preted as supporting Feenberg's suggestion that the plateau which Dempster had drawn in the region 180–210 should be shifted to the region 108–124.

A detailed discussion of the effect on the packing fraction curve of the present measurements and others in progress will be given in a later paper.

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Spectroscopic Isotope Shift and Nuclear Polarization*

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Staggering of term values of odd isotopes with respect to those of the even ones is discussed. The validity of the static picture of nuclei as applied to their interaction with electrons is examined. It is found that the partial excitation of nuclei by atomic electrons results in polarization effects which lower the energy by amounts comparable to the observed irregularities and staggering. Correlations of observed shifts with the formation of stable shells are also discussed in a tentative way.

NOTATION

Ψ = wave function of nucleus and atomic electrons or electron.
N_i = nuclear functions; N_0 = nuclear ground state; N_1 = nuclear perturbing state.
$H = H^N + H^e + H' =$ Hamiltonian of the whole system.
E_i^N = energy of nuclear level.
E = total energy.
$E_i = E - E_i^N$.
$(\mathbf{r}, \mathbf{s}) \cdots$ Cartesian and spin coordinates of electrons taken collectively.
φ_i defined by $\Psi = \Sigma_i N_i \varphi_i(\mathbf{r}, \mathbf{s})$.
$\psi = \varphi_0$, $\varphi = \varphi_1$, $H_{ij}' = (N_i, H' N_j)$.
Operators: $H_0 = H^e + H_{00}'$, $H_1 = H^e + H_{11}'$.
(f, g) = radial functions for ψ.
(f_φ, g_φ) = radial functions for φ.
$G = rg$, $G_\varphi = r g_\varphi$, $\chi = \begin{pmatrix} G \\ G_\varphi \end{pmatrix}$.
$-U$ = potential energy of electron inside the nucleus (approximated by a constant).
$\hat{E}_0 = E_0 + U$, $\hat{E}_1 = E_1 + U$; a = nuclear radius.
$y = f/g$, y_φ / g_φ.
$V = H_{01}'$ (approximated by a constant).
θ defined by $-2V/[(E_0 - E_1)^2 + 4V^2]^{\frac{1}{2}} = \sin\theta$.
k_1, k_2 = the two possible values of $2\pi \times$ wave number for χ inside nucleus; values of k_1, k_2 are obtainable from Eq. (3.6).
$z_1 = k_1 a$.
$z_2 = k_2 a$.
ξ_1, ξ_2 are defined by Eq. (3.2).
$a' = amc/\hbar$, $\gamma = Ze^2/\hbar c$.
$\rho = (1 - \gamma^2)^{\frac{1}{2}}$.
$\Delta(\delta y) \equiv y_{a+\delta a}(a + \delta a) - y_a(a + \delta a)$.
A = mass number.
$\delta_e E$ = change in the electron's energy $\delta_e E$ caused by $A \rightarrow A + \delta A$.
$s = \delta_e E / \delta U$.
$\mathfrak{M}$ defined by Eq. (6.5).
κ_0 defined by Eq. (6.7); κ_0 = value of k_1 for $V = 0$.
κ defined by Eq. (7).
n = principal quantum number.
δ = quantum defect.
F = relativistic correction factor for electron density at nucleus.
$\mathfrak{R}$ = ratio of electron density at nucleus to that for a free electron.
p = momentum of electron in units mc.
$C(E)$ coefficient of lowest power of r in formula for linear density of s electron for unit linear density at $r = \infty$.
$S(r)$ = wave function of s nucleon in ground state.
z_N = charge of nuclear particle interacting with electron.

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I. INTRODUCTION

IT is usually supposed that the hyperfine structure of spectroscopic terms can be understood sufficiently well by considering only the static features of the nucleus. A marked exception has been pointed out by A. Bohr who found that the deuteron has to be considered in terms of its constituent parts rather than as a static system. Conditions in the deuteron are somewhat exceptional because the whole nuclear charge is carried by the proton, while in heavier nuclei the charge on any one of the nuclear protons is a small fraction of the whole. The centering of the electronic wave function on a proton is not likely to be as important in these cases. It appears, nevertheless, that the static picture is not necessarily a good one and may be inadequate in discussions of isotopic displacements of spectroscopic terms. In the usual theory[1] of these displacements the change in nuclear radius which is held responsible for the effect is only a small fraction ($\sim 1/600$) of the whole radius. The change in potential energy between the electron and the nucleus is correspondingly small in comparison with the whole deviation from Coulomb energy which is expected from customary nuclear models. It would not be too surprising, therefore, if other effects than changes in the nuclear radius were found to be important. One such effect has been suggested by Brix and Kopfermann[2] in connection with

[1] G. Racah, Nature **129**, 723 (1932); J. E. Rosenthal and G. Breit, Phys. Rev. **41**, 459 (1932); G. Breit, Phys. Rev. **42**, 348 (1932).
[2] P. Brix and H. Kopfermann, Zeits. f. Physik **126**. 344 (1949).

