changes P into $(P_{12}-P_{21})/2$, Q_1 into Q_2, Q_2 into $-Q_1$, Q_1' into Q_2', Q_2' into $-Q_1'$. These relations will be helpful to those who wish to verify the calculations. It is found that

$$d(\delta \ln A)/dr = A^{-2}\Sigma\chi_i(\delta R_{ij})\chi_j - 2Q_1'^0\delta_1 - Q_2'^0\delta_2 + Q_1'^0\delta_3 \quad (6)$$

and for the special case of c numbers for the P_{ij} the corresponding formula is

$$d(\delta \ln A)/dr = \delta Q_2' - 2Q_1'\delta_1 - Q_2'\delta_2 + Q_1'\delta_3. \quad (6.1)$$

The calculation of changes in the amplitude A is thus reducible to the evaluation of simple expressions.

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Electron-Nuclear Potential Fields from Hyperfine Structure

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Theoretical predictions for the effects of nuclear size on hyperfine structure are compared with experimental data. New data show that isotope shifts of *ns* levels in Tl III are proportional to $\psi^2(0)$ as predicted. The fractional change in nuclear radius for the addition of two neutrons, determined from s electron shifts in Hg II, Tl III, Pb IV, is the same for the three elements. Köhler's results for Tl II are consistent with those for Tl III when allowance is made for the mutual screening of the valence electrons.

Corrections for the approximation of the perturbation method and for screening of inner electrons by the valence electron are considered and found to be appreciable. Even after applying the corrections, the fractional change in nuclear radius is smaller than expected if the charge is uniformly distributed throughout the nucleus and the volume is proportional to the mass.

Values of nuclear magnetic moments of thallium deduced from hyperfine structure measurements are compared with those measured by radiofrequency induction and found to be 15 percent lower. This discrepancy is removed by the correction for finite nuclear size assuming either a uniform charge distribution or a concentration of charge toward the surface of the nucleus. Thus both the isotope shift and the magnetic effect indicate that the electron-nuclear potential is consistent with a charge distribution of this form and that the non-electrical forces between electrons and nuclei are relatively small.

1. INTRODUCTION

A RELATIVISTIC theory of the effects of finite nuclear size, with a consequent departure from a Coulomb field, on the atomic energy levels has been formulated by Rosenthal and Breit[1,2] and Racah.[3] The first two authors have also considered the effect of a finite nucleus on the interaction between electrons and the nuclear magnetic moment. The first effect leads to an isotope shift, and the second to a correction for the nuclear magnetic moment deduced from hyperfine structure splittings. Previous comparisons[2,4,5] of the theory with experimental data on isotope shifts agreed only as to order of magnitude; in general, the theoretical and observed values differed by a factor of the order of three. In many of these cases the comparison was complicated by the mutual screening of several electrons outside closed shells and by inter-configuration perturbations. It is therefore desirable to consider unperturbed levels arising from one-electron configurations, preferably those of penetrating s electrons. Such configurations occur in the Hg II, Tl III, Pb IV sequence and their isotope shifts are analyzed here.

The analysis shows that significant information about electron-nuclear potential fields can be obtained from the absolute magnitude of the shifts. The corrections for the approximations in the perturbation method and for the screening of electrons in completed shells are found to be important.

Hitherto the effect of nuclear radius on the magnetic interaction between electrons and the nuclear spin has not been confirmed experimentally. Evidence confirming this effect is presented. Both the isotope shifts and the magnetic effect are more consistent with a uniform charge distribution in the nucleus than with a well-type potential for the electron-nuclear interaction.

2. ISOTOPE SHIFT

The isotope shift for a single s electron as derived by Rosenthal and Breit[1] using the perturbation method is

$$\Delta\delta W = \frac{4\pi R a_H^3 \psi^2(0)}{Z} \frac{1+\rho}{[\Gamma(2\rho+1)]^2} y_0^{2\rho} \frac{\Delta y_0}{y_0} \cdot B, \quad (1)$$

where R is the Rydberg constant,

$a_H = h^2/4\pi^2 me^2$ is the radius of the first Bohr orbit for hydrogen,
Z is the nuclear charge,
$\psi^2(0)$ is the square of the non-relativistic atomic wave function at the center of the nucleus,
$\rho = (1-Z^2\alpha^2)^{\frac{1}{2}}$,
$\alpha = 2\pi e^2/hc$ is the fine structure constant
$y_0 = 2Zr_0/a_H$ where r_0 is the radius of the nucleus,

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

[2] G. Breit, Phys. Rev. **42**, 348 (1932).

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

[4] P. Köhler, Zeits. f. Physik **113**, 306 (1939).

[5] S. Mrozowski, Phys. Rev. **61**, 605 (1942).

$\Delta y_0/y_0$ is the fractional change in y_0 for two isotopes,
B is a factor depending on the potential within the nucleus.

The datum for the shifts given by Eq. (1) is zero shift when the s electron is completely removed. Following Goudsmit,[6] Breit,[2] and Fermi and Segrè,[7]

$$\psi^2(0)=\frac{Z_iZ_0^2}{\pi a_H^3 n_0^3}\left(1-\frac{d\sigma}{dn}\right), \tag{2}$$

where Z_i is the effective nuclear charge in the inner region and can be put equal to Z for an s electron,
Z_0 is the effective nuclear charge in the outer region,
n_0 is the effective principal quantum number,
σ is the quantum defect.

Since the term value

$$T=RZ_0^2/n_0^2, \tag{3}$$

$$n_0^3=(R/T)^{\frac{3}{2}}Z_0^3. \tag{4}$$

Substituting Eq. (2) and Eq. (4) in Eq. (1),

$$\Delta\delta W=\frac{4T^{\frac{3}{2}}}{Z_0R^{\frac{1}{2}}}\left(1-\frac{d\sigma}{dn}\right)\frac{1+\rho}{[\Gamma(2\rho+1)]^2}y_0^{2\rho}\frac{\Delta y_0}{y_0}\cdot B. \tag{5}$$

Case 1. For a constant potential within the nucleus[1]

$$B=[1+vy_0/2a^2], \tag{6}$$

where $a=Z_i\alpha$, $v=V/mc^2$ and V is the potential energy of the electron inside the nucleus.

