

Isotope Shift in the First Spectrum of Atomic Lithium*

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The isotope shift in Li I has been studied in the hollow cathode spectrum from separated isotopes with the aid of a Fabry-Perot interferometer. Specific shifts have been determined for the $2s$, $2p$, $3s$, $3p$, $3d$, $4s$, $4d$, $5s$, and $5d$ levels. The inadequacy of the Hughes-Eckart approximation is pointed out.

I. RESUMÉ OF THEORY

THE isotope shift in the atomic spectra of light elements is considered to result exclusively, within the limits of measurements, from the finite mass of the nucleus. Hughes and Eckart¹ were the first to treat mass effects in atoms with more than one electron. Relativistic and nuclear structure effects being neglected, the expression for the kinetic energy of an atom with a nucleus of finite mass differs from that of an atom with the same charges and an infinite mass nucleus by the additional terms $(2M)^{-1}(\sum p_i^2 + \sum' p_i \cdot p_j)$, where M is the nuclear mass and p_i the momentum of the i th electron, and \sum' means sum only over pairs $i \neq j$. The coordinates are measured relative to the nucleus.

The first sum results in the normal mass effect, which contracts the energy level spectrum of the atom with the finite mass nucleus by the ratio of the reduced mass to the electronic mass. The second sum is the specific mass effect, the expectation value of which must be calculated. Hughes and Eckart, using linear combinations of products of hydrogen-like wave functions as their approximation and neglecting interconfiguration mixing, calculated the specific mass effect for two- and three-electron spectra. In their approximation the specific shift occurs only for those configurations that have electrons differing by unity in l -value, e.g., among the lightest atoms, for p -terms only.

II. EXPERIMENTAL APPARATUS

The light sources used throughout were liquid air-cooled hollow cathode discharge tubes of the Mack-Arroe design.² Separated isotopes³ with abundance 99.91 and 95.4 percent of Li⁷ and Li⁶, respectively, were used. Resolution was obtained by crossing a Fabry-Perot interferometer with a special Hilger constant-deviation spectrograph or a Bausch and Lomb medium quartz spectrograph.

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¹ D. S. Hughes and C. Eckart, *Phys. Rev.* **36**, 694 (1930).

² O. H. Arroe and J. E. Mack, *J. Opt. Soc. Am.* **40**, 386 (1950).

³ Obtained on loan from the Y-12 plant, Oak Ridge National Laboratory, on AEC allocation.

III. TREATMENT OF DATA

In this paper, the whole shift of each level is assumed to consist of only two parts: the normal mass effect, which can be calculated with negligible uncertainty, and the specific mass effect. Thus, for each line, the observed total shift minus the calculated normal mass shift is considered to be the "observed specific mass shift", which must be the difference between the specific mass shifts of the two levels.

The following sign convention is used: For a line, the normal shift is positive; for a level, positive shift implies the relative depression of the heavier isotope, the matching point being the series limit, Li II $1s^2 \ ^1S_0$.

The magnitude of the specific shift of a level considered as a member of a series, is assumed to be a monotonically decreasing function of the principal quantum number, if the levels are arbitrarily matched at the series limit. (The behavior of the shifts in the line series $2p$ - ns and $2p$ - nd will be seen below to tend to justify this assumption.) The consequent asymptotic vanishing of the shift is used as a criterion to fix the otherwise undetermined zero point for the shift of the common level.

No account has been taken of the hyperfine structure splitting of the lines, which, being in every case less than the Doppler width, has not been observed and is believed not to have affected the measurements appreciably.

The presence of the weaker isotope (4.6 percent of Li⁷ in Li⁶, and 0.09 percent of Li⁶ in Li⁷) has been neglected; this we believe to be fairly safe, since none of our lines was overexposed.

Wave numbers are measured in kaysers, K ($1\text{K} \equiv 1\text{ cm}^{-1}$), and shifts in millikaysers, mK.

The errors in this work, indicated by the \pm sign, are estimated limit (high-confidence) errors.

IV. RESULTS

The experimental results of the work, some of which have been reported upon,⁴ are shown in Table I. In the transition $2s$ - $2p$ at $\sigma = 14\,904\text{ K}$ ($\lambda = 6708\text{ \AA}$) it was found, in disagreement with Jackson and Kuhn,⁵ that within the limits of error of $\pm 3\text{ mK}$, there is no isotopic

⁴ R. H. Hughes, *Phys. Rev.* **91**, 457(A) (1953); **95**, 621(A) (1954).

⁵ D. A. Jackson and H. Kuhn, *Proc. Roy. Soc. (London)* **A173**, 278 (1939).

TABLE I. Observed doublet separation and isotope shift of lithium lines (in mK).

