hyperfine energies

$$H_{so} + H_{ss} + H_c + H_{md} + H_q, \quad (13)$$

with the terms given by Eqs. (8), (11), and (12), is still correct as long as  $LS$  coupling holds. This is the case for our states as evidenced by the configuration interaction wave functions,<sup>17–19</sup> which give excellent electrostatic energies and are pure  $LS$  functions. Hence our calculation should be considered a first approximation to the values of the constants. The parametrization along with our values of the constants will be used in the following paper to determine the actual values and, thence, the fine and hyperfine structure.

### C. Lifetimes

In order to calculate lifetimes we use a projection-operator technique we have devised. This method has been discussed in detail previously,<sup>20,32</sup> so we shall just outline it here. The first step is to obtain the Hartree-Fock solution to the initial state  $\psi_i$  and construct an operator to  $H_0$  to which it is an eigensolution. Using this operator we find a final-state wave function  $\psi_f$  (which turns out to be very close to the Hartree-Fock final function)<sup>32</sup> and get the transition matrix element of the total Hamiltonian  $H - H_0$  between the initial and final states. The decay rate (the inverse of the lifetime) is then given by

$$R = (2\pi/\hbar) |\langle \psi_i | H - H_0 | \psi_f \rangle|^2 \rho, \quad (14)$$

where  $\rho$  is the density of final states. Then to obtain the decay rates of the  $^4P$  states we use the wave functions obtained in the diagonalization of the energy matrices in the structure calculations of Sec. II B. The  $J = \frac{5}{2}$  states ( $^4P_{5/2}$ ) will be connected to the  $(1s^2, \epsilon f)^2F_{5/2}$  continuum only through the spin-spin Hamiltonian. The  $^4P_{3/2}$  and  $^4P_{1/2}$  states will decay to the  $(1s^2, \epsilon p)^2P_{3/2}$ ,  $^2P_{1/2}$  continua via the spin-orbit plus spin-other-orbit plus spin-spin interactions, so that they very likely decay some-

TABLE II. Calculated fine- and hyperfine-structure parameters in  $\text{cm}^{-1}$  for Li and  $\text{He}^-$ .

	$C_{so}$	$C_{ss}$	$a_c$	$C_{md}$	$C_q$
$\text{He}^{3-}$			-0.101	$0.187 \times 10^{-3}$	...
$\text{He}^{4-}$	-0.0613	0.0114	...	...	...
$\text{Li}^6$			0.065	$0.775 \times 10^{-3}$	$0.185 \times 10^{-5}$
$\text{Li}^7$	-0.325	0.185	0.172	$0.205 \times 10^{-2}$	$0.105 \times 10^{-3}$

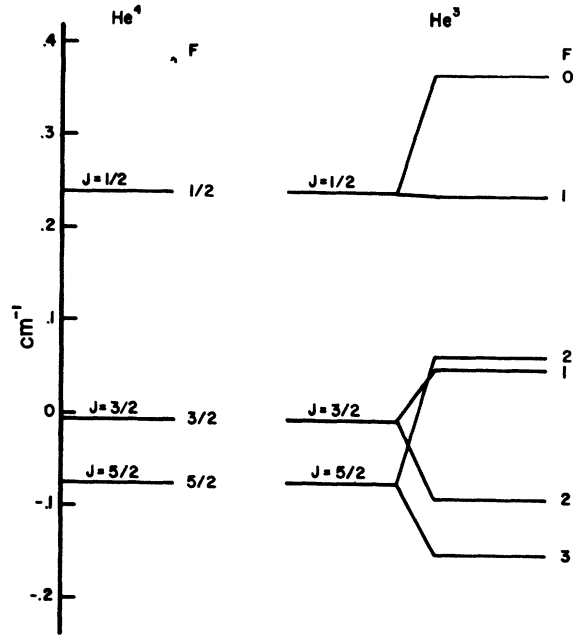


FIG. 4. Calculated fine and hyperfine structure of  $(1s, 2s, 2p) ^4P$  in  $\text{He}^{3-}$  and  $\text{He}^{4-}$ .

what more quickly than the  $^4P_{5/2}$  states. We must however, further, consider the mixing of the  $^4P$  states with the  $^2P_+$  and  $^2P_-$  states, since the coupling of the  $^4P$  states to the continuum directly is *a priori* of the same order of magnitude as their coupling to the continuum via the doublet states. This is because the quartet states are directly coupled to the continuum by the fine-structure Hamiltonian and the coupling is thus of order  $\alpha^2$ ; while the coupling to the doublets is by the fine and hyperfine Hamiltonians, also of order  $\alpha^2$ ; and the doublets are coupled directly to the continuum by the electrostatic operators of order unity. This mixing only occurs, of course, for the  $J = \frac{3}{2}$  and  $\frac{1}{2}$  states since the  $^2P$ 's do not have a  $J = \frac{5}{2}$  component. Further, this mixing does not affect the  $^4P$  fine or hyperfine structure very much since the fine and hyperfine structure in the  $^2P$ 's are of the same order of magnitude as in the  $^4P$  so that, when multiplied by the rather small ( $\approx 10^{-4}$ ) mixing coefficient, their contribution is negligible.

