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Lamb Shifts in Two-Electron Atoms

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From an absolute wavelength measurement of the $2s\,^3S_1$-$2p\,^3P_1$ transition in ^{7}Li II we deduce a Lamb shift of 1.274 ± 0.015 cm^{-1}, compared with a theoretical value of 0.99 ± 0.04 cm^{-1} for the $2s\,^3S_1$ level. We suggest that the difference is due to a Lamb shift of the $2p\,^3P_1$ level and show that other measurements in isoelectronic two-electron spectra are in accord with this prediction.

INTRODUCTION

Measurements of Lamb shifts in two-electron atoms are difficult to make, primarily because the nondegeneracy of the ns, np excited states prohibits the applicability of microwave techniques. The principal existing measurements are by Herzberg[1] in He I and by Edlén and Löfstrand[2] in C V which have accuracies of about 10%. A summary of these measurements has been given by Accad *et al.*[3] The only accurate calculations of Lamb shifts in excited states of two-electron atoms are by Suh and Zaidi[4] for the $2s\,^{1,3}S$ states in He I. The recent calculations of the energies of such states by Accad *et al.*[3] include relativistic effects but exclude radiative corrections. Hence, through a direct energy-difference measurement, we can derive the differential Lamb shift of the two states involved. The best examples of such transitions are the $ns\,^{1,3}S$-$n'p\,^{1,3}P$ transitions with $n=n'$, where the Lamb shifts remain a significant fraction of the total energy difference. We shall describe an accurate measurement of the Lamb shift in such a transition with $n=2$ in ^{7}Li II, and compare our result with existing data in other two-electron atoms.

EXPERIMENT

The ^{7}Li II transition $2s\,^3S - 2p\,^3P$ at 5485 Å was excited in a liquid-nitrogen-cooled double-anode hollow cathode and observed in high resolution with a HYPEAC[5] spectrometer. The cathode walls were "dressed" with different compounds[6] (Li, Li_2CO_3, LiOH). The grating premonochromator was centered on, and transmitted light of, a single Fabry-Perot fringe, the two systems being scanned synchronously in wave number. A second Fabry-Perot, in parallel with the first, provided calibration fringes which were compared with a thorium standard source for the absolute wavelength measurements. Optically contacted spectrosil spacers ensured the necessary stability. Since the $2p\,^3P$ term of Li II is more than 65 V above the neutral lithium ground state, the excitation is very weak and the consequent light intensity is low. In addition, the transition is very wide (6.5 cm^{-1}), due to fine and hyperfine structures, and a single scan took approximately 12 h. The stability of the spectrometer, which was in a temperature-controlled box, was checked with the calibration fringes, compared to thorium spectra.

In this first work the absolute wavelength accu-

racy is limited by the low signal-to-noise ratio. Relative line positions are found to within 0.003 cm^{-1}, but the exploration time and source instability give possible absolute errors of less than 0.015 cm^{-1}. New measurements with steadier sources now in progress will reduce these errors to within 0.002 cm^{-1}.

RESULTS

Figure 1 shows the energy levels involved in this transition, which has been partially resolved previously by Herzberg and Moore.[7] Using photoelectric detection and higher resolution, we have been able to resolve most components directly and have obtained all level energies by an iterative least-squares fitting of the spectrum.

Since the components *a*, *b*, and *c* from $^3P_0(F=\frac{3}{2})$ shown in Fig. 1 are completely resolved, we have used their wave numbers in our measurement of the Lamb shift. The common upper level ($J=0$, $F=\frac{3}{2}$) is shifted by 0.027 cm^{-1} by the hyperfine mixing of the other levels of $F=\frac{3}{2}$. In this calculation we have used the off-diagonal matrix elements of the nuclear magnetic dipole interaction as introduced by Güttinger and Pauli,[8] and the theoretical fine structure including the singlet-triplet mixing of Ermolaev and Jones.[9] Our initial measurements of the fine-structure separations are in good agreement with the theory. We have used the magnetic hyperfine coupling constant $A=0.240\pm0.002$, recently measured by Berry *et al.*[10] with the beam-foil Fourier-transform spectroscopy technique, for which these measurements also show good agreement. The nuclear quadrupole moment of ^{7}Li is small,[11] and we estimate the consequent shift of the $^3P_0$ components to be 1.0×10^{-5} cm^{-1}, which may be neglected.