Transition	σ (K)	Separation ^a	Observed shift ^a	Normal shift	Residual shift ^a	H ^b	Previously observed shift		Mc ^e
							JK ^c	MMS ^d	
2s-2p	14 904	337 ±3	+350.9± 3	+194.0	+156.9± 3	+347	{+345 ₁ +365 ₁ }	(+356±2) ₁	f
2s-3p	30 925	g	+482.7±15	+402.5	+ 80.2±15	+555			
2p-3s	12 302	336.8±2	+ 30.6± 2	+160.1	-129.5± 2				
2p-3d	16 379	302.7±3 ^e	+ 92.0± 3	+213.2	-121.2± 3	h			
2p-4s	20 108	336 ±3	+140.3± 3	+261.7	-121.4± 3				
2p-4d	21 719	322.8±4 ^e	+163.8± 4	+282.7	-118.9± 4				
2p-5s	23 396	336 ±4	+186.1± 4	+304.5	-118.4± 4				
2p-5d	24 191	327.8±4 ^e	+195.8± 4	+314.8	-119.0± 4				

^a The digit after the decimal point is carried along for computational purposes although its significance is slight.

^b D. S. Hughes, Phys. Rev. **38**, 857 (1931).

^c See reference 5.

^d See reference 6.

^e J. R. McNally, Jr., Am. J. Phys. **20**, 152 (1952).

^f Identical with the doublet separation.

^g Fine structure unresolved or only partly resolved.

^h Undetected.

difference in the 2p doublet separation, i.e., the isotope shift has no dependence upon the total angular momentum, J . (In agreement with our finding, there appears to be no place in the theory for the fine structure to be so strongly mass-dependent.)

The specific shift data for the levels are gathered in Table II. The values in the line series 2p-ns and 2p-nd converge to -119 ± 4 mK, which is therefore assigned to the 2p-levels. With this assignment to start with, the specific shift values for the remaining levels are determined.

The observed specific s - and p -shifts are approximately $+1.4\times 10^{-1} \text{ K}\times n_{\text{eff}}^{-2.8}$ and $-6.4\times 10^{-1} \text{ K}\times n_{\text{eff}}^{-2.5}$, respectively, where $n_{\text{eff}}=(\text{Rydberg constant})^{\frac{1}{2}}(\text{term value})^{-\frac{1}{2}}$. The exponents are equal, well within the limits of error. It is not evident *a priori* that such a simple relationship should occur.

The doublet separations in all our measured members of the sharp series, including the first member of the principal series, agree with the atomic-beam values of both Jackson and Kuhn⁶ (337.2 ± 0.5 mK) and Meissner, Mundie, and Stelson⁶ (336.6 ± 0.5 mK), within our larger (and differently specified—see Sec. III) uncertainty.

The 2p-nd transitions confirm the values of Meissner, Mundie, and Stelson for the 3d, 4d, and 5d doublet

TABLE II. Observed and calculated specific shift in Li I levels (in mK).

n	$ns\ ^2S$		$np\ ^2P$			$nd\ ^2D$	
	Obs	Calc HE ^a	Obs	HE ^a	Calc b	Obs	Calc HE ^a
2	+38±7	0	-119± 4	-80	-90		
3	+11±6	0	- 42±22		-24	+2±7	0
4	+ 3±7	0				0 ^c	0
5	0 ^c	0				0 ^c	0

^a See reference 1.

^b Calculated with modern mass values of the atomic masses, and using Morse-Young-Haurwitz functions [Phys. Rev. **48**, 948 (1935)] (with Z_1, Z_2 extrapolated to 2.69, 1.00 for 3p).

^c Bases for the assignment of the 2p-shift.

⁶ Meissner, Mundie, and Stelson, Phys. Rev. **74**, 932 (1948); erratum, **75**, 891 (1948).

separations. Although the 2D structure was not resolved, the splittings can be calculated from the quantum-statistical weights as 38 ± 4 mK, 16 ± 5 mK, and 10 ± 5 mK, respectively. Here Meissner's 2p doublet separation value of 336.6 ± 0.5 mK has been used. The 3p 2P structure was unresolved, a circumstance which accounts for the large uncertainty in the 3p-shift.

V. DISCUSSION

It would be difficult to find an explanation for the s -shifts outside of the specific mass effects. The field effects give a shift in the opposite direction, which is commonly expected to be very small in any case, for such light nuclei. (The nuclear volume effect would give the correct sign only if the Li⁶ nucleus were the larger.) We are led to question the validity of the Hughes-Eckart approximation for the wave function. It is interesting to note the effect on the calculated specific shift for He I of improved wave functions. Fred, Tompkins, Brody, and Hamermesh⁷ point out that, although their use gives finite values for s -shifts, they are at this stage hardly adequate to explain the experimental values.

Burke⁸ has found a large departure from the Hughes-Eckart calculation in the resonance line 2s-2p of the lithium-like spectrum B III. The discrepancy is in the normal effect direction and can be at least partially explained by a positive shift in the 2s level.

The calculated specific shifts in the 2p and 3p levels in Li I are too small by factors of about 3/4 and 4/7, respectively, which would not bear out the expectation of the relative improvement of the Hughes-Eckart approximation with increasing n ; but the large uncertainty in the 3p-shift prevents a final conclusion now concerning this n -dependence.

The evidence is overwhelming against the adequacy of the Hughes-Eckart approximation. If the present

⁷ Fred, Tompkins, Brody, and Hamermesh, Phys. Rev. **82**, 406 (1951).

