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The Isotope Displacement in Hyperfine Structure

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With Goudsmit's extension of Landé's formula for $(\overline{1/r^3})$ it is possible to explain the order of magnitude of the isotope displacements in Hg, Tl, Pb arc and spark spectra on the hypothesis of small changes in nuclear radii. The nuclear radius is supposed to be proportional to the 1/3 power of the atomic weight. The effective nuclear charge is supposed to be distributed with a roughly uniform density through the interior of the nucleus. The spectra Hg I, Hg II, Tl I, Tl II, Pb II, are in agreement with the above theory. The larger displacements are due to the addition or removal of a $6s$ or $7s$ electron to the electron configuration. The direction of the shift is in agreement with the supposition that the nuclear radius increases with atomic weight, the heavier isotope having the looser binding for the s and $p_{1/2}$ electrons. In order to explain the shifts of the $6p^2$, $6p7s$, $6p8s$, $d6p$, $6p8p$ configurations of PbI it is supposed that in this case the displacements are due principally to changes in the penetration to the nucleus of the $6s^2$ subgroup. These changes are presumably caused by differences in screening of the two $6s$ electrons from the nucleus as the valence electron is excited from the $6p$ state to the ionization limit.

THE elements Hg, Tl, Pb show in their hyperfine structure a number of components which are ascribed to the different isotopes of these elements. The observed displacements are considerably larger than would be expected according to the simple mass correction to the Rydberg formula given by the factor $(1+m/M)^{-1}$. The suggestion has been made that these isotope displacements are due to deviations of the electric field of the nucleus from the inverse square law. Calculations by Racah[1] and also by Rosenthal and the writer[2] indicated however that on such a hypothesis the displacement would be expected to be several times larger than that observed. In addition, in the case of Tl, it appeared impossible[2] to reconcile the observed direction of the displacement in the spark with that in the arc spectrum.

It has since been found possible to interpret the troublesome terms of Tl in such a way that the direction of the displacement in its arc and spark spectrum fits in with that observed in Hg and Pb. For these three elements, the large displacements can be attributed consistently to differences of binding of s electrons and particularly those of the deeply penetrating $6s$ electron. It was furthermore found that a simple formula used by Goudsmit[3] in the calculation of hyperfine structure separations gives in these cases smaller values for the probability of finding an electron at the nucleus than the numerical calculations of Racah which have been used by Rosenthal and the writer as well. It appears possible that the numerical calculations may be sub-

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[1] G. Racah, Nature **129**, 723 (1932).

[2] J. E. Rosenthal and G. Breit, Phys. Rev. **41**, 459 (1932).

[3] Pauling and Goudsmit, *Structure of Line Spectra*. See also J. C. McLennan, A. B. McLay and M. F. Crawford Proc. Roy. Soc. **A133**, 652 (1931).

ject to cumulative errors and it is at all events of interest that Goudsmit's application of the Landé formula for $\overline{(1/r^3)}$ leads to a reasonable agreement of the expected and observed isotope displacements.

In order to obtain an expression for the square of the Shroedinger function at $r=0$ we use Landés approximate formula

$$l(l+1)\overline{\left(\frac{1}{r^3}\right)} = \frac{R\alpha^2 Z_i Z_0^2}{\mu_0^2(2l+1)n_0^2} \tag{1}$$

where l is the azimuthal quantum number, R the energy corresponding to the Rydberg constant, $\alpha = 2\pi e^2/hc$, μ_0 is the Bohr magneton, Z_i is the effective nuclear charge in the inner part of the orbit, Z_0 is the effective charge in the outer part of the orbit and n_0 is the effective quantum number defined by equating the term energy to $-R\, Z_0^2/n_0^2$. This formula has been derived by Landé by means of classical considerations with penetrating orbits. One may expect it, however, to be at least qualitatively correct also in quantum mechanics. For s terms the meaning of the left side of (1) is known to be[4]

