

from the experimental line scans and the uncertainty in its magnitude led to the uncertainties in  $\Delta E_P$  shown in Table I.

The contribution to the uncertainty of the rf power calibration was estimated to be  $\pm 0.02$  MHz. Other possible sources of error which were found to be negligible ( $<0.01$  MHz) were Doppler shift, time dilation, rf Stark shifts, stray electric fields, and residual magnetic fields.

Table I summarizes the results of each run. The weighted average result  $\Delta E_P = 59.22(14)$  MHz is in good agreement with the theoretical prediction of  $59.1501(1)$  MHz.<sup>9</sup> The experimental precision indicates that techniques of subnatural-linewidth spectroscopy can be successfully used for the measurement of unresolved features of atomic structure.

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## Electron Density at the Nucleus and the Lamb Shift of $^3P$ Levels of Two-Electron Ions\*

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The Lamb shifts of the  $2^3S$  and  $2^3P_1$  levels in He I and Li II have been calculated by a method of effective-oscillator-strength sums. The computed shifts are in a good agreement with experiment. For Li II, the theoretical Lamb shift of the  $2^3P_1$  level is  $+0.291 \pm 0.041$  cm<sup>-1</sup> to be compared with the experimental value of  $+0.230 \pm 0.060$  cm<sup>-1</sup> derived from the  $2^3S-2^3P_1$  interval measured by Bacis and Berry. A significant Lamb shift of  $^3P$  levels is attributed to an anomalously low electron density at the nucleus in these states.

Recently the author gave<sup>1</sup> a theoretical discussion of the Lamb shift in excited states of two-electron ions. Numerical calculations performed for the ions of nuclear charge  $Z \geq 4$  predicted a significant Lamb shift of  $^3P$  atomic levels. Independently, Berry and Bacis<sup>2</sup> reported hfs measurements which could suggest a similar effect in the singly ionized lithium atom. Since that time, high-resolution studies of the  $2^3S-2^3P$  transition have been accomplished<sup>3</sup> for  $^6,7\text{Li II}$ . The experiment shows a difference,

$$D_L^{\text{expt}} = -1.2547 \pm 0.0040 \text{ cm}^{-1}, \quad (1)$$

between the observed value of the  $2^3S-2^3P_1$  interval in  $^7\text{Li II}$  and that calculated by Accad, Pekeris, and Schiff<sup>4</sup> to order  $\alpha^2$  and corrected with re-

spect to the singlet-triplet mixing of the  $P$  states<sup>5</sup> as well as with respect to hf interactions.<sup>3</sup> Berry and Bacis estimate the Lamb shift of the  $2^3S$  level to be  $-0.99 \pm 0.04$  cm<sup>-1</sup>. This leaves the difference

$$D_L' = +0.2647 \pm 0.04 \text{ cm}^{-1} \quad (2)$$

to be accounted for.

The difference  $D_L'$  is appreciably bigger than an expected Lamb shift of  $\pm 0.007$  cm<sup>-1</sup> for a  $2p$  electron in the hydrogenic ion of  $Z=2$ . Therefore the suggestion that this difference can still be attributed to the Lamb shift of the  $2^3P_1$  level needs an independent justification. Berry and Bacis pointed out<sup>2</sup> that an underestimation of the  $S$  shift and a slow convergence of the method of

Accad, Pekeris, and Schiff<sup>4</sup> for nonrelativistic S states could be other possible explanations of the significant difference  $D_L'$ .

In this communication we shall discuss the effect and we shall find that  $D_L'$  is, in fact, in good agreement with the theoretical value of the  $2^3P_1$  Lamb shift obtained here.