anomalies in the isotopic displacements for Sm and Nd. Kopfermann's suggestion that these anomalies are caused by the deviation of the nuclear charge distribution from spherical symmetry is not literally tenable in the form stated by him because nuclei of spin O must have spherical symmetry. The essential idea is applicable, however, because the value zero for the total angular momentum can be secured by having the wave function in the form of a linear combination of space coordinate and spin functions none of which correspond to zero angular momentum. The charge distribution could be reasonably supposed to be determined by the space coordinate factors and the deviation from spherical symmetry which corresponds to these is independent of the magnetic quantum numbers. Thus, *e.g.*,

$$\psi = 3^{-\frac{1}{2}}(u_1 S_{-1} - u_0 S_0 + u_{-1} S_1)$$

with u_1, u_0, u_{-1} and S_1, S_0, S_{-1} standing for space coordinate and spin functions of angular momentum 1 with magnetic quantum numbers 1, 0, -1, respectively, is a wave function for a state of resultant angular momentum zero. The charge density is obtainable from

$$|u_1|^2 + |u_0|^2 + |u_{-1}|^2,$$

which is spherically symmetric. The charge density for a spinless state described by one of the u_m can have a quadrupole moment, however, and the mean electrostatic energy of the electron can be affected by a deviation from spherical symmetry of the charge distribution of the states u_1, u_0, u_{-1}. In order that this revision of Kopfermann's attempt to correlate anomalies in the isotopic shift with quadrupole moments be applicable to nuclei of zero total angular momentum, it is necessary to suppose that the coupling of the space coordinate functions to the sum of the spins does not affect the charge distribution. This is true for the wave function as it is written above. It will be remembered, however, that such a wave function is modified by spin-orbit and spin-orbit-spin (tensor) forces which are often supposed to be large in nuclei.[3] A dilemma seems to present itself at this point: One must either discard the view that large spin-orbit interactions are responsible for shell structure or else one must consider the connection between the isotope displacement and the occurrence of quadrupole moments as accidental for nuclei of zero spin. It is not clear, however, that the conditions of nuclear structure which are favorable for a large quadrupole moment are necessarily dissociated from irregularities in the average electrostatic energy of the electron which may exist quite apart from the direct geometrical effects on charge distribution associated with the existence of a quadrupole moment. Kopfermann's assumption of equal progressions in total volume of nuclei independently of their shape is an appealingly simple one. It cannot be considered, however, to be a necessary consequence of nuclear theory. Other possible sources of irregularities in the isotopic shift deserve consideration as well, therefore.

Another interpretation of Kopfermann's viewpoint brought out in a discussion by Dr. A. Bohr is that the nucleus has an intrinsic angular momentum and quadrupole moment with respect to an axis definable by internal coordinates and that the condition of zero spin arises from a factor in the wave function containing the polar coordinate angles of the spin axis. But also on this view Kopfermann's explanation implies an absence of dynamic interaction between the rotation of the spin axis and the internal coordinates, in addition to the constant volume assumption. While these hypotheses have plausibility their validity appears to require justification.

The isotopic shift of heavy elements shows a striking difference between even and odd isotopes of elements with even Z. The odd isotopes behave as though their volume were anomalously small in the language of the volume effect explanation. An increase in nuclear volume amounts to a decrease of the attraction between the electron and the nucleus and the staggered position of the term values of the odd isotopes suggests that there might be some specific source of attraction between an electron and the nucleus of an odd isotope. It will be recalled here that the direction of the effect is such as though for the odd isotopes the nuclear radius were somewhat smaller than would be expected from the observed term values of the even ones. On a naive view the smaller stability of odd isotopes suggests an abnormally large nuclear radius, in accordance with the virial theorem. It is perhaps conceivable that an odd neutron dangles more or less on the outside of the nucleus without affecting the proton charge distribution to a large degree. Such an explanation appears a forced one, however, because the question arises as to why a pair of neutrons should not behave similarly to a single one. It appears natural to investigate the order of magnitude of polarization effects of a nucleus by atomic electrons because such effects should lower the energy and because the observed density of nuclear levels for odd isotopes is usually larger for odd isotopes than for even ones.[4,5] It is found in the estimates presented that the polarization effects can conceivably be large enough to have an influence on the phenomenon and may possibly be one of the main contributing factors.

II. GENERAL EXPANSION

The wave function Ψ will be expanded in terms of products of a normal orthogonal complete set of nuclear functions N_i. The coefficients of the N_i are functions of

[3] M. G. Mayer, Phys. Rev. **74**, 235 (1948).

[4] A. C. G. Mitchell (private communication); also Kern, Mitchell, and Zaffarano, Phys. Rev. **76**, 94 (1949); Brolley, Sampson, and Mitchell, Phys. Rev. **76**, 624 (1949); Mitchell, Mei, Maienschein, and Peacock, Phys. Rev. **76**, 1450 (1949), and other papers.