Equation (6) is based on the assumption that v is the same for both nuclei.

Case 2. If v is a constant for a given nucleus, but a function of y_0, then by the perturbation method

$$B=\left[1+\frac{vy_0}{2a^2}+\frac{1}{2a^2}\frac{y_0^2}{2\rho+1}\frac{dv}{dy_0}\right]. \tag{7}$$

Case 3. If the non-electrical forces between the electron and the nucleus are negligible and all the charge is concentrated at the surface of the nucleus, then $V=-Ze^2/r_0$, and $v=-2a^2/y_0$ and is different for each isotope. For this case,[3] from Eq. (7),

$$B=\left[1-\frac{2a^2y_0}{2a^2y_0}+\frac{1}{2\rho+1}\right]=\frac{1}{2\rho+1}. \tag{8}$$

If the forces are purely electrical, any other charge distribution will give $V<-Ze^2/r_0$ inside the nucleus. $V>-Ze^2/r_0$ implies the existence of non-electrical forces.

Case 4. If V is the same for each isotope and equal to $-Ze^2/r_0$ for one of the isotopes, then $dv/dr_0=0$ and from either Eq. (6) or Eq. (7),

$$B=0. \tag{9}$$

This corresponds to the case where the addition of neutrons does not change the proton distribution.

Case 5. If the non-electrical forces are negligible but, in contrast to *Case 3*, the charge is uniformly distributed throughout the nucleus,[1]

$$V=\left[-\frac{3}{2}+\frac{1}{2}\left(\frac{r}{r_0}\right)^2\right]\frac{Ze^2}{r_0}=\left[-\frac{3}{2}+\frac{1}{2}\left(\frac{y}{y_0}\right)^2\right]\frac{2a^2}{y_0},$$

and

$$B=3/(2\rho+1)(2\rho+3). \tag{10}$$

Figure 1 shows the potential energy distributions discussed above. In each case the curve for the heavier isotope is represented by a broken line where it differs from that of the lighter isotope.

A. Experimental Data

To test Rosenthal and Breit's theory it is best to study the ns term sequences of one-electron spectra of elements with relatively heavy, and therefore relatively large nuclei. Since the contributions of non-s electrons to the shifts are small, these data can be supplemented by those for terms of more complex configurations with one or two s electrons. Mrozowski[5] has given shifts for

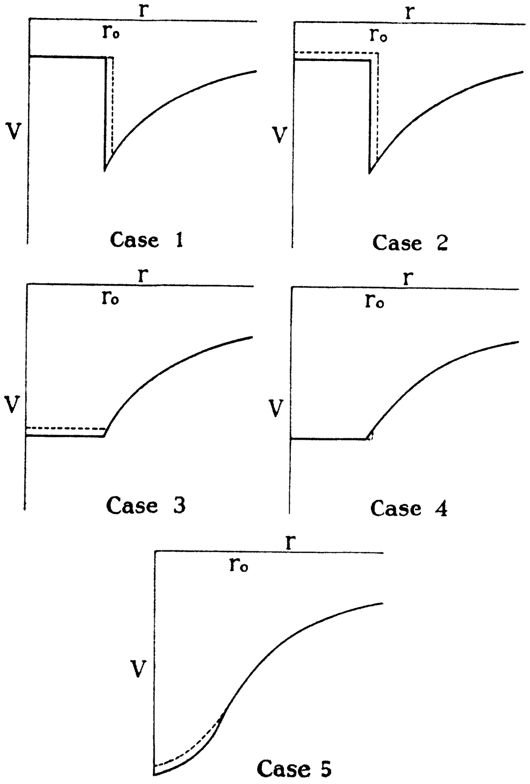

FIG. 1. Potential energy of the valence electron for five nuclear models.

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[6] L. Pauling and S. Goudsmit, *The Structure of Line Spectra* (McGraw-Hill Book Company, Inc., New York, 1930); S. Goudsmit, Phys. Rev. **43**, 636 (1933).

[7] E. Fermi and E. Segrè, Zeits. f. Physik **82**, 729 (1933).

TABLE I. Isotope shifts in Tl III.

Term	Term value cm^{-1}	Isotope shift cm^{-1}
$5d^96s^22_{1\frac{1}{2}}$	156,001.0	0.710
$5d^96s6p3_{2\frac{1}{2}}{}^0$	113,220.0	0.385
$5d^96s6p4_{1\frac{1}{2}}{}^0$	111,436.2	0.343
$7s\ {}^2S_{\frac{1}{2}}$	101,377.5	0.090
$5d^96s6p10_{\frac{1}{2}}{}^0$	97,224.5	0.407
$5d^96s6p13_{\frac{1}{2}}{}^0$	89,746.2	0.397
$5d^96s6p14_{1\frac{1}{2}}{}^0$	84,739.4	0.378
$5d^96s6p18_{1\frac{1}{2}}{}^0$	80,585.4	0.410
$6d^96s6p22_{\frac{1}{2}}{}^0$	65,858.7	0.422
$8s\ {}^2S_{\frac{1}{2}}$	56,402.0	0.046

Hg II; Crawford, McLay, and Crooker[8] have given shifts for eight terms of Pb IV involving a $6s$ electron. Shifts have been measured by Crawford and Convey[9] as part of an extensive analysis of the hyperfine structures of Tl III. This spectrum was excited in an electrodeless discharge and the hyperfine structures were resolved by a 21-foot concave grating of 80,000 lines in the third to eight orders. Table I gives the isotope shifts observed by Crawford and Convey for terms involving one unpaired s electron and for one level of $5d^96s^2$. The shifts are relative to a datum of zero shift for the $7d\ {}^2D_{5/2}$ level which shows no magnetic splitting. For all levels listed the lighter isotope has the greater binding energy.