*Electron density term.*—Following the notations used by the author earlier,<sup>1</sup> we shall write the Lamb shift  $E_l$  of the relativistic potential of ionization of a two-electron ion in a  $|nLSJ\rangle$  state as

$$E_{l,\alpha^3} = \delta E(nLS) - E_{L,2}''(nLS) - E_{L,2}'''(nLSJ), \quad (3)$$

where all corrections of orders  $Z^4\alpha^3$ ,  $Z^3\alpha^3$ , and  $Z^3\alpha^3 \ln\alpha$  have been included in (3) (energies are in rydbergs). The main contribution to the shift  $E_l$  comes from  $\delta E = \delta E_1 + \delta E_2$ :

$$\delta E_1 = - (8\alpha^3 Z^4 / 3\pi) [2 \ln(1/\alpha) + \frac{19}{30}] \Delta(Z) \quad (4)$$

and

$$\delta E_2 = - (\alpha^3 / 2\pi) [P(Q) - P(q)], \quad (5)$$

where

$$P(Q) = \sum_{Q'} F_{Q'Q} (E_{Q'} - E_Q)^2 \ln |(E_{Q'} - E_Q)| \quad (6)$$

is related to the hydrogenic ion with nuclear charge  $Z$ ,  $F_{Q'Q}$  being oscillator strengths for electric dipole transitions from the initial state  $|Q\rangle = |1s\rangle$  to all other states  $|Q'\rangle$  of the ion. The second term in (5) has an analogous meaning for the two-electron ion of the same  $Z$ ,  $|q\rangle$  being the initial state  $|nLS\rangle$ .

The electron density at the nucleus in the initial state  $|q\rangle$  of the two-electron ion is determined by  $\langle q | \delta^{(3)}(\vec{r}_1) | q \rangle$ . This quantity enters the term  $\delta E_1$ , formula (4), since the correlation function  $\Delta(Z)$  is given by

$$\Delta(Z) = 2\pi \langle q | \delta^{(3)}(\vec{r}_1) | q \rangle / Z^3 - 1. \quad (7)$$

The functions  $\Delta(Z)$  computed from the data of Ref. 4 for  $n^{1,3}S$  and  $n^{1,3}P$  states,  $n \leq 5$ , of the ions with  $Z \leq 10$  are presented in Fig. 1, scaled by a factor of  $n^3$ . It can be asserted that, for low  $Z$ , these functions differ considerably from the asymptotic values  $\Delta(\infty)$  for all but  $n^1P$  states.

In the case of  $n^{1,3}S$  and  $n^1P$  states,  $\Delta(Z) > 0$ , which corresponds to a regular situation when the electron density at the nucleus in a  $|q\rangle$  state of the two-electron ion is higher than that in the  $|1s\rangle$  state of the hydrogenic ion. For a positive  $\Delta(Z)$ , the term  $\delta E_1$ , formula (4), is negative and the resulting shift decreases the potential of ionization. For S states, the departure of  $\Delta(Z)$  from

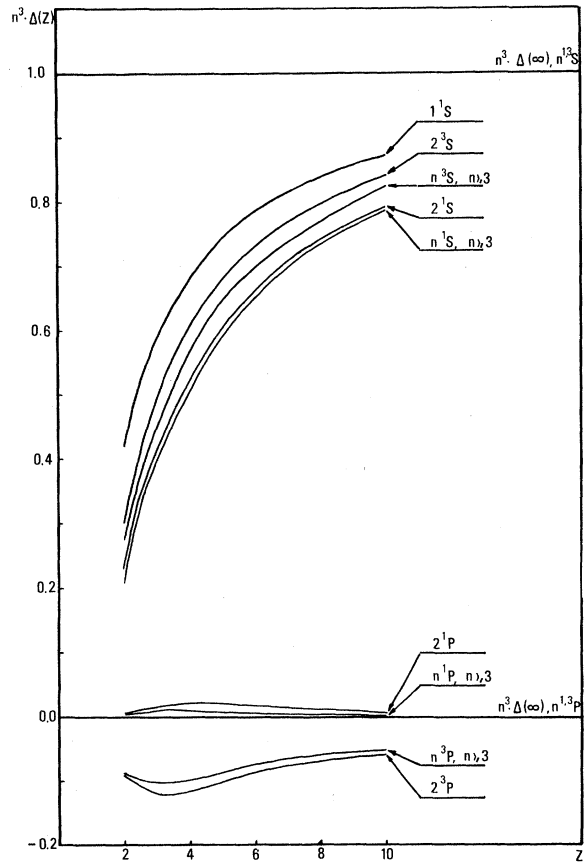


FIG. 1. The correlation functions  $n^3\Delta(Z)$  for  $n^{1,3}S$  and  $n^{1,3}P$  states of two-electron ions.