[5] Pollard, Sailor, and Wylie, Phys. Rev. **75**, 725 (1949); Davison, Buchanan, and Pollard, Phys. Rev. **76**, 890 (1949); L. D. Wylie, Phys. Rev. **76**, 316 (1949); R. J. Creagan, Phys. Rev. **76**, 1769 (1949), and other papers.

the electronic coordinates. These functions are denoted here by φ_i. The expansion is

$$\Psi=\Sigma_i N_i\varphi_i(\mathbf{r}, \mathbf{s}), \tag{1}$$

where r, s denote the Cartesian and spin coordinates of the electrons. The Hamiltonian is represented as

$$H=H^N+H^e+H', \tag{1.1}$$

where superscipts N, e refer, respectively, to the nucleus and electron. The operator H^N contains no electronic coordinates and spins. Similarly H^e is free of nuclear quantities. The total energy of the system is denoted by E so that

$$(H-E)\Psi=0. \tag{1.2}$$

The functions N_i satisfy the orthogonality relations

$$(N_i, N_j)=\delta_{ij}. \tag{1.3}$$

The eigenvalues of H^N corresponding to the N_i will be designated by E_i^N so that

$$(H^N-E_i^N)N_i=0. \tag{1.4}$$

The E_i^N will be referred to as the energy values of nuclear levels i. As in all perturbation calculations the spectrum of the unperturbed problem is affected by the choice of the complete set of functions in terms of which the expansion is made. The energies E_i^N thus depend on the choice of the operator H^N. This arbitrariness may be supposed to be not very serious, however, in the present problem because the forces exerted on a nuclear particle by the electrons are not as effective as those originating in other nuclear particles. The operator H^N may include, for instance, some of the electrostatic potential produced by the electrons in the nucleus. It will be seen, however, that the calculation as carried out below will bring in such effects of its own accord so that the results are largely independent of additions to H^N and corresponding subtractions from H' or H^e.

Substitution of the form of Ψ given by Eq. (1) into the complete wave equation gives

$$(H^e-E_i)\varphi_i+\Sigma_j H_{ij}'\varphi_j=0, \tag{1.5}$$

where

$$E_i=E-E_i^N \tag{1.6}$$

is the energy left over for the electrons when the nucleus is in the state i. Here

$$H_{ij}'=(N_i, H'N_j)_N \tag{1.7}$$

with the understanding that

$$(\ )_N$$

designates a scalar product in the space of nuclear variables only, i.e., with the convention of treating the electron variables as fixed parameters. The H_{ij}' are functions of the electronic variables. They have the significance of matrix elements of H' for a dynamic consideration of the nuclear system and a static consideration of the electrons. Equation (1.5) gives in a sense the reaction of the nuclear system on the electronic one. If the non-diagonal H_{ij}' could be neglected one would have only the correction terms $-H_{ii}'$ to the E_i which correspond to a picture of the nucleus in which its effect on the electrons is describable by a static field. In fact for this approximation

$$(H^e+H_{ii}'-E_i)\varphi_i=0, \tag{1.8}$$

so that for each i there is an effective Hamiltonian H^e+H_{ii}' which determines E_i, φ_i. The energy of the system is in this approximation

$$E=E_i^N+E_i=(\varphi_i N_i, H\varphi_i N_i)/(\varphi_i N_i, \varphi_i N_i), \tag{1.9}$$

as is readily verified from the previous formulas. This energy is independent of the breakup of H into H^N, H', H^e except insofar as this breakup affects the wave function $\varphi_i N_i$. Since the right side of Eq. (1.9) is the expectation value of H, it is approximately independent of the choice of $\varphi_i N_i$ in accordance with the Ritz variational principle. The errors in the energy E involve the errors in the wave function only quadratically. The approximation of Eq. (1.8) gives in a sense a static picture of the action of the nucleus on the electrons, for it corresponds to the elimination of an explicit consideration of internal nuclear coordinates and a picture of an effective Hamiltonian H^e+H' containing electronic coordinates only. From a calculational viewpoint the present paper is concerned with estimates of some of the inaccuracies resulting from the application of Eq. (1.8).

The effect of the non-diagonal terms in Eq. (1.5) can be taken into account with sufficient accuracy by a perturbation calculation which is practically identical with the standard second-order calculation of the energy. This fact will be first established by an examination of a special case for which an explicit solution can be worked out.

III. TWO NUCLEAR LEVELS; ONE ELECTRON

In the present section the influence of only one excited nuclear level will be considered. The consideration of the electronic system will be simplified also by taking into account only one electron and bringing in, therefore, some contributions to the energy which have to be modified so as to be in agreement with the exclusion principle. The state N_0 will denote the nuclear ground state, N_1 the perturbing state. The corresponding functions φ_0, φ_1 will be now called ψ, φ. The coupled equations are

$$H_0\psi+H_{01}'\varphi=E_0\psi, \quad H_{10}'\psi+H_1\varphi=E_1\varphi, \tag{2}$$

where

$$H_0=H^e+H_{00}', \quad H_1=H^e+H_{11}'. \tag{2.1}$$

The functions ψ, φ are four-component functions for Dirac's electron. In order to simplify calculation it will be assumed that: (a) H_{01}' does not operate on the

electronic spin coordinates which is the case for electrostatic interactions, (b) inside the nucleus H_0 is of the form of Dirac's electron Hamiltonian with a constant potential energy, (c) it is sufficiently accurate to replace H_{01}' and H_{10}' by a real constant V through the nuclear interior and zero outside the nucleus. The calculation will be carried through as though $H_0=H_1$. The latter simplification does not restrict the range of applicability of the results because the difference between H_1 and H_0 is equivalent according to (b) to a difference between E_1 and E_0.