Since the shift of the $6s\ {}^2S_{\frac{1}{2}}$ level was not observed directly, it is evaluated here as 0.38 cm^{-1} by reducing the average shift of the $6s6p$ levels by 2 percent to allow for the contribution of the p electron. This 2 percent correction follows from Rosenthal and Breit's theory which, for Tl III, gives the shift of a $6p_{\frac{1}{2}}$ electron as about 1/20 of that of a $6s$ electron and gives a negligible shift for a $6p_{3/2}$. In this way we get 0.38 cm^{-1} for the shift of the $6s\ {}^2S_{\frac{1}{2}}$ level. As a further check, the 0.710 cm^{-1} shift of $5d^96s^22_{1\frac{1}{2}}$ gives a shift of 0.355 cm^{-1} per s electron in $6s^2$ and thus indicates a shift somewhat greater than 0.355 cm^{-1} for a single unscreened $6s$ electron.

B. Comparison with Theory

To test the theory, the value of $\Delta y_0/y_0$ has been computed from the experimental data for ns levels of Hg II, Tl III, and Pb IV using the value of B for uniform charge density given by Eq. (10). y_0 used in the calculation was obtained from the approximate formula[10]

$$r_0 = 1.5\times 10^{-13}A\ \text{cm}, \tag{11}$$

where A is the mass number. $(1-d\sigma/dn)$ was evaluated from a plot of quantum defect, σ, against term value. If the terms are unperturbed they should fit a Rydberg-Ritz equation[11]

$$T = RZ_0^2/(n-\alpha-\beta T)^2, \tag{12}$$

so that

$$\sigma = \alpha+\beta T, \tag{13}$$

and

$$d\sigma/dn = \beta dT/dn.$$

But from Eq. (12),

$$(n-\alpha-\beta T) = R^{\frac{1}{2}}Z_0/T^{\frac{1}{2}}.$$

Differentiating,

$$1-\beta\frac{dT}{dn} = -\frac{R^{\frac{1}{2}}Z_0}{2T^{\frac{3}{2}}}\frac{dT}{dn}$$

so that

$$dT/dn = 1/(\beta - R^{\frac{1}{2}}Z_0/2T^{\frac{3}{2}}).$$

Finally

$$d\sigma/dn = \beta/(\beta - R^{\frac{1}{2}}Z_0/2T^{\frac{3}{2}}) = \beta/(\beta - n_0/2T). \tag{14}$$

To evaluate β and check for perturbations, σ was plotted against T. By Eq. (13), this graph for an unperturbed series is a straight line of slope β.

The values obtained for the apparent fractional change in nuclear radius, $\Delta y_0/y_0$, for the addition of two neutrons, are tabulated in Table II. These values are termed apparent because, as will be shown, they must be corrected for the approximations in the perturbation method and for the effect of the decrease in screening of the inner electrons by removal of the outer s electron.

Within the precision of the measured intervals, the shifts of the $6s$, $7s$, and $8s$ levels in Tl III give the same value of $\Delta r_0/r_0$. This confirms the predicted variation of the isotope shift with $T^{\frac{3}{2}}(1-d\sigma/dn)$ and hence with $\psi^2(0)$, and shows that the isotope shift in the heavy elements is primarily due to the finite size of the nucleus.

In the case of Hg II, the $6s$ and $7s$ levels give equal values of $\Delta y_0/y_0$. The other three levels give much larger values of the ratio, but these are not free from perturbations since the plot of quantum defect against term value starts to depart from a straight line at $8s$ and is curving strongly at $9s$ and $10s$. This shows that they are perturbed by at least one level above the $10s$. Although levels of the configuration $5d^96s6d$ have not been identified, they are expected in this position and some of them are capable of producing the perturbation. Furthermore, these levels would have large isotope shifts and on sharing their properties with the $8s$, $9s$, and $10s$ would increase the shifts of the latter and account for the large values of $\Delta y_0/y_0$. Therefore the $8s$, $9s$, and $10s$ levels are not suitable for testing the theory.

Table II shows another confirmation of the field effect theory. The addition of two neutrons to a nucleus of each of the three elements causes the same fractional

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[8] Crawford, McLay, and Crooker, Proc. Roy. Soc. **A158**, 455 (1937).

[9] J. Convey, Ph.D. thesis, Toronto (1940).

[10] H. Bethe, *Elementary Nuclear Theory* (John Wiley and Sons, Inc., New York, 1947). See also E. Amaldi and B. N. Cacciapuoti, Phys. Rev. **71**, 739 (1947).

[11] A. G. Shenstone and H. N. Russell, Phys. Rev. **39**, 415 (1932).

change in nuclear radius, as would be expected since the binding energies for the addition of two neutrons are equal within a few percent[12] for thallium and lead. Binding energies for mercury are not available.

Köhler[4] has analyzed the shifts observed by him for the 6*sns* sequence of Tl II and concluded that for a reasonable choice of datum they could be fitted to a $(1-d\sigma/dn)/n_0^3$ law as predicted by Eq. (1) and Eq. (2). Mrozowski[5] has pointed out that the higher members of the $^1S_0$ sequence are known to be perturbed by a term that is capable of lowering their isotope shifts. Furthermore, Köhler made no estimate of the effect on the shifts of the change in screening of the 6*s* electron by the removal of the outer *ns* electron. Until such an estimate is made this confirmation of theory is not as conclusive as the results of Table II.

In the following, the shifts for the 6*sns* sequence of Tl II are calculated making allowance for screening and using the value of $\Delta y_0/y_0=1.1\times10^{-3}$ established in Tl III. This is done primarily to show that the shifts in Tl II are not inconsistent with the value of $\Delta y_0/y_0$ obtained from Tl III when calculated on the same basis [Eqs. (5), (10), and (11)]. The results of the calculations are summarized in Table III. The shifts of the 6*sns* levels, tabulated in the third column, were calculated treating the outer *ns* electron as a one-electron system and using the term values from Tl II. The datum for the calculated shifts is zero shift for 6*s* of Tl III. The shift listed in the third column for the $5d^96s^26p$ is that given in Table II as the measured shift of the 6*s* level of Tl III. This value is in accord with $\Delta y_0/y_0=1.1\times10^{-3}$.