$\Delta(\infty)$  tends to diminish this effect.

The  $^3P$  states are a rather special case:  $\Delta(Z) < 0$ ; that is, the electron density at the nucleus is lower in these states than that in the  $|1s\rangle$  state of the hydrogenic ion. The function  $\Delta(Z)$  attains a minimum at  $Z \approx 3.5$  where its magnitude is about 25% of that for S states, instead of approaching the asymptotic value  $\Delta(\infty) = 0$ . This leads to a significant shift  $\delta E_1$  which increases the potential of ionization. We can expect that the behavior of functions  $\Delta(Z)$  of  $L > 1$  states will be similar to that of the P states.

For both S and P states of low  $Z$ , the electron-density term  $\delta E_1$  gives the main contribution to the total Lamb shift  $E_l$ . The term  $\delta E_2$ , depending upon the oscillator-strength sums, constitutes about 30% of  $\delta E_1$ .

*Effective-oscillator-strength sums.*—For calculation of two-electron oscillator sums (6) we shall use the following method. Let us assume that the initial state  $|q\rangle$  is given by

$$|q\rangle = 2^{-1/2} \mathcal{G}(1, 2) u_{1s}(1, Z_1) u_{nL}(2, Z_2) \quad (8)$$

and that

$$|q'\rangle = 2^{-1/2} \alpha(1, 2) \hat{C}(\beta, \gamma) |q\rangle u_\beta(1, Z_i) u_\gamma(2, Z_a), \tag{9}$$

where  $u_\beta(1, Z_i)$  is the hydrogenic function of electron 1 in a  $|\beta\rangle$  state for the Coulomb field of charge  $Z_i$ , and  $\hat{C}$  is a coupling operator for transitions from  $|q\rangle$  to  $|q'\rangle$ . The term  $\delta E_2$  given by (5) and (6) then becomes, for a fixed value of  $Z$ , a two-parameter function of  $Z_i$  and  $Z_a$ :

$$\delta E_2(Z_i, Z_a) = - (8\alpha^3 Z^4 / 3\pi) \times \{ \ln[K_0(1s)Z^2] - (Z_i/Z)^4 \ln[K_0(1s)Z_i^2] - (1/n^3)(Z_a/Z)^4 \ln[K_0(nL)Z_a^2] \pm A_L(Z_i, Z_a) \}, \tag{10}$$

$K_0(nl)$  being the Bethe average excitation energy of an electron in an  $|nl\rangle$  state with  $Z=1$ .

The last term in (10), that is  $A_L(Z_i, Z_a)$ , accounts for electron exchange. This term vanishes when  $Z_i = Z_a$ .

We specify the numerical values of  $Z_i$  and  $Z_a$  by the condition

$$S_k(Z_i, Z_a) = S_k(Z), \quad k=1, 2. \tag{11}$$

In this equation,  $S_k(Z)$  is the oscillator-strength sum  $\sum_{q'} f_{q',q} (\mathcal{E}_{q'} - \mathcal{E}_q)^k$  for the  $|q\rangle$  state of the two-electron ion. With  $|q\rangle$  being the *exact* wave function of the state, the sums  $S_k(Z)$ ,  $k=1, 2$ , are equivalent to the expectation values given by Eqs. (12) and (13) below, provided energies  $\mathcal{E}_q$  are expressed in rydbergs:

$$S_1(Z) = \frac{4}{3} \langle q | (\vec{p}_1 + \vec{p}_2)^2 | q \rangle, \tag{12}$$

$$S_2(Z) = (16\pi Z/3) \langle q | \delta^{(3)}(\vec{r}_1) + \delta^{(3)}(\vec{r}_2) | q \rangle. \tag{13}$$

The left-hand side of Eq. (11) denotes the expectation values (12) and (13), obtained with wave functions (8) and (9). The values of parameters  $Z_i$  and  $Z_a$  obtained from (11) are then used to compute the effective sum (10) which gives the contribution to the Lamb shift.