The radial wave functions for ψ will be designated by f, g in the customary manner [see Eqs. (12.3a)] and those for φ by f_φ, g_φ.

In terms of the abbreviations

$$G=rg, \quad G_\varphi=rg_\varphi, \quad \chi=\begin{pmatrix} G \\ G_\varphi \end{pmatrix} \tag{2.2}$$

there results the convenient equation

$$\frac{d^2\chi}{dr^2}+\frac{1}{c^2\hbar^2}\begin{pmatrix} \hat{E}_0^2-m^2c^4+V^2, & -(\hat{E}_0+\hat{E}_1)V \\ -(\hat{E}_0+\hat{E}_1)V, & \hat{E}_1^2-m^2c^4+V^2 \end{pmatrix}\chi=0, \tag{2.3}$$

where

$$\hat{E}_0=E_0+U, \quad \hat{E}_1=E_1+U. \tag{2.4}$$

Here U is the negative of the potential energy between the electron and the nucleus. The nuclear radius is denoted by a. As an approximation U is taken to be zero for $r>a$. For $r<a$ it will be approximated by

$$U\cong Ze^2/a. \tag{2.5}$$

By straightforward calculation it is found that the region $0<r<a$ gives the following connection between

$$y=f/g, \tag{2.6}$$

and

$$y_\varphi=f_\varphi/g_\varphi, \tag{2.7}$$

$$y=(\alpha+\beta y_\varphi)/(\gamma+\delta y_\varphi), \tag{3}$$

where

$$\begin{aligned} \alpha&=-(\hbar c/a)\eta_1\eta_2, \\ \beta&=\eta'(a_{11}'\mathbf{c}+a_{12}'\mathbf{s})+\eta''a_{11}', \\ \gamma&=\eta'(-a_{21}'\mathbf{s}+a_{22}'\mathbf{c})-\eta''a_{22}', \\ \delta&=(a/\hbar c)(a_{11}'a_{22}'-a_{12}'^2). \end{aligned} \tag{3.1}$$

Here

$$\eta_i=\xi_i-1, \quad \xi_i=k_ia\cot(k_ia), \quad (i=1,2) \tag{3.2}$$

$$\eta'=(\eta_1-\eta_2)/2, \quad \eta''=(\eta_1+\eta_2)/2, \tag{3.3}$$

$$a_{11}'=\hat{E}_1+mc^2, \quad a_{22}'=\hat{E}_0+mc^2, \quad a_{12}'=a_{21}'=V, \tag{3.4}$$

$$\begin{aligned} \mathbf{s}&=\sin\theta=-2V/[(E_0-E_1)^2+4V^2]^{\frac{1}{2}}, \\ \mathbf{c}&=\cos\theta=(E_0-E_1)/[(E_0-E_1)^2+4V^2]^{\frac{1}{2}}, \end{aligned} \tag{3.5}$$

$$k_1^2=c_{11}+c_{12}\tan(\theta/2), \quad k_2^2=c_{22}-c_{12}\tan(\theta/2); \tag{3.6}$$

with

$$\begin{aligned} c_{11}&=(\hat{E}_0^2-m^2c^4+V^2)/(c^2\hbar^2), \\ c_{22}&=(\hat{E}_1^2-m^2c^4+V^2)/(c^2\hbar^2), \\ c_{12}&=c_{21}=-V(\hat{E}_0+\hat{E}_1)/(c^2\hbar^2), \end{aligned} \tag{3.7}$$

where the c_{ij} are the elements of the matrix occurring in Eq. (2.3).

By means of the equations listed, one can obtain y at $r=a$ in terms of y_φ at the same point. On the other hand, the boundary condition at $r=\infty$ when applied to g, f and g_φ, f_φ determines y and y_φ at $r=a$ for an assumed E. With these values of y and y_φ, Eq. (3) determines the energy.[6] A complete solution along these lines is not necessary, however, because the variation of y_φ with E is important on a much coarser scale than that within which there is any question as to the value of E. The value of y_φ is essentially determined by the nuclear excitation energy $E_1^N-E_0^N$ and the change in y caused by V can be used to estimate the energy change by comparison with the corresponding change for the central field problem.

Expanding in V^2 and retaining only terms of first power in V^2 one has the approximation

$$\begin{aligned} y\cong(\hbar c/a)(\zeta_1/a_{22}')\{1+(\delta\xi_1/\zeta_1)+\zeta'\delta_1/(\zeta_1a_{11}') \\ +V^2/(a_{11}'a_{22}')+(\hbar c/a)[\zeta'\zeta_2\delta_1/(\zeta_1a_{11}') \\ -\zeta'\delta_2/a_{22}'+V^2\zeta_2/(a_{11}'a_{22}')]/D\}, \end{aligned} \tag{4}$$

where

$$D=a_{11}'y_\varphi-(\hbar c/b)\zeta_2, \tag{4.1}$$

and

$$\zeta_i=(\eta_i)_{V=0}, \quad \zeta'=(\eta')_{V=0}, \quad (i=1,2) \tag{4.2}$$

$$\delta_i=-2V^2(\hat{E}_{i-1}+mc^2)/(E_0-E_1)^2. \tag{4.3}$$

The quantities

$$\delta\xi_1=[\cot z_1-(z_1/\sin^2z_1)]z_1V^2\hat{E}_0/[(\hat{E}_0^2-m^2c^4)(\hat{E}_0-\hat{E}_1)], \tag{4.4}$$