$$\overline{l(l+1)r^{-3}} = 2\pi\psi^2(0) \tag{2}$$

so that

$$\psi^2(0) = \frac{Z_i Z_0^2}{\pi a_H^3 n_0^3} = 2.16 \times 10^{24}\frac{Z_i Z_0^2}{n_0^3}\ \mathrm{cm}^{-3} \tag{3}$$

where a_H is the Bohr radius. It will be noted that *for Coulomb fields Eq. (3) is exact.* The fact that for $l=0$ the left side of (2) is indeterminate does not concern us because in the relativistic theory of hyperfine structure this expression is replaced by one having a perfectly definite meaning. Also Eq. (3) may be interpreted along the lines of Landé's penetrating orbits by regarding $(Z_0/Z_i)^2/n_0^3$ as the factor by which the normalization constant in the region of effective nuclear charge Z_i is decreased on account of the presence of the region with effective nuclear charge Z_0. Thus (3) is a reasonable approximation. We do not pretend, however, to regard it as exact and the ultimate test of its validity lies in comparing it with accurate numerical calculations. Computing $\psi^2(0)$ for the normal states of the alkalies by means of (3) we have the following comparison (Table I) with values of $\psi^2(0)$ obtained by means of numerical calculations of the eigenfunctions:

TABLE I.

Element:	Na	Cs	Rb
$\psi^2(0)$ by (3):	5.6×10^{24}	1.8×10^{25}	1.4×10^{25}
$\psi^2(0)$ according to Fermi[5]:	2.4×10^{24}	2.7×10^{25}	0.88×10^{25}
$\psi^2(0)$ according to Nile:		$1.7(5)\times10^{25}$	

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[4] G. Breit, Phys. Rev. **37**, 51 (1931).

[5] E. Fermi, Zeits. f. Physik **60**, 320 (1930).

For the lighter elements $\psi^2(0)$ is smaller when computed numerically. For Cs the very careful as yet unpublished calculations of Nile agree very well with (3) while Fermi's value is appreciably higher.

It will be seen that in the case of Tl the comparison of the magnitude of the hfs splitting of the $7s$ state is in much better agreement[6] with that of the $6p_{1/2}$ using (3) than the numerical calculations of $\psi^2(0)$ for this state made by Racah. One may regard the hfs splitting as an empirical determination of $\psi^2(0)$ and it appears that this determination fits in with the magnitude of the isotope shift and with the value for $\psi^2(0)$ obtained by means of (3).

In mercury the isotope displacement has been observed both for the spark and the arc spectra. In the spark spectrum Schüler and Jones[7] arrive at an interpretation according to which the largest displacement is that of the $^2D_{5/2}$ term belonging to the $5d^9\ 6s^2$ configuration. The other terms belong to the $5d^{10}\ 6s$, $5d^{10}\ 6p$, $5d^{10}\ 7s$ arrangements. The displacement between Hg^{204} and Hg^{202} is 0.52 cm^{-1} and it is significant that the energy of Hg^{204} is higher than that of Hg^{202}. This shows that a change of an electron from the $5d$ to the $6s$ state produces a larger energy increase in Hg^{204} than in Hg^{202}. The $6s$ electron may be thus thought of as less tightly bound in Hg^{204} than in the lighter isotopes. Similarly in the arc spectrum[8] of Hg the largest displacement is assigned to $6s^2\ {}^1S_0$, the shift between Hg^{204} and Hg^{202} being 0.15 cm^{-1} while that between Hg^{201} and Hg^{199} is reported to be 0.21 cm^{-1}. The direction of the shift is again such that Hg^{204} has the highest energy. The $6s\ 7s$ configuration also shows a shift in the same direction but of a smaller magnitude, the displacement between Hg^{204} and Hg^{202} being 0.03 cm^{-1} both in the $^1S_0$ and $^3S_1$ states.