To find the wave functions of the  $^4P$  states including the doublet contribution, perturbation theory can be used, since the quartet-doublet matrix elements are of the order of  $1 \text{ cm}^{-1}$ , whereas the separation of the states is of the order of eV. Then using the well-known formula from perturbation theory

$$\psi_i^{\text{new}} = \phi_i^{\text{old}} + \sum_{j, j \neq i} \frac{\langle \phi_i^{\text{old}} | H_1 | \phi_j^{\text{old}} \rangle}{E_i - E_j} \phi_j^{\text{old}}, \quad (15)$$

we obtain the wave functions of the system.

We now note that all of the states of different  $F$  and  $J$  within a given doublet will have essentially the same coupling to the continuum, since the electrostatic operators are four orders of magnitude larger than the fine-structure operators. We shall denote these matrix elements for  ${}^2P_+$  and  ${}^2P_-$  by  $M_+$  and  $M_-$ , respectively. Further, within the  ${}^4P$  state all the different  $F$  levels arising from a given value of  $J$  will have the same coupling to the continuum, since the auto-ionization is carried by the fine-structure Hamiltonian which is diagonal in  $J$  but independent of  $F$ . We denote the three matrix elements for  $J = \frac{5}{2}, \frac{3}{2},$  and  $\frac{1}{2}$  as  $M_{5/2}, M_{3/2},$  and  $M_{1/2}$ .

As an example of how the calculation goes, consider a state of  $\text{Li}^7$  with  $F = 3, M_F = 3$  of the form

$$\begin{aligned} \psi = & a |{}^4P, J = \frac{5}{2}, F = 3, M_F = 3\rangle \\ & + b |{}^4P, J = \frac{3}{2}, F = 3, M_F = 3\rangle \\ & + c |{}^2P_+, J = \frac{3}{2}, F = 3, M_F = 3\rangle \\ & + d |{}^2P_-, J = \frac{3}{2}, F = 3, M_F = 3\rangle. \end{aligned} \quad (16)$$

The auto-ionization rate of this state is then

$$R = (2\pi/\hbar)(a|^2M_{5/2}|^2 + |bM_{3/2} + cM_+ + dM_-|^2)\rho(E). \quad (17)$$

The fact that different hyperfine states have differing amounts of  $J = \frac{5}{2}, \frac{3}{2},$  and  $\frac{1}{2}$  character, as well as of  ${}^2P_+$  character, means that, in general, they will have differing metastable lifetimes, i. e., the phenomenon of differential metastability. Further, since the  $J = \frac{5}{2}$  states are only coupled to the  ${}^2P$ 's through the hyperfine Hamiltonian and are coupled directly to the continuum only through the spin-spin Hamiltonian, it is expected that these states will be most weakly coupled to the continuum and, thus, have the longest lifetimes. It is important to note, however, that this may not always be the case. Since the  $J = \frac{3}{2}, \frac{1}{2}$  components of the  ${}^4P$  and  ${}^2P$  states auto-ionize to the *same* final states, their transition matrix elements add up coherently [as in the second term in Eq. (17)] and thus, depending upon the signs of the mixing coefficients and transition matrix elements, the decay rates of some of these lower  $J$  states could be anomalously small and their lifetimes correspondingly large.

The results of our calculations are shown in Table III for  $\text{Li}^6, \text{Li}^7, \text{He}^3,$  and  $\text{He}^4$ . Here can be seen the effects of coherent mixing in the  $J = \frac{1}{2}$  states of  $\text{He}^4$  and  $\text{Li}$  designated by asterisks. Due to cancellation between the contributions, the decay rate is small and the lifetime thus anomalously large. Unfortunately the cancellations are so large that, when considered in conjunction with the uncertainty in each of the component matrix elements due to the nature of the simple model we are using, these lifetimes are not at all reliable. Relatively small changes in the component matrix elements can

change these asterisked lifetimes by more than an order of magnitude. Thus, we reemphasize, these results show the type of effects that can occur under certain circumstances, but are not of sufficient accuracy to necessarily agree with experiment. The other lifetimes should be rather better, but are still not to be taken too seriously. The results for the states associated with  $J = \frac{5}{2}$  are more accurate than the lower  $J$  states, and the  $\text{Li}$  results are more reliable than those of  $\text{He}$ .