$$\delta\xi_2=[\cot z_2-(z_2/\sin^2z_2)]z_2V^2\hat{E}_1/[(\hat{E}_1^2-m^2c^4)(\hat{E}_1-\hat{E}_0)], \tag{4.5}$$

are the first-order changes in ξ_1, ξ_2. Here the $z_i=k_ia$, with k_i taken for $V=0$. It was found that Eq. (4) is a sufficiently good approximation to Eq. (3) and that effects of higher powers of V^2 are, therefore, not serious.

Substitution of numbers gives

$$y\cong-0.205[1+0.00012V^2-0.0016V^2/(1+4.98y_\varphi)], \tag{4.6}$$

where V is expressed in mc^2 and the following values of parameters have been used

$$\begin{gathered} a=1.5\times(208)^{\frac{1}{3}}\times10^{-13}\text{ cm}, \\ U=82e^2/a=26.0mc^2, \quad E_0=mc^2, \quad E_1=mc^2/2. \end{gathered}$$

These values of the parameters are intended to represent conditions for Pb^{208}.

The change in y caused by V may be compared with that produced by cutting off the Coulomb potential at $r=a$. The cut-off will be supposed to be made in such a way as to replace the Coulomb energy in $0<r<a$ by the constant value $-Ze^2/a$. One finds for the cut-off

[6] G. Breit and G. E. Brown, Phys. Rev. **76**, 1307 (1949).

field

$$[y(a)]_{\text{cut-off}}=-(\gamma/3)-\gamma^2(2+\gamma/a')a'/45+\cdots, \quad a'=amc/\hbar, \quad \gamma=Ze^2/\hbar c. \tag{5}$$

For the solution of the Dirac equation in a Coulomb field one has, on the other hand,

$$[y(a)]_{\text{Coulomb}}=-[\gamma/(1+\rho)]\times\{1+2\gamma a'/[(2\rho+1)(\rho+1)]+\cdots\}, \quad \rho=(1-\gamma^2)^{\frac{1}{2}}. \tag{5.1}$$

For the values of the parameters employed in Eq. (4.6) these formulas give -0.334 as the value of $y(a)$ for the straight cut-off field and -0.204 for the unmodified Coulomb case. The change caused by the cut-off is $0.334-0.204=0.130$.

It is not fair to use this change as a criterion of sensitivity of energy to changes in y because the experimental energy shift, on the nuclear volume change picture, is more closely related to changes in y produced by changing the nuclear radius. The value of y at the increased nuclear radius $a+\delta a$ undergoes the change

$$\Delta(\delta y)\equiv y_{a+\delta a}(a+\delta a)-y_a(a+\delta a)\cong[-(2\gamma a'/15)+1]\gamma(\delta a'/3a')\cong\gamma\delta a'/3a', \tag{5.2}$$

in accordance with Eqs. (5), (5.1). For $Z=82$ this formula gives

$$\Delta(\delta y)\cong 0.199\delta a/a. \tag{5.3}$$

If the nuclear volume is supposed to be proportional to the mass number A then $\delta a/a=\delta A/3A$ and for a change of A from 207 to 208 one obtains

$$\Delta(\delta y)\cong 0.00032. \tag{5.4}$$

If, instead, one employed the number 0.130, obtained by direct application of Eq. (5.1), one could estimate $\Delta(\delta y)$ as $0.130/624=0.00021$, which agrees approximately with Eq. (5.4) but underestimates the effect. The crudeness of the latter estimate is caused by the change in the shape of the electronic wave function inside the nucleus which is produced by the cut-off. For $E_1=0.5$ with a Coulomb field in $a<r<\infty$ the value of y_φ may be estimated approximately to be -2. Using this value and requiring that the effect of V^2 in Eq. (4.6) be equal to one-half of the amount in Eq. (5.4) one obtains for V the value $1.6\ mc^2$. The sign of the change in y produced by either sign of V is positive while the cut-off of the Coulomb potential increases y as in Eq. (3.4). The effect under discussion is seen to oppose the nuclear volume effect, in accordance with expectation.

If instead of $y_\varphi=-2$ one had used a value corresponding approximately to the vanishing of the denominator in Eq. (4.6) one would have obtained a much smaller value of V. Such a value of y_φ corresponds to a stationary state of the electron in the condition described by the wave function φ. Thus, for example, the straight cut-off gives according to Eq. (5.1) the value -0.204 which makes the denominator very small and this value would have to be reproduced by the branch of the wave function which is regular at $r=\infty$ if the level is a stationary one. Such a condition corresponds to a resonance of the nuclear excitation energy with a jump of the electron to a lower energy level. It would be incorrect to make use of it because nuclear levels have larger spacings than those between optical energy levels while the x-ray levels are occupied, so that transitions into them cannot take place. The unoccupied shells which are left in the building up of the periodic system do not have the azimuthal quantum number $L=0$ or 1. Transitions to the unoccupied levels may be assumed to be improbable, because the wave functions do not penetrate to the nucleus. The value $y_\varphi=-2$ is very different from those corresponding to approximate resonance and the effect computed above is, therefore, not especially concerned with forbidden transitions to occupied electron states. In order to have greater certainty concerning this point calculations by the standard second-order perturbation formula have been carried out and the results are presented in Section IV. The application of the second-order perturbation method for approximate calculation is justifiable because the approximate Eq. (4) agrees with Eq. (3) reasonably up to $V=10\ mc^2$.