It has been observed by Shenstone and Russell[9] that the large displacement of the ^1P terms of this spectrum finds a natural interpretation in a perturbation of these terms by the $5d^9\ 6s^2\ 6p$ configuration. In particular the $8\ {}^1P_1$ term[9] shows an isotope displacement of practically the same amount as the $6s^2\ {}^1S_0$ term. The direction of the displacement is again the same and corresponds to a tighter binding of the $6s$ electron in the lighter isotope.

For Tl it appeared at first difficult[2] to interpret the displacement in terms of nuclear fields because the directions of the shift in the spark and arc spectrum did not agree. A further examination of the data[10] showed that the terms with large displacements are the X_2 and the term previously designated as $6s\ 7p\ {}^1P_1$. According to McLennan and Crawford[11] this designation is incorrect and it is therefore called by them $1_1{}^0$. In this term as well as in X_2 the lighter isotope Tl^{203} has a tighter binding between the electrons and the nucleus than Tl^{205}. The analogy between this and Hg suggests that X_2 and $1_1{}^0$

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[6] This has been observed first by Goudsmit who kindly informed the writer of the fact.

[7] H. Schüler and E. G. Jones, Zeits. f. Physik **76**, 14 (1932), see Fig. 1, p. 17.

[8] H. Schüler and J. E. Keyston, Zeits. f. Physik **72**, 423 (1931), see Fig. 16, p. 438. H. Schüler and E. G. Jones, Zeits. f. Physik **74**, 631 (1932).

[9] A. G. Shenstone and H. N. Russell, Phys. Rev. **39**, 415 (1932), see p. 427. The "$8\ {}^1P_1$" term practically belongs to the $5d^9\ 6s^2\ 6p$ configuration.

[10] H. Schüler and J. E. Keyston, Zeits. f. Physik **70**, 1 (1931).

[11] J. C. McLennan and M. F. Crawford, Proc. Roy. Soc. **A132**, 10 (1931).

belong to a configuration involving two $6s$ electrons. Professor Goudsmit kindly examined the data on Tl II and Tl III, and it appears in fact quite logical to interpret the X_2 (McLennan and Crawford's $3_2{}^0$) and the $1_1{}^0$ terms of Tl II as belonging to the $5d^9\ 6s^2\ 6p$ configuration, the difference in term values of $5d^9\ 6s\ 6p\ {}^4F^0$ and $5d^{10}\ 6s$ of Tl III being $\stackrel{\frown}{=} 124{,}000\ \mathrm{cm}^{-1}$ while the difference in term values of $1_1{}^0$, X_2 from $5d^{10}\ 6s^2$ in Tl II is respectively 126,204 and 125,437 cm^{-1}. With this interpretation, the observed senses of the displacements in Tl I and Tl II are in agreement provided one supposes that $5d^{10}\ 6s^2\ 6p\ {}^2P_{3/2}$ of Tl I is undisplaced so that the largest displacement is to be assigned to $5d^{10}\ 6s^2\ 7s\ {}^2S_{1/2}$ and a somewhat smaller displacement to $5d^{10}\ 6s^2\ 6p\ {}^2P_{1/2}$. This view appears to be in disagreement with the reported fact that combinations of the higher ${}^2P$ terms with $5d^{10}\ 6s^2\ 7s\ {}^2P_{1/2}$ show no isotope shift. The experimental difficulties involved are apparently very high, however, as shown by the disagreement between Jackson and Schüler and Keyston on the isotope shift of $\lambda 3776$. Since the direction of the displacement in Tl II is the same as in Hg I, II and Pb I, II, it would be surprising if Tl I were different. [See discussion of Pb I below.]

The displacements in Pb II have been discussed previously.[2] The view that the large shifts are to be attributed to the $6s$ electrons is seen to be in agreement with the similar cases in Tl and Hg both with respect to the direction of the shift and its order of magnitude.