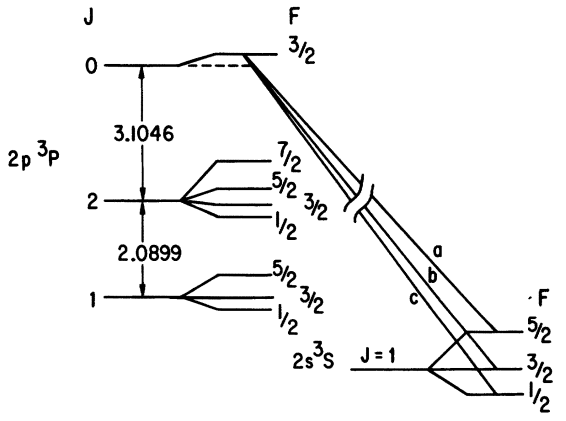

FIG. 1. Energy diagram for the $2s\,^3S$-$2p\,^3P$ transition complex (not to scale). The fine-structure separations are indicated in cm^{-1}. The small shift of the $J=0$ component by the hyperfine coupling is 0.027 cm^{-1}.

We then obtain for the wave-number difference

$$2s\,^3S_1\text{-}2p\,^3P_1 = 18\,226.093 \pm 0.015\ cm^{-1}, \quad (1)$$

to be compared with the theoretical value[3]

$$2s\,^3S_1\text{-}2p\,^3P_1 = 18\,227.367 \pm 0.001\ cm^{-1}. \quad (2)$$

The difference

$$D_L = -1.274 \pm 0.015\ cm^{-1} \quad (3)$$

should represent the Lamb-shift corrections to the two levels.

COMPARISONS WITH THEORY AND EXPERIMENT

Dalgarno[12] has estimated the Li II $2s\,^3S$ Lamb shift as 1.14 ± 0.1 cm^{-1}, in approximate agreement with experiment. To the authors' knowledge, no other calculations of this Lamb shift have been published. However, the calculations of Suh and Zaidi[4] for the Lamb shift of the $2s\,^3S_1$ state in He I can be used as a basis for Lamb-shift estimates in ions of the isoelectronic sequence. They show that the radiative corrections of order α^3Ry can be written as a sum of four terms, the first three of which were suggested earlier[13,14]:

$$I_L = E_{L1} - E_{L2} - E'_{L2} - E''_{L2}. \quad (4)$$

In the above equation,

$$E_{L1} = \frac{8}{3}Z^4\frac{\alpha^3}{\pi}\left(2\ln\frac{1}{Z\alpha} - \ln\frac{K_0}{Z^2} + \frac{19}{30}\right)\ \text{Ry}, \quad (5)$$

where K_0 is the average excitation energy of the one-electron ion ($K_0 = 19.77Z^2$),[15] and

$$E_{L2} = \frac{8}{3}Z\alpha^3\left(2\ln\frac{1}{\alpha} - \ln k_0 + \frac{19}{30}\right)2\langle\delta(\vec{r}_1)\rangle\ \text{Ry}, \quad (6)$$

where k_0 is the average excitation energy of the two-electron excited state. E'_{L2} is zero for the $2s\,^3S$ state and E''_{L2} is less than 10^{-4} of E_{L1} for all two-electron ions. Since our experimental accuracy is not better than one part in 10^3, E''_{L2} can be neglected.

In the limit of high Z, we can expect $k_0 \to K_0$. Already for He I ($Z=2$), k_0 is close to K_0; i.e.,

$$k_0(Z=2) = 79.84\ \text{Ry}, \quad K_0 = 79.08\ \text{Ry}; \quad (7)$$

therefore, as suggested by Bethe and Salpeter,[16] we have written

$$k_0(Z) = 19.77(Z+b)^2. \quad (8)$$

By fitting the calculated k_0 for $Z=2$, we obtain $b=0.009$.