The estimates made in the present section do not take into account the fact that negative energy states of the electron are occupied. This is clear from the fact that there is in principle no difference between the occupied atomic electron shells and the occupied negative energy states. While of little value for direct quantitative application they are included in this paper because they indicate the approximate validity of the second-order perturbation theory and also because their approximate agreement with other estimates is an indication that the effect of pair theory is not too pronounced.

IV. SECOND-ORDER PERTURBATION ENERGY

The second-order energy will be first estimated in a model which neglects the Coulomb interaction outside the nucleus. The crude character of this procedure is partly offset by calculating the volume effect for the same model and expressing the answer in terms of the ratio of the two effects. The normalization factor of the initial electronic state cancels out as a result. The object of this calculation is more that of locating the energy region which contributes principally to the effect rather than of obtaining a precise number for the effective value of V.

The ratio of the second-order perturbation energy $E^{(2)}$ to the change in the electron's energy $\delta_c E$ caused by a fractional increase $\delta A/3A$ in nuclear radius can be expressed in the following form:

$$\frac{E^{(2)}}{\delta_c E}=-\frac{V^2}{\pi}\frac{3A}{\delta A}\frac{a}{Ze^2 s}\int\frac{N^2|\mathfrak{M}(E)|^2}{E_1-E}dk, \tag{6}$$

where

$$s=\delta_c E/\delta U=\int_0^a (f_0^2+g_0^2)r^2dr, \tag{6.1}$$

with f_0, g_0 denoting the radial functions for the ground state. The normalization convention regarding integration over angles is such that

$$\int_0^\infty (f_0^2+g_0^2)r^2dr=1. \tag{6.2}$$

The remaining undefined symbols in Eq. (6) will now be explained. The change in energy $\delta_c E$ is supposed to be produced by a change δU in U through the distance a and the value

$$\delta U=(Ze^2/a)(\delta a/a) \tag{6.3}$$

is used with

$$\delta a/a=\delta A/3A. \tag{6.4}$$

These relations give the first-order change in energy for a straight horizontal cut-off of the Coulomb potential. At this point there is an apparent inconsistency in the model because the effect of the Coulomb potential is omitted for the wave functions. The inconsistency does not involve anything more than the approximation of substituting wave functions outside the nucleus for $Z=0$ for those with the true Z, affecting somewhat the relative weights of different parts of the continuum.

The matrix element $\mathfrak{M}$ for the continuum is defined by

$$VNN_0\mathfrak{M}=\int_0^a (ff_0+gg_0)Vr^2dr, \tag{6.5}$$

where the normalization constants N, N_0 are introduced by

$$\begin{gathered}(rg_0)=N_0\sin\kappa_0 r, \quad (r<a),\\ \langle r^2(f^2+g^2)\rangle_{Av}=1,\\ (rg)=N\sin\kappa r, \quad (r<a).\end{gathered} \tag{6.6}$$

The values of the quantities are obtainable from:

$$s=a/2-s_0c_0/2k_0+(\hbar^2c^2/a)[\kappa_0 a s_0c_0/2-s_0^2+(\kappa_0 a)^2/2]/(\hat{E}_0+mc^2)^2, \tag{6.7}$$

$$\kappa_0=[(E_0+U)^2-m^2c^4]^{\frac{1}{2}}/\hbar c, \quad s_0=\sin(\kappa_0 a), \quad c_0=\cos(\kappa_0 a),$$
$$1/N^2=[E/(E+mc^2)](1+C^2)\sin^2(\kappa a), \tag{7}$$

$$\kappa=[(E+U)^2-m^2c^4]^{\frac{1}{2}}/\hbar c, \tag{7.1}$$

$$C=\left[\frac{(\hat{E}-mc^2)(E+mc^2)}{(\hat{E}+mc^2)(E-mc^2)}\right]^{\frac{1}{2}}\left[\cot\kappa a-\frac{1}{\kappa a}\right]+\frac{1}{\kappa a}, \tag{7.2}$$

$$\hat{E}=E+U,$$

$$\mathfrak{M}(E)=\frac{\hbar^2c^2/a}{(\hat{E}+mc^2)(\hat{E}_0+mc^2)}\times\left[\frac{\hat{E}+mc^2}{E-E_0}(\kappa_0 a)sc_0+\frac{\hat{E}_0+mc^2}{E_0-E}(\kappa a)s_0c-ss_0\right], \tag{7.3}$$

$$s=\sin(\kappa a), \quad c=\cos(\kappa a). \tag{7.4}$$

Computation for $E_0=mc^2$, $E_1=mc^2/2$ and otherwise for the same values of the parameters as in Section III yields for V the approximate value 1.7 mc^2 if it is desired that the effect of V be $\frac{1}{2}$ of the absolute value of the volume effect. The contributions from $E>180\ mc^2$ have been neglected and the number is, therefore, an overestimate for V. Only the contributions to the integral arising from the continuum have been taken into account so that the exclusion principle does not affect this part of $E^{(2)}$. Most of the effect comes from high excitation energies of about 50 mc^2.