The isotope displacements in Pb I fit into the above theory only partly. Taking the $6p^2\ {}^1D_2$ level as having no displacement, and letting $\Delta W = W(\mathrm{Pb}^{208}) - W(\mathrm{Pb}^{206})$ we obtain, using the data of Kopfermann,[12] Rose and Granath,[13] and of Schüler and Jones[14] the following approximate values for ΔW in cm^{-1}: $6p^2\ {}^1S_0 + 0.01$; $6p^2\ {}^3P_{0,1,2} + 0.01$; $7s\ 6p\ {}^3P_{0,1} + 0.09$; $d\ {}^3D_{2,1} + 0.07$; $d\ {}^3F_3 + 0.07$; $8s\ 6p\ {}^3P_{1,2} + 0.09$; $7s\ 6p\ {}^1P_1 + 0.07$; $6p\ 8p\ {}^3P_1 + 0.08$; $6p\ 8p\ {}^3P_0 + 0.07$. The fact that all levels of the $6p^2$ configuration have approximately the same isotope displacement indicates that ΔW for $6p_{1/2}$ is small and of the order of 0.01 cm^{-1} so that $\Delta W(6p_{3/2})$ can be neglected altogether. The relatively large displacement of the $d\ 6p$ terms is therefore rather puzzling. It may possibly be due to a perturbation by the $6p\ 7s$ configuration, and it may also be that there is as a consequence a perturbation with $6p\ 8s$. Such perturbations make it possible to explain why the displacements of $6p\ 7s$ and of $6p\ 8s$ are of the same order of magnitude. With the above mutual perturbations of $d\ 6p$ by $6p\ 7s$ and of $6p\ 8s$ by $d\ 6p$, the approximately equal shifts of the three configurations may be understood and should then be ascribed mainly to the influence of the $7s$ electron.

It is more difficult, however, to interpret the relatively large shifts of $6p\ 8p\ {}^3P_{0,1}$ which follow from the observed structure[14] of $\lambda\lambda 6059$, 6012, 5896. On the present theory we should expect the shifts to be of the same order as

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[12] H. Kopfermann, Zeits. f. Physik **75**, 363 (1932); Naturwiss. **19**, 400 (1931); **19**, 675 (1931).

[13] John L. Rose and L. P. Granath, Phys. Rev. **40**, 760 (1932). With the later data of Schüler and Jones $a' = 0.012$, $a'' = 0.372$ for $6p^2$.

[14] H. Schüler and E. G. Jones, Zeits. f. Physik **75**, 563 (1932).

those of $6p^2\ {}^3P_{1,2}$ while actually they are approximately the same as those of the $6p\ 7s$ configuration. It is not possible that the $6p\ 8p$ configuration could be perturbed by $6p\ 7s$ or $d\ 6p$ so that another explanation must be looked for.

It should be remembered in this connection that the subgroup $6s^2$ is present in all of the Pb I spectrum. A change in the screening constant of the two $6s$ electrons would lead to an isotope shift. It appears possible, although it is not certain, that the screening of the nucleus by $8p$ is sufficiently weaker than the screening by $6p$ to produce a larger penetration of $6s$ and a consequent isotope shift. The existences of such effects is also suggested by the apparent absence of isotope shifts in the lines $7s\ mp$ of Tl I which would otherwise be expected to show the full shift of the $7s$ electron. As has already been mentioned in connection with Tl I we do not feel very confident that a shift of the $7s\ mp$ lines could have been detected with certainty since there appears to be some contradiction between different observers of λ3776. It appears nevertheless reasonable to suppose that in Pb I the $6s$ electrons have a smaller $\psi^2(0)$ when the valence electron is in a low energy state, because from the point of view of our theory this fits in with the presence of isotope shifts in all the higher terms in the Pb I spectrum. The mass effect considered by Hughes and Eckart for Li can hardly have much to do with the observed shifts in Pb I since there appears no reason why it should give the same shifts for the five ground levels and since it should give equal spacings between Pb^{206}, Pb^{207}, Pb^{208} which is not the case experimentally. It thus seems that changes in $\psi^2(0)$ of $6s$ and perhaps other underlying groups should be considered as mainly responsible for the isotope shifts in Pb I. In Pb II, however, we deal primarily with shifts due to the addition or subtraction of a $6s$ electron and we are thus not concerned with the smaller effects of differences in penetration.