The shifts in the last column of Table III are obtained from those in column 3 by correcting for screening. The change in the screening of the 6*s* by the *ns* can be estimated from the change in the magnetic hyperfine structure of the 6*sns* $^3S_1$ sequence because both the magnetic hyperfine structure and the isotope shift depend on $\psi^2(0)$ of each electron. The interaction constant of the 6*s* electron in the 6*sns* configuration was evaluated from the observed interval factors[13] by treating the outer *s* electron as a one-electron system and calculating its contribution to the interval factor. The interaction constant, a_{ns}, of the outer electron was evaluated by the Goudsmit expression

$$a_{ns}=8\pi R\alpha^2 a_{\mathrm{H}}^3\kappa g(I)\psi^2(0)/3\times1837$$

using $g(I)$ deduced from $a_{6s}(\text{Tl III})=5.85\text{ cm}^{-1}$. This interval factor is a reliable limiting value obtained from the hyperfine structures of 6*sng* levels and 6*sns* $^3S_1$ levels of Tl II, and also by calculation from the structures of higher members of the *ns* sequence of Tl III (see Section 3). It is found that for the 6*s*7*s* level a_{6s} is reduced 3 percent at most by the presence of the 7*s* electron. Thus the corrected shifts of the 6*s*7*s* levels are smaller than the calculated by not more than 0.011 cm^{-1}, 3 percent of 0.38. For the 6*s*8*s* and 6*s*9*s* the screening correction is negligible.

TABLE II. Apparent change in nuclear radius (uniform charge distribution).

Level	Hg II Isotope shift cm^{-1}	Hg II $\frac{\Delta y_0}{y_0}=\frac{\Delta r_0}{r_0}$ apparent	Tl III Isotope shift cm^{-1}	Tl III $\frac{\Delta y_0}{y_0}=\frac{\Delta r_0}{r_0}$ apparent	Pb IV Isotope shift cm^{-1}	Pb IV $\frac{\Delta y_0}{y_0}=\frac{\Delta r_0}{r_0}$ apparent
6*s*	0.276	1.05×10^{-3}	0.38	1.13×10^{-3}	0.5	$1.(2)\times10^{-3}$
7*s*	0.050	1.02×10^{-3}	0.090	1.01×10^{-3}		
8*s*	0.080*	4.2×10^{-3}	0.046	1.2×10^{-3}		
9*s*	0.10±0.025*	11×10^{-3}				
10*s*	0.05±0.03*	10×10^{-3}				

* Perturbed—see text.

For the $5d^96s^26p$ levels the important screening correction will be the mutual screening of the 6*s* electrons. The isotope shift due to a 6*s* electron is $5d^{10}6s^2$ can be evaluated from the isotope shift of a single 6*s* electron (Tl III) by approximating to the Z_0 and n_0 of a $6s^2$ as follows. Consider the two *s* electrons of $6s^2$ as a single electron of charge 2. For them Z_0 is 2.5 since the probability of either 6*s* being nearer the nucleus than the other is one-half and their charge distribution is spherically symmetrical. From this value of Z_0 and the sum of the ionization potentials of Tl II and Tl III, which is the energy required to remove the pair to infinity, one obtains $n_0=1.840$ for either electron of the pair. For the 6*s* electron of Tl III, $Z_0=3$, $n_0=2.026$ and its isotope shift is 0.38 cm^{-1} relative to ionization. A shift of 0.352 cm^{-1} for each 6*s* electron of $6s^2$ of Tl II is obtained from these data by the relation $\Delta\delta W\propto Z_0^2/n_0^3$, which follows from Eqs. (1) and (2) assuming a constant Fermi-Segrè correction. That is, the mutual screening of the two 6*s* electrons decreases the shift per 6s electron by 7 percent. The shift for $6s^2$ of Tl II then is 0.704 cm^{-1} relative to ionization of Tl III (double ionization of Tl II). This shift agrees well with the 0.710 cm^{-1} shift observed for the $5d^96s^2$ of Tl III, which differs from $5d^{10}6s^2$ only by the absence of a *d* electron.

But the datum for the calculated shifts is 6*s* of Tl III. To get the shift relative to this datum it is necessary to subtract the shift produced by taking a 6*s* electron in Tl III to infinity. Thus the shift of the $6s^2$ configuration of Tl II relative to the 6*s* level of Tl III is $0.704-0.38=0.32$ cm^{-1}. For a $5d^96s^26p$ configuration the shift will be from 0 to 5 percent greater because of the presence of the 6*p* electron; the absence of a *d* electron should have a negligible effect.

The agreement between the observed values and the values corrected for screening is very good except for 6*s*8*s* and 6*s*9*s*, for which the observed shifts are smaller. But, as pointed out by Mrozowski,[4] these levels are perturbed, presumably by $6p^2\ ^1S_0$,[14] which would reduce

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[12] J. Mattauch, *Nuclear Physics Tables* (Interscience Publishers Inc., New York, 1946).

[13] S. Smith and J. Convey, Can. J. Research **A14**, 139 (1936). The intervals given by Smith and Convey for 6*s*8*s* and 6*s*10*s* are incorrect; they are 4.68 and 4.47 cm^{-1}, respectively, from our unpublished data.

[14] C. B. Ellis and R. A. Sawyer, Phys. Rev. **49**, 145 (1936).

TABLE III. Isotope shifts in Tl II.