This fact would seem to indicate that the energy change is not sensitive to the position of perturbing nuclear levels of moderate excitation energy. Calculations described in Section V show, however, that the model used underestimates the importance of the smaller electron excitations.

V. EFFECT OF COULOMB FIELD

The effect of the Coulomb field at electron distances $r>a$ has not been considered so far. This produces an increase in the contribution to $E^{(2)}$ from the region of excited electron states close to ionization. The situation can be understood qualitatively in terms of discrete states just below ionization. For a screened nuclear field, with effective internal and external charges Z, Z_0 the non-relativistic electron density for s states at $r=0$ is

$$\psi^2(0)=ZZ_0^2/[\pi a_H^3(n-\delta)^3]$$

where a_H is the Bohr radius and δ the quantum defect, which is assumed to be independent of the principal quantum number n. The spacing between adjacent levels is

$$\Delta E=Z_0^2e^2/[a_H(n-\delta)^3].$$

The density at the nucleus per unit energy range of electron states is, therefore,

$$\psi^2(0)/\Delta E=(Z/a_H)(m/\pi\hbar^2). \tag{8}$$

On the other hand, in the absence of the Coulomb field, the corresponding quantity for states having momentum p is

$$pEdE/(2\pi^2c^2\hbar^3), \tag{8.1}$$

relativistically. Formula (8) underestimates the density, being non-relativistic. The appropriate correction factor taking account of relativistic effects will be called F. The ratio of the Coulombian density to that for a free electron will be called $\mathfrak{R}$ so that according to Eqs. (8), (8.1)

$$\mathfrak{R}=2\pi F(\hbar/p)(Z/a_H). \tag{8.2}$$

For small values of p this ratio increases. Allowing F to have the value 2 the value of $\mathfrak{R}$ following from the above estimate for $p=mc/2$, $Z=80$ is $\cong 20$. An omission of the effect of the large concentration of electron density per unit energy range is seen to underestimate the influence of the low excitation states of the electron

and to give an underestimate of the effect of low nuclear excitations in comparison with the high ones.

The effect of the Coulomb field is calculated here relativistically but with the omission of effects of deviations from the Coulomb law at small distances. Arguments can be produced to indicate that the latter effect is not serious up to $E=10$ or 20. The calculation as made applies to a model which precludes the possibility of an isotopic nuclear volume effect due to static causes but allows for nuclear polarization effects. The solution of Dirac's radial equations along standard lines due to Dirac,[7] Gordon,[8] and Darwin[9] and the application of standard relations of these solutions to Whittaker's confluent hypergeometric function gives for small values of r

$$(rf)^2+(rg)^2=C(E)r^{2\rho}, \tag{9}$$

where γ and ρ are given by Eqs. (5), (5.1), and

$$C(E)=(2p)^{2\rho}[1+(\rho/E)]\,|\,\Gamma(\rho+i\sigma)/\Gamma(2\rho+1)\,|^2 e^{\pi\sigma} \tag{9.1}$$

with

$$\sigma=E\gamma/p, \tag{9.2}$$

$$p=(E^2-1)^{\frac{1}{2}}. \tag{9.3}$$

The normalization is such as to give unit average linear density for large r, i.e., such that $\langle(rf)^2+(rg)^2\rangle=1$. The unit of energy is here mc^2 and that of length is $\hbar/mc$. The momentum in units mc is designated by p. Higher powers of r are omitted in Eq. (9). The expression on the right of Eq. (9.1) has been obtained by an independent calculation along the lines mentioned. It can also be obtained from Eq. (40) in Fermi's classic paper[10] on β-ray theory, which makes use of Hulme's work[11] on Dirac's equation. In comparing Eq. (9) with Fermi's result, account must be taken of the following circumstances: (a) Fermi's problem includes the consideration of both spin directions while in the present work only one spin direction enters; for this reason a factor $\frac{1}{2}$ must be applied to Fermi's expression in the comparison; (b) in β-ray theory the emission of electrons in $p_{\frac{1}{2}}$ states has to be considered while in the present problem only $s_{\frac{1}{2}}$ states perturb the initial state. The effect of the latter circumstance is to bring in a factor $2E/(E+\rho)$ to be applied to $C(E)$. The origin of this factor is as follows. From the symmetry properties of Dirac's radial equations one finds that a change of f into g, g into $-f$, E into $-E$ and r into $-r$ changes the equations for $s_{\frac{1}{2}}$ into those for $p_{\frac{1}{2}}$. Since the argument of the hypergeometric functions is $2(1-E^2)^{\frac{1}{2}}r$, a change of the sign of r is equivalent to changing the sign of p and leaving r unchanged. The quantity σ is thus unchanged and the factor $1+\rho/E$ is replaced by $1-\rho/E$ for $p_{\frac{1}{2}}$ states. Summation over $s_{\frac{1}{2}}$ and $p_{\frac{1}{2}}$ states replaces, therefore, $1+\rho/E$ by 2 and this replacement is equivalent to multiplication by $2E/(E+\rho)$. Finally there is a factor 4π to be applied to the right of Eq. (9) because in the present calculation $\langle(rf)^2+(rg)^2\rangle=1$ while in Fermi's the corresponding average is 4π. Since it is possible to derive Eq. (9) in this way, further details concerning mathematical relations need not be gone into.