*Lamb shifts in He and Li<sup>+</sup>.*—I have computed Lamb shifts for  $n=2$ ,  $^3S$  and  $^3P$  states of He I and Li II. The numerical values of  $S_k(Z)$ , required for calculation of  $Z_i$  and  $Z_a$ , have been obtained from the expectation values of Ref. 4.

TABLE I. The S states of He I. Comparison of different computational methods for the shift  $\delta E = \delta E_1 + \delta E_2$  (in  $\text{cm}^{-1}$ ).

State	Present method with $A(Z_i, Z_a) = 0$	Direct summation over $ q'\rangle$
$1^1S$	-1.497	-1.475 ± 0.021 <sup>a</sup>
$2^1S$	-0.103	-0.119 ± 0.016 <sup>b</sup>
$2^3S$	-0.133	-0.129 ± 0.011 <sup>b</sup>

<sup>a</sup>Ref. 7.

<sup>b</sup>Ref. 8.

For neutral helium, the present method can be compared with previous calculations<sup>7,8</sup> of Lamb shifts in S states. Table I gives values of  $\delta E$  for  $1^1S$  and  $2^{1,3}S$  states of He, which have been obtained by the present method with the exchange terms  $A(Z_i, Z_a)$  being neglected in (10), (12), and (13). Comparison with calculations by Salpeter and Zaidi<sup>7</sup> and by Suh and Zaidi<sup>8</sup> shows that for low-lying S states the present method without exchange terms leads to  $\delta E$  which coincide, within the stated probable error, with the values of  $\delta E$  obtained by direct summation of the oscillator-strength terms.

In view of this, I have also neglected the exchange terms  $A(Z_i, Z_a)$  in my calculations of Lamb shifts for  $^3P$  states.<sup>9</sup>

The computed Lamb shifts to order  $\alpha^3$  are presented in Table II. The total shift  $E_I$  also includes

TABLE II. The Lamb shifts in triplet states of He I and Li II.  $E_I = \delta E_1 + \delta E_2 - E_{L,2}'' - E_{L,2}''' - E_{L,2}''''$ . All shifts are given in inverse centimeters.

Term	He I		Li II	
	$2^3S$ $Z_i = 2.012$ $Z_a = 1.126$	$2^3P_1$ $Z_i = 1.994$ $Z_a = 0.972$	$2^3S$ $Z_i = 3.023$ $Z_a = 2.114$	$2^3P_1$ $Z_i = 2.989$ $Z_a = 1.954$
$\delta E_1$	-0.224	0.070	-1.905	0.444
$\delta E_2$	0.091	-0.032	0.910	-0.155
$-E_{L,2}'' - E_{L,2}'''$	0.000	-0.001	0.000	-0.006
$-E_{L,2}''''$	-0.002	0.001	-0.030	0.008
$E_I$	-0.135	+0.038	-1.025	+0.291
$E_I(S-P)$	-0.173		-1.316	
Experiment	-0.175 ± 0.01 <sup>a</sup>		-1.255 ± 0.004 <sup>b</sup>	

<sup>a</sup>Ref. 10.

<sup>b</sup>Ref. 3.

the leading term

$$-E_{L,2}''' = -8\alpha^4 Z^5 \left(1 + \frac{11}{128} - \ln 2/2 + \frac{5}{192}\right) \Delta(Z) \quad (14)$$

of order  $\alpha^4$  which is a generalization of the term<sup>10</sup> for relativistic corrections to the Lamb shift in the one-electron ion to the case of a two-electron ion.

Comparison with experimental results for the  $2^3S-2^3P_1$  transition in  $\text{He I}^{11}$  and in  $\text{Li II}^3$  shows that inclusion of the Lamb shift of the  $P$  level is essential to bring the experimental and theoretical total shifts  $E_I(S-P)$  in agreement with each other. The  $J$ -dependent term  $-E_{L,2}'''$  contributes only 2% to the shift  $E_I(2^3P_1)$  so that the latter is determined, for low  $Z$ , mainly by correlation effects in  $\delta E_1$ .