The expectation value of $\delta(\vec{r}_1)$ is given by Accad *et al.*[3], and the resulting value for the Lamb shift of Li II is

$$I_S = -0.99 \pm 0.04\ cm^{-1}. \quad (9)$$

The error limit is three times the change in I_S in replacing k_0 by K_0.

The difference of D_L from Eq. (3) and I_S from Eq. (9) is significant, and we suggest that it is due to the Lamb shift of the $2p\ ^3P_1$ level, which is thus shifted downward in energy by

$$I_P = 1.274 - 0.99 = 0.28 \pm 0.05\ \text{cm}^{-1}. \quad (10)$$

A calculation of I_P does not exist for any two-electron atom, and would be difficult to perform primarily because evaluation of k_0 involves summations over all electric dipole transitions from $2p\ ^3P$ to discrete and continuum states. We should note that this p-state contribution to the $2s$-$2p$ Lamb shift (~20%) is much larger than that found in one-electron systems, where it is only about 2%.

In the absence of a theoretical verification of a $2p\ ^3P$ Lamb shift, we have tested our value against previous measurements in two-electron atoms. We assume that the $np\ ^3P$ Lamb shifts scale as Z^4/n^3. This is a reasonable assumption, since both E_{L1} and E_{L2}, apart from the logarithmic terms, closely follow this scaling law. The $2s\ ^3S$ Lamb shifts are calculated using k_0 defined by Eq. (8) and using a $1/n^3$ scaling law for $n \neq 2$. The comparisons are given in Table I.

A measurement by Herzberg and Moore[7] of the energy of the $2p\ ^3P$-$3s\ ^3S$ transition in Li II shows better agreement with the theory when the $2p\ ^3P$ Lamb shift is included.

In He I, the best experimental wave number for the $2s\ ^3S$ - $2p\ ^3P$ transition is from Meggers and Humphreys.[17] They provide no estimate of the precision, but it can be expected to be approximately $\pm 0.010\ \text{cm}^{-1}$. There appears to be definite evidence for a $2p\ ^3P$ Lamd shift with the value

$$I_P(\text{He I}) = 0.046 \pm 0.023\ \text{cm}^{-1}, \quad (11)$$

in good agreement with the scaled value of 0.051 cm^{-1}. The residual Lamb shifts of other transitions are compared in Table I, and although the precision is not as good, the shifts agree quantitatively with the adjusted theory. The unresolved fine structure has been accounted for by assuming statistical populations, but the limiting precision in these cases comes from the calculations of Accad *et al.*[3]

Table I also shows that a $2p\ ^3P$ Lamb shift in B IV and C V improves the agreement between theory and experiment.

It appears from the wave-number differences of the $2s\ ^1S$ - $2p\ ^1P$ transitions in He I and C V that the $2p\ ^1P$ Lamb shift may be much smaller than the $2p\ ^3P$ Lamb shift.

CONCLUSIONS

We have shown that our measured Lamb shift of $-1.274 \pm 0.015\ \text{cm}^{-1}$ in the $2s\ ^3S$ - $2p\ ^3P$ tran-

TABLE I. Lamb shifts in two-electron atoms.

Transition	Wave-number difference[a] between theory and experiment (cm^{-1})	Calculated Lamb shift (cm^{-1})		
		S state[b]	*P* state[c]	Total
Li II $2s\ ^3S_1$-$2p\ ^3P_1$	-1.274 ± 0.015	-0.99 ± 0.04	0.28	−1.27
$2p\ ^3P_1$-$3s\ ^3S_1$	0.46 ±0.10	−0.29	0.28	0.57
He I $2s\ ^3S_1$-$2p\ ^3P_1$	-0.175 ± 0.010	-0.129 ± 0.013[d]	0.051	−0.180
$2s\ ^3S_1$-$3p\ ^3P_1$	-0.148 ± 0.02	−0.129[d]	0.016	−0.145
$2s\ ^3S_1$-$4p\ ^3P_1$	-0.156 ± 0.02	−0.129[d]	0.006	−0.135
$2s\ ^3P_1$-$3s\ ^3S_1$	-0.083 ± 0.01	−0.039	0.051	−0.090
$2s\ ^1S_0$ - $2p\ ^1P_1$	-0.096 ± 0.01	-0.106 ± 0.018[d]	...	...
B IV $2s\ ^3S_1$-$2p\ ^3P_1$	−10.7 ±1	−7.71	2.16	−9.87
C V $2s\ ^3S_1$-$2p\ ^3P_1$	−21.6 ±1	−16.6	4.5	--21.1
$2s\ ^1S_0$-$2p\ ^1P_1$	−16 ±4	−12.8	...	...
Be III $2s\ ^3S_1$-$2p\ ^3P_1$	−4.2 ±0.2[e]	−3.16	0.88	−4.04