Level	Isotope shift Observed (datum 6s9s of Tl II) cm^{-1}	Calculated (datum 6s of Tl III) cm^{-1}	Calculated with screening correction cm^{-1}
$5d^96s^26p4_2{}^0$	0.348*	0.38	0.32–0.34
$5d^96s^26p8_1{}^0$	0.338*		
$5d^96s^26p5_1{}^0$	0.302*		
$6s7s\ {}^3S_1$	0.059	0.066	0.055
$6s7s\ {}^1S_0$	0.060	0.063	0.052
$6s8s\ {}^1S_0$	0.015	0.023	0.023
$6s9s\ {}^1S_0$	0.000	0.011	0.011

* There is some perturbation between these levels and those of $6s7p$ and it would reduce the observed shifts. This spread in the shifts is probably caused by this perturbation.

their shifts and, in particular, make the shift of $6s9s$ less than the calculated 0.011 cm^{-1}. As a result of this perturbation, Köhler's original datum of zero shift for $6s9s$ is probably equivalent to zero shift for $6s$ of Tl III, the datum for the calculated values. Thus the shifts in Tl II as well as those listed in Table II are consistent with the field effect theory.

C. Validity of the Perturbation Method

Because the fields responsible for the energy perturbation are so large, even though they act only in a small region, it is necessary to examine the accuracy of the perturbation method. Rosenthal and Breit[1] have considered the case where v is constant and the same for both nuclei, but their method is not suitable for cases where the v's are different. An alternative treatment by E. K. Broch[15] avoids the use of the perturbation method and permits the derivation of an expression for the isotope shift which is not dependent on the assumption that the perturbed wave functions differ only slightly from the unperturbed in the region of the perturbation. By Broch's method the change in energy due to the finite nuclear radius is

$$\delta W=-2\left(\frac{C-}{C}\right)C^2Ze^2\frac{\rho}{\Gamma(1+2\rho)\Gamma(1-2\rho)},\tag{15}$$

where $C-$ and C are the coefficients used by Rosenthal and Breit in the solution of the wave equations for $y>y_0$. Equation (15) differs from Broch's Eq. (4–3) only by a factor $a_{\mathrm{H}}/2Z$ which converts Broch's normalization to that of Rosenthal and Breit.

The wave functions are

$$\phi_1/a=CJ_{2\rho}(2y^{\frac{1}{2}})+C_-J_{-2\rho}(2y^{\frac{1}{2}}),\tag{16}$$

$$\phi_2=CA_{2\rho}(2y^{\frac{1}{2}})+C_-A_{-2\rho}(2y^{\frac{1}{2}}),\tag{17}$$

where

$$A_{2\rho}(2y^{\frac{1}{2}})=(j-\rho)J_{2\rho}(2y^{\frac{1}{2}})+y^{\frac{1}{2}}J_{2\rho+1}(2y^{\frac{1}{2}}),\tag{18}$$

$$A_{-2\rho}(2y^{\frac{1}{2}})=(j-\rho)J_{-2\rho}(2y^{\frac{1}{2}})-y^{\frac{1}{2}}J_{-2\rho-1}(2y^{\frac{1}{2}}),\tag{19}$$

the J's are Bessel functions,
j is the quantum number taking the values -1, 1, -2, 2, -3, $\cdots$ for $s_{\frac{1}{2}}$, $p_{\frac{1}{2}}$, $p_{3/2}$, $d_{3/2}$, $d_{5/2}$, $\cdots$ electrons, respectively,
C is a constant and equals $(-a_{\mathrm{H}}\psi(0)/2Z)$,
C_- depends on y_0 and on the potential inside the nucleus.

From Eq. (15), by differentiating, the isotope shift is

$$\Delta\delta W=-2Ze^2C^2\frac{2\rho}{\Gamma(1+2\rho)\Gamma(1-2\rho)}\times\left[\frac{d}{dy_0}\left(\frac{C-}{C}\right)\right]y_0\frac{\delta y_0}{y_0},\tag{20}$$

where[1,15]

$$\frac{C_-}{C}=\frac{(\phi_1/a\phi_2)_{y0}A_{2\rho}(2y_0{}^{\frac{1}{2}})-J_{2\rho}(2y_0{}^{\frac{1}{2}})}{J_{-2\rho}(2y_0{}^{\frac{1}{2}})-(\phi_1/a\phi_2)_{y0}A_{-2\rho}(2y_0{}^{\frac{1}{2}})}.\tag{21}$$

$(\phi_1/a\phi_2)_{y0}$ is obtained by putting $y=y_0$ in the solutions of the wave equation for $y\leqslant y_0$. These solutions for v constant are given by Rosenthal and Breit; those for the uniform charge distribution were obtained as power series in y. It can be shown that $(\phi_1/a\phi_2)_{y0}$ is very nearly independent of y_0 so that its derivative can be set equal to zero in the differentiation.

The isotope shift for an s electron of thallium has been evaluated by Eq. (20) for *Case 3* ($V=-Ze^2/r_0$) and *Case 5* (uniform charge density), and compared with the shift calculated by the perturbation method, Eq. (5). The error in the perturbation method was found to be 36 percent for *Case 3* and 34 percent for *Case 5*. Thus for this reason alone the values of $\Delta y_0/y_0$ (apparent) in Table II must be multiplied by 1.35.

D. Screening of Inner Electrons by the Valence Electron

Since a penetrating s-type valence electron has a finite probability of being near the nucleus, it has an appreciable probability of being inside the orbit of any of the inner electrons. For that fraction of the time when the valence electron is inside the orbit of the inner electron, the effective nuclear charge for the inner electron is reduced by one unit. Thus the binding of the inner electron to the nucleus is reduced by the presence of the valence electron and thus the contribution of the inner electron to the isotope shift of the entire atom is reduced.

The change caused by this screening of an inner electron by the valence electron is a small fraction of the isotope shift in the binding energy of the inner

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[15] E. K. Broch, Archiv. f. Mat. o. Nat. **48**, 25 (1945). J. Smorodinsky, J. Phys. U.S.S.R. **10**, 419 (1946), has used essentially the same method, but his result is inaccurate because of the approximations used.

electron. But the inner electron is closely bound to the nucleus, and a small fractional change in its isotope shift is an appreciable fraction of the isotope shift of the valence electron.