For  $\text{Li II}$  the value  $E_{I,\alpha^3}(2^3S) = -0.995 \text{ cm}^{-1}$  confirms the estimate<sup>2</sup> by Berry and Bacis. The main uncertainty in the shift  $E_I(2^3S)$  is due to an error  $\eta_1$  in  $\delta E_2$ . We shall adopt  $\eta_1(2^3S) = \pm 0.040 \text{ cm}^{-1}$  stated in Ref. 2. The uncertainty  $\eta_2(2^3S)$ , due to terms of orders  $\alpha^4$  and  $\alpha^3(m/M)$  neglected in (14), is probably  $\pm 0.015 \text{ cm}^{-1}$ . The volume-isotope correction contributes about  $0.0008 \text{ cm}^{-1}$ .

For the  $2^3P_1$  state of  $\text{Li II}$ , no other calculations of the oscillator-strength sums  $\delta E_2$  are available. We shall obtain a crude estimate of the error  $\eta_1$  by assuming that the calculation of  $\delta E_2$  doubles the uncertainty brought in the term  $\delta E_2$  of  $2^1,^3S \text{ He}$  by the method of Suh and Zaidi.<sup>8</sup> This gives  $\eta_1(2^3P_1) = \pm 0.037 \text{ cm}^{-1}$ . The probable error  $\eta_2(2^3P_1)$  is  $\pm 0.004 \text{ cm}^{-1}$ , and the volume-isotope correction may definitely be neglected.

Within these estimates of uncertainties in the theoretical shifts, one obtains for  $^7\text{Li II}$

$$E_I(2^3S) = -1.025 \pm 0.055 \text{ cm}^{-1} \quad (15)$$

and

$$E_I(2^3P_1) = +0.291 \pm 0.041 \text{ cm}^{-1}. \quad (16)$$

The experimental value of the Lamb shift of the  $2^3P_1$  level is then found thus:

$$E_I^{\text{expt}}(2^3P_1) = E_I(2^3S) - D_L^{\text{expt}} \\ = +0.230 \pm 0.059 + \eta_3 \text{ cm}^{-1}, \quad (17)$$

where  $D_L^{\text{expt}}$  is given by (1) and  $\eta_3$  accounts for the uncertainty in the nonrelativistic position of the two levels, mainly of the  $2^3S$  level. Despite slow convergence of the Pekeris method for low-lying  $S$  states,<sup>12</sup> it appears that the Pekeris estimate

$\eta_3 = \pm 0.001 \text{ cm}^{-1}$  for  $2^3S \text{ Li II}$  is reliable. This brings us to

$$E_I^{\text{expt}}(2^3P_1) = +0.230 \text{ cm} \pm 0.060 \text{ cm}^{-1} \quad (18)$$

which is in good agreement with the theoretical value (16). I shall emphasize that the main error in the present experimental value (18) is due to the uncertainty in the theoretical value of the Lamb shift of the  $2^3S$  level.

For  $^1P$  states, the terms  $\delta E_1$  and  $\delta E_2$  are of comparable magnitude and opposite signs so that they nearly cancel each other. This results in a *small* total shift of the  $^1P$  level. Recent experiments<sup>13</sup> for two-electron ions of low  $Z$  support this conclusion.

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<sup>6</sup>Numerical values of the Lamb shifts reported in Ref. 1 for the ions of  $Z \geq 4$  correspond with  $Z_i = Z$ ,  $Z_a = Z - 1$ , and  $A(Z_i, Z_a) = 0$ . For  $Z < 4$ , this choice of the effective nuclear charges  $Z_i$  and  $Z_a$  brings in an error of 30% to the computed shifts  $\delta E$ .

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<sup>9</sup>For  $2^1,^3P$  states, the neglect of the exchange terms  $A(Z_i, Z_a)$  may lead to an error in  $\delta E_2$  which is bigger than that for  $2^1,^3S$  states. For instance, transitions  $1s2p \ ^1,^3P \rightarrow 2s6s \ ^1,^3S$  are not quite adequately represented in (10) unless the exchange terms are taken into account.

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