Both the isotope shifts and the nuclear spin term splittings depend on the penetration of the electrons to the nucleus. We discuss, therefore, briefly the theoretical interpretation of the nuclear spin term splittings for Pb I in order to see whether it can be made consistently.

Using (jj) coupling and supposing that ${}^3P_0$ belongs to $6p_{1/2}\ 8p_{1/2}$ while ${}^3P_1$ belongs to $6p_{1/2}\ 8p_{3/2}$, we derive from the observed level splitting of -0.155 cm^{-1} the value[15] $A=-0.103$ cm^{-1} and $a''(6p)=A(6p_{1/2})=0.41$ cm^{-1} which compares reasonably well with the value[13] 0.37 cm^{-1} derived by means of the sum rule from the splittings of the $6p^2$ configuration. The interpretation of $6p\ 8p\ {}^3P_1$ as $6p_{1/2}\ 8p_{3/2}$ appears to be a natural one in view of the fact that it falls into the same series with $6p^2\ {}^3P_1$. Also the interpretation of $6p\ 7s\ {}^3P_1$ and $6p\ 8s\ {}^3P_1$ as $6p_{1/2}\ 7s\ (j=1)$ and $6p_{1/2}\ 8s\ (j=1)$ leads to reasonable values $a''(6p)+a(7s)=0.586$, $a''(6p)+a(8s)=0.386$ which gives on using $a''(6p)=0.372$, $a(7s)=0.214$ and $a(8s)=0.014$. Using the observed[14] splitting -0.060 cm^{-1} for $6p\ 7s\ {}^1P_1$ and interpreting this term as $6p_{3/2}\ 7s\ (j=1)$, we obtain $A=-0.040$ cm^{-1}, $5a'(6p)-a(7s)=-0.160$ cm^{-1}. Using here $a(7s)=+0.214$ cm^{-1} we get $a'(6p)=0.011$ cm^{-1} in good agreement with $a'(6p)$

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[15] S. Goudsmit, Phys. Rev. **37**, 663 (1931). For (jj) coupling
$A=\{[j(j+1)+j_1(j_1+1)-j_2(j_2+1)]a(j_1)+[j(j+1)+j_2(j_2+1)-j_1(j_1+1)]a(j_2)\}/2j(j+1)$.

$=0.007$ cm^{-1} which follows from the $6p^2$ configuration according to Rose and Granath's data[13] and 0.012 cm^{-1} according to Kopfermann's[12] and the latest of Schüler and Jones.[14] The $^3F_3$ level of the $d6p$ configuration must be interpreted as $d_{5/2}\cdot 6p_{1/2}$. For if the observed[12] splitting is 0.250 cm^{-1}, $A=0.0714$ cm^{-1} and $a''(6p)=0.43$ cm^{-1} again in fair agreement with 0.37 cm^{-1} from the $6p^2$ configuration. The hfs splittings do not call, therefore, for any change in the interpretation of the terms and we are thus unable to interpret the large displacements of the $6p$ $8p$ configuration[16,17] *except as a change in the effective screenings of* $6s^2$. Experimental material on other levels of the $6p$ mp series would be of value in arriving at a definite explanation.

The comparison of the observed and theoretically expected shifts is given in Table II.

TABLE II.