A direct evaluation of this screening would require a very accurate value of $\psi^2(0)$ for the inner electrons when the valence electron is present and when it is removed to ionization. The wave function of the 1*s* electron would need to be accurate to one part in 10^5 or 10^6 so that the uncertainty in its value of $\psi^2(0)$ would be a small fraction of $\psi^2(0)$ for the valence electron. This accuracy is far beyond the limit of the Hartree self-consistent field method.

However, an estimate of the screening effect can be obtained in the following way. From the Hartree wave functions for mercury[16] the probability, p, of a 6*s* valence electron being closer to the nucleus than each of the 1*s*, 2*s*, 3*s*, 4*s*, and 5*s* electrons is evaluated. From Eq. (1) the ratio of the isotope shift for the *ns* electron to the isotope shift for the 6*s* electron is

$$(\Delta\delta W)_n/(\Delta\delta W)_6=\psi_{ns}^2(0)/\psi_{6s}^2(0), \tag{22}$$

but $\psi_{ns}^2(0)=Z_iZ_0^2/\pi a_{\mathrm{H}}^3n_0^3$ from Eq. (2). During a fraction p of the total time, the valence electron is closer to the nucleus than the inner electron and reduces Z_0 by one unit. For this fraction of the time $\psi_{ns}^2(0)$ is reduced by the fraction $[Z_0^2-(Z_0-1)^2]/Z_0^2\simeq 2/Z_0$. Thus the change in the isotope shift of the *ns* electron due to the presence of the 6*s* electron, expressed as a fraction of the isotope shift of the 6*s* is

$$\frac{\psi_{ns}^2(0)}{\psi_{6s}^2(0)}\cdot\frac{2}{Z_0}\cdot p. \tag{23}$$

p is obtained by evaluating numerically the integral

$$p=\int_0^\infty\left[P_{ns}^2\int_0^{r_1}P_{6s}^2dr\right]dr_1 \tag{24}$$

using the Hartree wave functions to get P^2, the probability of the electron being between r and $r+dr$. $\psi_{ns}^2(0)$ and $\psi_{6s}^2(0)$ are taken from the Hartree wave functions. Z_0, from a shell model of the atom, is approximately 80 for 1*s* electrons, 78 for 2*s* electrons, 70 for 3*s* electrons, 52 for 4*s* electrons, and 20 for 5*s* electrons. These values of Z_0 are not inconsistent with the Hartree and Fermi-Thomas fields.

The values of p and of the change in the isotope shift of the atomic energy levels caused by the change in screening of each inner pair of *s* electrons, expressed as a fraction of the shift for the 6*s* electron, are given in Table IV.

Thus this calculation shows that the observed shifts should be 16 percent smaller than those calculated neglecting screening. It is difficult to assess the accuracy of this calculation, but it is believed that the correction should be of the right order of magnitude. It is realized that the Hartree wave function for ψ_{6s} does not give a good value of $\psi_{6s}^2(0)$ because the amplitude in the inner region is very sensitive to the normalization integral, which is determined mainly in the region of large r. However in the expression for the screening, Eq. (23), p appears in the numerator and $\psi_{6s}^2(0)$ in the denominator. Since they are both dependent on the amplitude of the 6*s* wave function, the error is reduced. This compensation is best for the 1*s* electron. For the 5*s* electron this compensation is worst since p is not as dependent on the amplitude of ψ_{6s} near the nucleus, but the error in $\psi_{6s}^2(0)$ probably is partially compensated by an error of the same sense in $\psi_{5s}^2(0)$.

In the calculation it has been assumed that n_0 is independent of the screening by the valence electron. This approximation is very good for the inner electrons, for which the effective field is nearly Coulombian, but is not as accurate for the outer electrons. As a result of these two effects the calculated screening corrections should be regarded as upper limits.

The 6*s* electron also screens inner p and d electrons, but since the latter have very small isotope shifts, the change in the screening of these electrons by the valence electron has a negligible effect on the shifts.

E. Conclusions

When the corrections for both the approximation of the perturbation method and the screening of the inner electrons are applied to the apparent $\Delta y_0/y_0$ for uniform charge density (*Case 5*), its value is raised from 1.1×10^{-3} (Table II) to $1.1\times10^{-3}\times1.35\times1.16=1.7\times10^{-3}$. This fractional change in nuclear radius is only half of 3.3×10^{-3}, the value expected on the assumption that the protons remain uniformly distributed throughout the volume of the nucleus, and that the volume is proportional to the mass. Therefore the isotope shifts indicate that the addition of two neutrons to a lead, mercury, or thallium nucleus does not cause a complete redistribution of the charge in the nucleus. This result favors the existence of some type of reasonably stable structure in the nucleus, such as the shell structures discussed by Feenberg and Hammack, Mayer, and Nordheim.[17]

If any of the other potentials (*Cases 1* to *3*) are assumed, $\Delta y_0/y_0$ calculated from the observed shifts is still smaller. For *Case 3*, charge on surface, $\Delta y_0/y_0$ is $\frac{2}{3}$ of that calculated assuming uniform charge density. For the deep potential well ($v\simeq 0$), $\Delta y_0/y_0$ is one-fourth that calculated on the basis of uniform charge distribution. Thus the deep potential well does not seem probable and the charge on surface is somewhat less satisfactory than the uniform charge density.

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[16] D. R. Hartree and W. Hartree, Proc. Roy. Soc. **A149**, 210 (1934).

[17] M. G. Mayer, Phys. Rev. **74**, 235 (1948); E. Feenberg and K. C. Hammack, Phys. Rev. **75**, 1877 (1949); L. Nordheim, Phys. Rev. **75**, 1894 (1949).

TABLE IV. Isotope shift screening correction.