The addition of a magnetic field will not be considered in detail, but its effects can be described qualitatively. The Zeeman Hamiltonian introduces no new mixing between quartet and doublet states, but it does have an interaction between states of the same  $M_F$ . Thus the degeneracies of the  $M_F$  states are removed and, as a function of magnetic field, the energy levels change. This in turn causes level "anticrossings" between states of the same  $M_F$  and crossings between states of differing  $M_F$ . These shall be discussed further in the following paper.<sup>26</sup>

The Zeeman interaction thus causes the wave function of a particular level to change as a function of magnetic field; in particular the amounts of  $J = \frac{5}{2}, \frac{3}{2},$  and  $\frac{1}{2}$  will vary. Hence the lifetimes of the levels will change if the magnetic field does, and the states that were long-lived at zero field will be mixed with shorter-lived ones, so that their decay rates will be, in general, increased. This will happen unless, of course, a particular value of the magnetic field causes a large amount of coherent cancellation of the matrix element, which is unlikely. This shortening of the lifetime of the various states as a magnetic field is turned on, is known as Zeeman quenching. Note that a relatively small field would quench long-lived lower  $J$  states, so that even if our results are correct, it is unlikely that these states would be seen unless they were looked for in a field-free region.

The states of highest  $F$  with  $M_F = \pm F$  are, however, never mixed with any other state. Thus, with a large magnetic field, after a short time essentially all of the other states will have decayed leaving only atoms in these states. Subsequent decays would then yield polarized electrons which could be used in a variety of ways.

### III. FINAL REMARKS

The formalism presented in this paper is not only useful in the interpretation of experimental data on the  $(1s, 2s, 2p) {}^4P$  states, but also provides some insight into the details of the decay and structure of these states. Further, it should be helpful in understanding metastable auto-ionizing states, which are found in other alkalis and alkalilike ions and which may occur in other atomic systems as well.

TABLE III. Calculated lifetimes in  $\mu\text{sec}$  of the states arising from  $(1s, 2s, 2p) {}^4P$  in  $\text{He}^3$ ,  $\text{He}^4$ ,  $\text{Li}^6$ , and  $\text{Li}^7$ , including the effects of the  $(1s, 2s, 2p) {}^2P$  levels. Those lifetimes marked by asterisks involved large cancellations and must be considered extremely unreliable.

$\text{He}^3$		$\text{He}^4$		$\text{Li}^6$		$\text{Li}^7$	
$ 3, 5/2\rangle$	1000	$ 5/2, 5/2\rangle$	1000	$ 7/2, 5/2\rangle$	5.88	$ 4, 5/2\rangle$	5.88
$ 2, 5/2\rangle$	370	$ 3/2, 3/2\rangle$	33	$ 5/2, 5/2\rangle$	5.88	$ 3, 5/2\rangle$	1.47
$ 2, 3/2\rangle$	65	$ 1/2, 1/2\rangle$	3500*	$ 3/2, 5/2\rangle$	5.05	$ 2, 5/2\rangle$	2.30
$ 1, 3/2\rangle$	29			$ 5/2, 3/2\rangle$	0.24	$ 1, 5/2\rangle$	5.87
$ 1, 1/2\rangle$	21			$ 3/2, 3/2\rangle$	0.25	$ 3, 3/2\rangle$	0.28
$ 0, 1/2\rangle$	80			$ 1/2, 3/2\rangle$	0.29	$ 2, 3/2\rangle$	0.30
				$ 3/2, 1/2\rangle$	100*	$ 1, 3/2\rangle$	0.32
				$ 1/2, 1/2\rangle$	29*	$ 0, 3/2\rangle$	0.35
						$ 2, 1/2\rangle$	20.0*
						$ 1, 1/2\rangle$	10.2*

The particulars of each of these states will be different, but they should all exhibit many of the features which we have discussed, such as differential metastability, Zeeman quenching, and anomalously long-lived states due to coherent mixing of matrix elements as in our treatment of the  $(1s, 2s, 2p) {}^4P$  states.