⁸ E. Burke, following paper [Phys. Rev. **100**, 1839 (1955)].

theory of the isotope shift in the light elements is complete, the agreement between calculation and experimental observation should improve as more adequate wave functions are used in the specific mass calculations. As pointed out by Mack *et al.*,⁹ such studies of the specific mass effect should prove to be useful in checking the accuracy of the wave functions adopted for the light elements.

⁹ Bernarda, Burke, Burnett, Hughes, and Mack, Rydberg Conference, Lunds University Årsskrift 50:21, 1954 (unpublished), p. 88.

Gailer¹⁰ reports that three lines in the lithium spectrum, at 3303 Å, 3650 Å, and 3720 Å, remain to be classified. We believe all three lines to be spurious. A probable explanation for at least two of these lines lies in the list of the persistent lines of the elements. The second member of the principal series of sodium lies at 3303 Å and the ultimate line of Fe I (iron was present in Gailer's system), at 3720 Å. The other line, at 3650 Å, could possibly be from Hg I.

¹⁰ K. Gailer, *Ann. Physik.* **126**, 583 (1949).

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Isotope Shift in the First Three Spectra of Boron*

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Isotope shifts have been observed in the first three spectra of boron, with separated isotopes. On the assumption that the total observed shift consists only of the (exactly calculable) normal mass effect and a specific mass effect, the results are as follows (a positive sign indicating a shift of B¹¹ toward the violet relative to B¹⁰):

	Total shift	$\frac{\Delta\sigma_{s, \text{obs}}}{\Delta\sigma_{s, \text{calc}}}$ (approx)
B I $1s^2 2s^2 2p^2 P_{\frac{1}{2}, \frac{3}{2}} - 1s^2 2s^2 3s^2 S_{\frac{1}{2}}$	$\begin{cases} -137 \pm 12 \text{ mK} \\ -139 \pm 6 \text{ mK} \end{cases}$	1.0 or 0.9,
B II $1s^2 2s 2p^2 P_1 - 1s^2 2p^2 D_2$	$+867 \pm 26 \text{ mK}$	1.3,
B III $1s^2 2s^2 S_{\frac{1}{2}} - 1s^2 2p^2 P_{\frac{1}{2}, \frac{3}{2}}$	$\begin{cases} +1170 \pm 120 \text{ mK} \\ +1210 \pm 90 \text{ mK} \end{cases}$	1.4,

where the calculated specific shift, $\Delta\sigma_{s, \text{calc}}$ is based on hydrogen-like wave functions of the Hughes-Eckart type.

I. INTRODUCTION

HUGHES and Eckart¹ inaugurated the theoretical study of the isotope shift in light polyelectronic atoms in 1930. Hughes² at the same time made an experimental determination for lithium, but the work was done without the benefit of separated isotopes and the experimental results were not sufficient for a close check with theory. The conclusion was that the agreement was reasonable. Hughes³ has recently investigated the isotope shift in neutral lithium with separated isotopes and found that observations give specific shifts larger than the calculated values.

The current investigation of boron was initiated to consider another three-electron system, B III. The only lines available are those of the resonance doublet at 48 392/58 K (kaysers, $1 \text{ K} = 1 \text{ cm}^{-1} = 10^3 \text{ mK}$), 2066/7 Å,

$1s^2 2s^2 S_{\frac{1}{2}} - 1s^2 2p^2 P_{\frac{1}{2}, \frac{3}{2}}$. The studies have been extended to repeat Mrozowski's⁴ measurements, which he made with unseparated isotopes, on the B II line 28 966 K (3451 Å), $1s^2 2s 2p^2 P_1 - 1s^2 2p^2 D_2$, and the B I doublet at 40 040/24 K (2497/8 Å), $1s^2 2s^2 2p^2 P_{\frac{1}{2}, \frac{3}{2}} - 1s^2 2s^2 3s^2 S_{\frac{1}{2}}$. The B II $1s^2 2p^2 D_2 - 1s^2 2s 3p^2 P_1$ line was not excited in our sources. Calculations have been made for the B I lines by Opechowski and Devries⁵ and by Vinti.⁶ A calculation for the B II line has been made by Vinti.⁶ Hughes' paper³ contains a brief outline of the theory.

II. EXPERIMENTAL

For excitation of the B III spectrum a special high-excitation, sharp-line source was required. The resonance doublet has been previously observed only in the hot spark, but high voltages in a highly condensed discharge could not be used since that would have produced broadened lines. A compromise was effected with a condensed-hollow-cathode source. The tube itself was

* Supported by the Office of Naval Research and the Office of Ordnance Research.

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¹ D. S. Hughes and C. Eckart, *Phys. Rev.* **36**, 694 (1930); the last equation on page 697 should be labeled "(13)".

² D. S. Hughes, *Phys. Rev.* **38**, 857 (1931).

³ R. H. Hughes, preceding paper [*Phys. Rev.* **99**, 1837 (1955)].

⁴ S. Mrozowski, *Z. Physik* **112**, 223 (1939).

⁵ W. Opechowski and D. A. Devries, *Physica* **6**, 913 (1939).

⁶ J. P. Vinti, *Phys. Rev.* **58**, 879 (1940).