Electron	$\psi^2(0)\cdot\pi a_H^3$ (Hartree)	p	Screening correction per ns^2 as a fraction of $(\Delta\delta W)_{6s}$
$1s$	5.06×10^5	2.034×10^{-5}	0.016
$2s$	5.56×10^4	1.912×10^{-4}	0.017
$3s$	1.23×10^4	9.010×10^{-4}	0.020
$4s$	3.06×10^3	3.846×10^{-3}	0.028
$5s$	6.10×10^2	2.090×10^{-2}	0.079
$6s$	3.2×10^1		
		Total	0.16

The specific mass effect has generally been neglected for heavy elements and has not been considered here. The best justification for this is experimental: in elements of intermediate mass only very small isotope shifts are observed, and in heavy elements different levels of an unperturbed configuration have practically the same isotope shifts (see Table I). If the specific mass effect were invoked to account for the smallness of $\Delta y_0/y_0$ obtained from the observed shift of the $6s$ level of Tl III in particular, it would have to be in the opposite sense to the field effect and have a magnitude of 0.2 cm^{-1}. Then differences of this order between shifts of the levels of the same configuration would be expected. Since such large differences do not occur, the specific mass effect must be relatively small.

3. EFFECT OF NUCLEAR SIZE OF MAGNETIC INTERACTION

Rosenthal and Breit have considered the effect of the finite size of the nucleus on the interaction of an electron with the nuclear magnetic moment and have shown that for heavy nuclei the effect may be appreciable. Thallium is the only heavy element whose nuclear magnetic moment has been measured by an induction method,[18] and the value so obtained is higher than any of the spectroscopic values. The correction factors to be applied to the spectroscopic values have been computed for a deep potential well with $v=0$ (*Case 1*), but not for *Case 3* and *Case 5*. Since the latter are more consistent with the observed isotope shifts than *Case 1*, their correction factors are evaluated here.

The coupling of the electron and the nuclear magnetic moment is proportional to the integral

$$I=\int_0^\infty \phi_1\phi_2 y^{-2}dy, \tag{25}$$

where ϕ_1 and ϕ_2 are the Darwin-Gordon radial functions. It is evident from the form of this integral that the values of the product $\phi_1\phi_2$ are weighted most heavily for small values of y where, for a nucleus of finite size, ϕ_1 and ϕ_2 depart most from their values in a purely Coulomb field.

For all the charge on the surface of the nucleus, *Case 3*, analytical expressions for ϕ_1 and ϕ_2 are given by Rosenthal and Breit. For uniform charge distribution, *Case 5*, ϕ_1 and ϕ_2 inside the nucleus were obtained as power series in y. The Rosenthal-Breit solutions with the value of C_-/C given by Eq. (21) apply outside.

The integrand $\phi_1\phi_2y^{-2}$ was evaluated and plotted against y for the range $0\leq y\leq 0.2$, taking $y_0=0.0271$, the radius used for isotope shifts. This plot was compared with a similar plot of the unperturbed $\phi_1{}^{(0)}\phi_2{}^{(0)}y^{-2}$, corresponding to a point nucleus. From this comparison a particular value $y=y_1$ is found such that the total area under the perturbed $\phi_1\phi_2y^{-2}$ curve is the same as the area under the unperturbed curve from y_1 to infinity. Thus,

$$\begin{aligned} I&=\int_0^\infty \phi_1\phi_2y^{-2}dy=\int_{y1}^\infty \phi_1{}^{(0)}\phi_2{}^{(0)}y^{-2}dy \\ &=I^{(0)}-\int_0^{y1}\phi_1{}^{(0)}\phi_2{}^{(0)}y^{-2}dy \\ &=\left\{1-\frac{2(j-\rho)\rho(2\rho+1)y_1{}^{2\rho-1}}{(2j-1)[\Gamma(2\rho+1)]^2}\right\}I^{(0)}. \end{aligned} \tag{26}$$

The values of y_1 and the correction factor, $I^{(0)}/I$, as obtained from Eq. (26), are given in Table V.

Spectroscopic values of μ, the magnetic moment of Tl^{205}, derived from splittings of unperturbed levels of the first three spectra, are given in Table VI. These have been calculated from the observed splittings by the method of Goudsmit[19] and Fermi and Segrè.[6] The interaction constants for the s electrons of Tl III are from Convey's thesis.[9] The origins of the others are indicated. The values of μ in column 4 of Table VI, multiplied by the appropriate value of $I^{(0)}/I$ from Table V, give the corrected values of μ listed in columns 5 and 6.

All the uncorrected values in column 4 of Table VI are appreciably lower than the induction measurement; 16 percent for s electrons and 9 percent for the $p_{\frac{1}{2}}$ electron. The discrepancy is almost completely removed by the corrections for both cases, with *Case 3* slightly closer. Since the difference between the correction factors for the two cases is smaller than the spread in the spectroscopic values, the comparison does not significantly discriminate between the two models. However, the deep potential well of *Case 1* gives a 30 percent correction and is thus untenable on the basis of this comparison.

TABLE V. Correction factors for thallium ($y_0=0.0271$).

	Case 3		*Case 5*	
	y_1	$I^{(0)}/I$	y_1	$I^{(0)}/I$
$^2S_{\frac{1}{2}}$	0.032	1.17	0.024	1.14
$^2P_{\frac{1}{2}}$	0.030	1.05	0.024	1.04

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[18] H. L. Poss, Phys. Rev. 72, 637 (1947).

[19] S. Goudsmit, Phys. Rev. 43, 636 (1933).

Although the correction decreases with decreasing atomic number, it appears to be significant for intermediate elements. For caesium, Millman and Kusch[20] obtained $\Delta(6^2S_{\frac{1}{2}})=0.30665$ cm^{-1}. This gives, by the Goudsmit-Fermi-Segrè formula, $g(I)=0.7025$. The directly measured value,[21, 22] $g(I)=0.7315$, is 3.9 percent higher. If we assume that $y_1=y_0$, as indicated by the values of y_1 in Table V, the corrected hyperfine structure value is $g(I)=0.728$, which differs from the directly measured value by only 0.4 percent. For lanthanum[23] $\Delta(6s\,^2S_{\frac{1}{2}}$ of La III$)=1.076$ cm^{-1} from which, by the Goudsmit-Fermi-Segrè formula, $g(I)=2.65$. The induction method[22] gives $g(I)=2.761$, which is 4.2 percent higher. The correction for nuclear radius, calculated as above, is 4.1 percent.