At this point it is worthwhile to consider how these calculations may be improved. The fine and hyperfine structure of the  ${}^4P$  state could be calculated quite accurately using one of the good correlated<sup>17,18</sup> or configuration-interaction<sup>19</sup> wave functions which are currently available. The results could be further improved by adding in radiative corrections and by amending the wave function to include deviations from  $LS$  coupling, i.e., mixing with doublet states. This calculation would be a tremendous amount of work, but it is conceivable that the results would be as accurate as hydrogen,  $n=2$  results. Then, since the splittings in this state in lithium are an order of magnitude larger than in hydrogen, a careful experiment could obtain an independent value of the fine-structure constant

better than is now known.

Improving the lifetime calculation is somewhat more difficult. The quartet states alone (ignoring the coupling to the doublets) could be treated more accurately by an extension of our technique to correlated wave functions, or by some other projection operator method, e.g., the Feshbach formalism.<sup>33</sup> The doublet states alone can be well calculated by the close-coupling technique<sup>34</sup> or by a projection-operator method.<sup>33</sup> To treat both, with the attendant fine and hyperfine mixing, on the same footing as close coupling, would lead to exceedingly complex coupling integrodifferential equations, which would be extremely difficult and time consuming, if at all possible, to solve. Thus the best prospect for a better calculation seems to be by a modification of an existing projection-operator method.

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<sup>1</sup>For example, E. N. Lassette, *Radiation Res. Suppl.* **1**, 530 (1959); G. J. Schulz, *Phys. Rev. Letters* **10**, 104 (1963); J. Arol Simpson, M. G. Menendez, and S. R. Mielczarek, *Phys. Rev.* **150**, 76 (1966); G. E. Chamberlain and H. G. M. Heideman, *Phys. Rev. Letters* **15**, 337 (1965); M. E. Rudd, *ibid.* **15**, 580 (1965); and J. F. Williams and J. W. McGowan, *ibid.* **21**, 719 (1968).

<sup>2</sup>Among the many papers are R. P. Madden and K. Codling, *Astrophys. J.* **141**, 364 (1965); G. V. Marr and R. Heppinstall, *Proc. Phys. Soc.* **87**, 547 (1966); K. Codling, R. P. Madden, and D. L. Eoerer, *Phys. Rev.* **155**, 26 (1967); W. R. S. Garton and K. Codling, *J. Phys. B* **1**, 106 (1968); J. Berkowitz and C. Lifshitz, *ibid.* **1**, 438 (1968).

<sup>3</sup>H. Beutler, *Z. Physik* **91**, 131 (1934); H. Beutler and K. Guggenheimer, *ibid.* **87**, 188 (1933); **88**, 25

(1934).

<sup>4</sup>P. Feldman and R. Novick, *Atomic Collision Processes*, edited by M. R. C. McDowell (North-Holland, Amsterdam, 1964), pp. 201-210.

<sup>5</sup>P. Feldman and R. Novick, *Phys. Rev. Letters* **11**, 513 (1963).

<sup>6</sup>P. Feldman and R. Novick, *Phys. Rev.* **160**, 143 (1967).

<sup>7</sup>P. Feldman, M. Levitt, and R. Novick, *Phys. Rev. Letters* **21**, 33 (1968).

<sup>8</sup>G. Sprott and R. Novick, *Phys. Rev. Letters* **21**, 336 (1968).

<sup>9</sup>P. Feldman, M. Levitt, S. T. Manson, R. Novick, and G. Sprott, *Physica* **33**, 278 (1967).

<sup>10</sup>I. S. Dmitriev, L. I. Vinogradova, V. S. Nikolaev, and B. M. Popov, *Zh. Eksperim. i Teor. Fiz. Pis'ma v Redaktskiya* **3**, 35 (1966). [*Sov. Phys. JETP Letters* **3**, 20 (1965)].