[a] Theoretical wave numbers are taken from Accad *et al.* (Ref. 3). Experimental wave numbers are taken from W. C. Martin, J. Res. Natl. Bur. Stand. (U.S.) 64, 19 (1960), for He I; from B. Edlén, Ark. Fys. 4, 441 (1952), for B IV; and from Edlén and Löfstrand (Ref. 2) for C V. For Li II, see text.

[b] From calculations in the text, except where otherwise indicated.

[c] Values are scaled as Z^4/n^3, based on the difference between the experimental total Lamb shift and the calculated $2s\ ^3S$ Lamb shift in the Li II $2s\ ^3S_1$-$2p\ ^3P_1$ transition.

[d] Suh and Zaidi (Ref. 4).

[e] *Footnote added in proof.* The authors thank B. Löfstrand for these results [private communication; Phys. Scr. (to be published)].

sition of Li II can be expressed as the sum of a Lamb shift in the $2s\,^3S$ state of -0.99 cm^{-1} and a Lamb shift in the $2p\,^3P$ state of $+0.28$ cm^{-1}. Previous measurements in other transitions in two-electron atoms verify our predictions.

Although the ^3P Lamb shifts produce good agreement between theory and experiment, we must admit the possibility of two other explanations for the observed Lamb shifts. The first is an increase of the theoretical $ns\,^3S$ Lamb shifts by 20%. This is unlikely, especially for the $2s\,^3S$ state of He I, where the estimated precision of Suh and Zaidi[4] is 10%. However, a similar discrepancy arises in the $1s^2\ ^1S$ Lamb shift of C V, as pointed out by Edlén and Löfstrand.[2] The observed Lamb shift is -178 ± 30 cm^{-1}, while theory[18] gives -132 cm^{-1}. The discrepancy could be considered as just within the bounds of the combined experimental and theoretical error limits. This leads us to another possible source of error. The total energies of the S states of two-electron atoms, as calculated by Pekeris[18] and Accad *et al.*[3] might be too high—by this small factor, which is proportional to Z^4/n^3, thus creating a spurious S-state "Lamb shift."

The principal exception to these last two possibilities is the close agreement between theory and experiment for the $2s\,^1S - 2p\,^1P$ transition in He I, and to a lesser extent in C V. The most reasonable explanation is to assume a very small Lamb shift for the ^1P terms.

A calculation of the $2p\,^3P$ Lamb Shift in He I and Li II would be invaluable for comparison with experiment. We hope to improve our precision for the measurements in Li II and also to remeasure the $2s\,^3S - 2p\,^3P$ transition in He I.

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Nuclear-Charge-Expansion Method for $(2s^a 2p^b - 2s^{a-1}2p^{b+1})$ Transitions*

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The nuclear-charge-expansion method is used to calculate the radiative probabilities of the dipole transitions $2s^a 2p^b - 2s^{a-1}2p^{b+1}$ of ionic systems. An extensive comparison with more-elaborate calculations and with experimental data shows that after a few stages of ionization the method gives results of uniformly high accuracy.

I. INTRODUCTION

The nuclear-charge-expansion method has been used by several authors to calculate atomic transition probabilities for isoelectronic sequences. Precise calculations performed so far have been limited to the helium[1-3] and lithium[4-5] sequences, although other systems have been examined in the Hartree-Fock approximation.[6-8] The Hartree-Fock approximation gives the leading term in the expansion of the transition probability in powers of Z^{-1} correctly, but not the second term. The second term can be calculated exactly provided zero-order mixing does not occur. In this paper