Element and spectrum	Electron state	$\psi^2(0)10^{-26}$	Method of computation	Shift as multiple of $A\Delta y_0/y_0$	Fractional change in nuclear radius $\Delta y_0/y_0$	Expected shift in cm^{-1}	Observed shift in cm^{-1}
Tl I	$7s$	0.17	Goudsmit		1/300	0.07	0.06
"	"	0.49	Racah	360	"	0.2	"
"	$7p_{1/2}$			49	"	0.03	0.01 ± 0.005
Tl II	$6s$	<1.6	Goudsmit from Tl III		"	<0.8	0.23
	"	2.8		2060	"	1.4	"
Pb I	$7s$				"		0.07
Pb II	$6s$		G. from Hg II		"	0.70	0.50
Hg I	$6s$				"		0.18
	$7s$	0.30	G. from Hg II		"		0.03
Hg II	$6s$	1.45	G. from Hg II	1060	"	0.70	0.52

$A=(n+1)/(2\rho+1)\ (2\rho+n+1)\backsim 1/5$ for $\rho=0.81$.

It will be noted that in the one electron spectra of Tl I, Hg II the agreement with Goudsmit's formula for $\psi^2(0)$ is quite satisfactory. Only in such cases is the use of this formula safe because the screening is then the same in the calculation of the effective quantum number and in the calculation of

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[16] The *relative* values of the isotope shifts which should be expected for $7s$ and $6p_{1/2}$ of Pb I are approximately the same as in Tl I because for Pb I, $a(7s)\backsim 0.22$, $a''\ (6p)\backsim 0.37$ while for Tl I, $a(7s)\backsim 0.40$, $a''(6p)\backsim 0.71$ so that the ratio $a(7s)/a''(6p)$ is nearly the same for the two spectra.

[17] The small disagreements which exist in the above comparison between theory and experiment for the hfs of Pb I can be easily explained by the influence of the penetration of the electrons on the coupling to the nucleus and by the fact that the coupling is intermediate between Russell-Saunders and jj. For the $6p^2$ configuration the Zeeman effect g values determine the $^1D_2$ term as $0.93\ 6p_{3/2}\ 6p_{3/2}+0.38\ 6p_{3/2}\ 6p_{1/2}$ and $^3P_2$ as $0.93\ 6p_{3/2}\ 6p_{1/2}-0.38\ 6p_{3/2}\ 6p_{3/2}$. The deviation from jj coupling measured by $(0.38)^2=0.14$ is quite large enough to account for the difference between $A(^1D_2)=0.026$ and $a'(6p)=0.012$. Neglecting matrix elements of the type $(p_{3/2}/H'/p_{1/2})$ we derive theoretically $A(^1D_2)=0.024$, $A(^3P_2)=0.089$ in excellent agreement with experiment. It is not quite certain that these matrix elements are sufficiently small to be neglected. Nevertheless it is clear that the deviations from jj coupling may easily account for the remaining discrepancies.

$\psi^2(0)$. With Goudsmit's value[6] for $\psi^2(0)$ of $7s$ Tl I the hfs splitting of this term gives $\mu_0/\mu=(0.17/0.49)4050=1.4\times10^3$ which is in much better agreement with the value $\mu_0/\mu=0.92\times10^3$ which follows according to Racah from the splitting of $6p_{1/2}$ Tl I than $\mu_0/\mu=4.0\times10^3$. The isotope shift and the hfs splitting agree with Goudsmit's formula.

SUMMARY

It is seen from the above discussion that the theory of isotope shifts as due to changes in nuclear radii is substantially in agreement with the observed facts. The apparent objections[1,2] to such a theory have been removed. The main changes with respect to previous work are: (1) changes in the probable values of $\psi^2(0)$; (2) the interpretation of electron configurations in Hg, Tl, Pb. The values of nuclear radii and their differences have a significance only so far as order of magnitude is concerned, on account of uncertainties in the values of $\psi^2(0)$.

The picture of the nucleus as having an approximately uniform charge density is expected to apply only to its action on extranuclear electrons and has presumably somewhat the same relation to reality as the Hartree central field has to the correct treatment of an atom in configuration space.