Thus when the values of the nuclear moments obtained from the interaction constants of s electrons by the Goudsmit-Fermi-Segrè formula are corrected for the finite size of the nucleus, they are in excellent agreement with those from direct induction measurements. The Goudsmit-Fermi-Segrè formula appears to be sufficiently accurate to warrant the use of $d\sigma/dn$, as obtained from Eq. (14), in the Fermi-Segrè factor rather than the rougher approximation $\Delta\sigma/\Delta n$.

Bitter[24] has pointed out that the ratio of the magnetic moments of the rubidium isotopes indicates that the spectroscopic values of the magnetic moments should be further corrected if the nuclear magnetic moment is distributed over the volume of the nucleus. It is indicated that this correction is of the same order as the Rosenthal-Breit correction. This is true only for Z small. For thallium, an upper limit for the correction arising from the distribution of magnetic moment within the nucleus can be determined as follows. As an extreme, the distribution of the magnetic moment could reduce the integrand of Eq. (25) to zero for $y<y_0$. A numerical calculation shows that this would increase the values of $I^{(0)}/I$ for an s electron, as given in Table V, by 3 percent. This additional correction is small because for a finite charge distribution the product $\phi_1\phi_2y^{-2}$ is much smaller in the region $y<y_0$ than it is for a point nucleus.

It is interesting to note that the formula for the magnetic distribution correction, $(2Zr_0/a_{\mathrm{H}})$, which is a justifiable approximation for light elements happens to be of the right order for heavy elements when the charge distribution is taken into account. On the other hand $(2Zr_0/a_{\mathrm{H}})$ is a fair approximation to the Rosenthal-Breit correction to the magnetic interaction only for light elements. For the heavy elements the Rosenthal-Breit correction increases much more rapidly with Z. Although the difference in the magnetic distribution correction for different isotopes may well account for the difference in the ratios of the magnetic moments determined spectroscopically and inductively, this correction is too small relative to the Rosenthal-Breit correction for heavy elements to modify our conclusions about the electron-nuclear potentials.

TABLE VI. Nuclear moment of thallium.

				μ, nuclear magnetons	
Spectrum	Term	Interaction constant, a_{ns} cm^{-1}	Uncorrected	Charge on surface	Uniform charge distribution
Tl III	$7s\,^2S_{\frac{1}{2}}$	1.348	1.37	1.60	1.56
	$8s\,^2S_{\frac{1}{2}}$	0.565	1.38	1.61	1.58
	$9s\,^2S_{\frac{1}{2}}$	0.295	1.39	1.63	1.59
Tl II	$6s5g$ $6sns$	5.88	1.44[b]	1.68	1.64
Tl I	$6p\,^2P_{\frac{1}{2}}$	0.710	1.49[c]	1.57	1.55
	$7s\,^2S_{\frac{1}{2}}$	0.400	1.35[d]	1.58	1.54
Average				1.61	1.58
Radio frequency induction[a]			1.628		

[a] See reference 18.

[b] Unpublished data by M. F. Crawford. In the $6s5g$ configuration, the multiplet structure is of the same order of size as the h.f.s. When the perturbations are taken into account, the separations of the hyperfine structure states of the configuration are consistent to within 0.010 cm^{-1} with $a_{6s}=5.88$. This value of a_{6s} is in agreement with that obtained from other high $6snx$ terms. μ was calculated taking 5.88 as the value of a_{6s} for Tl III.

[c] The value quoted in the table is that calculated by G. Breit (Phys. Rev. **38**, 463 (1931) increased by a 3 percent perturbation correction estimated by L. A. Wills (Phys. Rev. **45**, 883 (1934)). The Goudsmit-Fermi-Segrè method cannot be applied because the doublet splitting is required and the $^2P_{3/2}$ term is perturbed.

[d] Measurement by D. A. Jackson (Zeits. f. Physik **75**, 223 (1932)). calculation by H. Schüler and Th. Schmidt (Zeits. f. Physik **104**, 468 (1936)).

The effect of nuclear size on magnetic interaction is not consistent with a deep potential well, but is in agreement with either a uniform charge density or a concentration of the charge on the surface of the nucleus. The magnitude of the isotope shift is in best agreement with the uniform charge distribution. Even for this distribution it is necessary to conclude that the fractional change in the radius of the positive charge distribution for the addition of two neutrons is less than that given by radius $\propto$ (mass)$^{\frac{1}{3}}$. This suggests that the added neutrons do not cause a complete redistribution of the protons, and so may be considered as evidence for some form of stable shell structure in the nucleus. Both effects, particularly the magnetic interaction, lead to the conclusion that non-electrical forces between electrons and nuclei are small in comparison with the electrical forces. This conclusion is consistent with results on slow neutron scattering[25] which show that forces between neutrons and electrons are small.

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[20] S. Millman and P. Kusch, Phys. Rev. **58**, 438 (1940).

[21] Kusch, Millman, and Rabi, Phys. Rev. **55**, 1176 (1939).

[22] W. H. Chambers and D. Williams, Phys. Rev. **76**, 461 (1949).

[23] M. F. Crawford and N. S. Grace, Phys. Rev. **47**, 536 (1935); H. Wittke, Zeits. f. Physik **116**, 547 (1940).

[24] F. Bitter, Phys. Rev. **76**, 150 (1949); H. Kopfermann, *Kernmomente* (Akademische Verlagesellschaft, M.B.H., Leipzig, 1940), p. 17.

[25] Rainwater, Rabi, and Havens, Phys. Rev. **75**, 1295 (1949).