<sup>11</sup>I. S. Dmitriev, V. S. Nikolaev, and Ya. A. Teplova,

- Phys. Letters **26A**, 122 (1968).
- <sup>12</sup>S. E. Kuprivanov, Zh. Eksperim i Teor. Fiz. Pis'ma v Redaktsiyu **4**, 345 (1966) [Sov. Phys. JETP Letters **4**, 233 (1966)].
- <sup>13</sup>D. J. Nicholas, C. W. Trowbridge, and W. D. Allen, Phys. Rev. **167**, 38 (1968).
- <sup>14</sup>L. M. Blau, R. Novick, and D. Weinflash, Phys. Rev. Letters **24**, 1268 (1970).
- <sup>15</sup>Ta-You Wu and S. T. Shen, Chinese J. Phys. **5**, 150 (1944).
- <sup>16</sup>J. D. Gracia and J. E. Mack, Phys. Rev. **138**, A987 (1965).
- <sup>17</sup>E. Holóien and S. Geltman, Phys. Rev. **153**, 81 (1967).
- <sup>18</sup>E. Holóien and J. Midtdal, Proc. Phys. Soc. (London) **90**, 883 (1967).
- <sup>19</sup>A. Weiss (private communication).
- <sup>20</sup>S. T. Manson, Phys. Rev. **145**, 35 (1966).
- <sup>21</sup>J. L. Pietenpol, Phys. Rev. Letters **7**, 64 (1961).
- <sup>22</sup>S. T. Manson, Phys. Letters **23**, 315 (1966).
- <sup>23</sup>V. V. Balashov, V. S. Senashenko, and B. Tekou, Phys. Letters **25A**, 487 (1967).
- <sup>24</sup>C. Laughlin and A. L. Stewart, J. Phys. B **1**, 151 (1968).
- <sup>25</sup>G. Estberg and R. Labahn, Phys. Letters **28**, 420 (1968); **24**, 1265 (1970).
- <sup>26</sup>M. Levitt, R. Novick, and P. Feldman, preceding paper, Phys. Rev. A **3**, 130 (1970).
- <sup>27</sup>C. E. Moore, *Atomic Energy Levels*, NBS Circular No. 476 (U. S. GPO, Washington, D. C., 1949).
- <sup>28</sup>B. Brehm, M. A. Gusinow, and J. L. Hall, Phys. Rev. Letters **19**, 737 (1967).
- <sup>29</sup>H. Bethe and E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Springer-Verlag, Berlin, 1957), p. 181.
- <sup>30</sup>Reference 29, p. 193.
- <sup>31</sup>J. C. Slater, *Quantum Theory of Atomic Structure* (McGraw-Hill, New York, 1960), Vol. II, p. 268.
- <sup>32</sup>S. T. Manson, Ph. D. thesis, Columbia University, New York, 1966 (unpublished).
- <sup>33</sup>H. Feshbach, Ann. Phys. N. Y., **5**, 357 (1958); **19**, 237 (1962).
- <sup>34</sup>See, for example, P. Burke and D. Moores, J. Phys. B **1**, 575 (1968); P. Burke, S. Ormonde, and W. Whitaker, *ibid.* **92**, 319 (1967); K. Smith, R. Henry, and P. Burke, Phys. Rev. **157**, 51 (1967); and Refs. therein.

## Kinematics and Dynamics of Nonlinear Mode Coupling

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A general treatment is given for the interaction of two propagating modes when they are nonlinearly coupled by a large-amplitude driving wave. The equations describing the space-time development of the mode amplitudes have a certain symmetry due to the constraints of small-signal energy conservation. The wave solutions, given the vector coupling relations ( $\omega_d = \omega_a \pm \omega_b$ ,  $k_d = k_a \pm k_b$ ), are of four possible types, depending on the signs of the energy densities and group velocities of the individual modes. The periodicity imposed by the driving wave is used to construct a spatial-temporal harmonic dispersion diagram in which these interactions are displayed. The results are then shown to be generalizations of the wave-wave couplings of linear theory.

### I. INTRODUCTION

Many wave-interaction phenomena in nature can be adequately described by coupled mode equations. In the case of linear or direct coupling, the four possible two-mode solutions have a well-known symmetry.<sup>1</sup> Lately, nonlinear wave-wave or "parametric" interactions have become a subject of much interest in plasma physics.<sup>2-5</sup> In many of the problems which have been treated, including those of the greatest experimental relevance, similar underlying mode-coupling symmetries operate. The following is a development of the form of these constraints.

The nonlinear effects which are to be described are those caused by the impression of a high-level driving wave, which, in relation to other low-level signal waves, may be considered to have a substantially constant amplitude. This assumption

allows a quasilinear treatment of the second-order terms in the equations. Under the common conditions of harmonic excitation and weak coupling these equations may be reexpressed in terms of the quiescent normal modes of the system with small intermode interaction coefficients. The treatment of this generalized class of dynamical equations in the linear case was conceived by Pierce<sup>6</sup> and is called the coupling-of-modes theory.

We will consider an extension of this theory in which a nonlinear interaction may be accurately described by the parametric coupling of two  $z$ -directed modes ( $a, b$ ). This coupling is effected by the impression of a driving or "pump" wave  $d$  satisfying [Fig. 1(a)] the Fourier-analysis vector relations

$$\omega_d \cong \omega_a + \Pi_d \omega_b, \quad k_d \cong k_a + \Pi_d k_b, \quad (1)$$

where all frequencies are positive and  $\omega_d \gg \omega_b$ . The