For the same convention concerning normalization one can compare Eq. (9) with the corresponding expression in the absence of the Coulomb field. The ratio of the two is

$$\mathfrak{R}=\frac{(E+\rho)(2p)^{2\rho}}{(E+1)(E^2-1)}\left|\frac{\Gamma(\rho+i\sigma)}{\Gamma(2\rho+1)}\right|^2 e^{\pi\sigma}\gamma^{2\rho-2} \tag{9.4}$$

for the case of small distances, keeping only the first non-vanishing power of r. The elements of special interest have values of Z approximately equal to 80 so that $\gamma=0.6$, $\rho=0.8$ may be used. For large E the complex Γ-function approaches $\Gamma\,(0.8+0.6i)$, for small p the σ becomes infinite. It is found by numerical trial that for the crude object in hand one obtains a satisfactory representation of $|\,\Gamma(\rho+i\sigma)\,|^2$ by means of Stirling's formula so that

$$C(E)\cong 2^{2\rho+1}\pi\gamma^{2\rho-1}(E+\rho)E^{2\rho-2} \times[\Gamma(2\rho+1)]^{-2}p/[1-\exp(-2\pi\sigma)] \tag{9.5}$$

and

$$\mathfrak{R}=[E/(E+1)]p^{-2}r^{2\rho-2}C(E). \tag{9.6}$$

Since p enters as p in Eq. (9.5) and as p^{-1} in $\mathfrak{R}$ the quantities $C(E)$ and $\mathfrak{R}$ vanish and become infinite, respectively, at low electron energies. The infinity of $\mathfrak{R}$ at $E=1$ enhances the importance of low electron excitations and is in agreement with the estimates at the beginning of Section V. Employing the schematic representation of the interaction of the electron with the nucleus by means of a constant V, and approximating the wave function for the normal state of the electron by the term in the first non-vanishing power of r, one has

$$f_0=-N_0[(1-\rho)/(1+\rho)]^{\frac{1}{2}}r^{\rho-1},\quad g_0=N_0r^{\rho-1}, \tag{9.7}$$

$$E^{(2)}=-(2/\pi)N_0{}^2V^2(1+\rho)^{-1}[a^{2\rho+1}/(2\rho+1)]^2 \times\int C(E)\,|\,E_1-E\,|^{-1}dE, \tag{9.8}$$

where N_0 is a normalizing factor for the bound state which will be eliminated by comparison with the volume effect on the isotope shift. The latter will be approximated by the value of the first-order perturbation energy caused by cutting down the negative of the Coulomb energy from the value γ/r to the constant value γ/a within $0<r<a$ and changing the nuclear radius from a to $[1+(1/3A)]a$ for isotopes with mass numbers A, $A+1$. The distortion of the wave function by the nuclear potential well is neglected in the present

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[9] C. G. Darwin, Proc. Roy. Soc. **A118**, 654 (1928).
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[11] H. R. Hulme, Proc. Roy. Soc. **A133**, 381 (1931).

qualitative considerations. The resultant change in E is called $\delta_c E$. One finds

$$\delta_c E=[2\gamma N_0^2/a(1+\rho)][a^{2\rho+1}/(2\rho+1)](\delta a/a) \quad (9.9)$$

and hence

$$E^{(2)}/\delta_c E\cong-(aV^2/\pi\gamma)(3A/\delta A)[a^{2\rho+1}/(2\rho+1)] \times\int C(E)|E_1-E|^{-1}dp. \quad (10)$$

For $\gamma=0.6$, $\rho=0.8$, $r\hbar/mc=1.5A^{\frac{1}{3}}\ 10^{-13}$ cm, $r=1/43.5$ substitution gives in round numbers

$$E^{(2)}/\delta_c E\cong-(V^2/6200)\int C(E)|E_1-E|^{-1}dp \quad (10.1)$$

and for small p

$$(V^2/6200)C(E)\cong(V^2/910)(E+0.8)E^{-0.4}p/[1-\exp(-3.8E/p)]. \quad (10.2)$$

The bracket with the exponential has a value close to unity. The approximations of Eq. (10.2) yield a simple estimate of contributions to the right side of Eq. (10) from the region $1<E<10$. The region from $E=1$ to $E=2$ contributes

$$\sim(V^2/910)\{2+(E_1+0.8)\ln[(2-E_1)/(1-E_1)]\},$$

and for E between 2 and 10 with $E_1\cong1$ the contribution is $\sim V^2/29$. If $E_1\cong0.9$ then the contribution from $E=1$ to $E=2$ is $\sim V^2/150$. For $E>10$ the parameter $2pr$ which is the argument of the hypergeometric function becomes too large to make the omission of all but the first term in the hypergeometric series a crude approximation. According to these numbers a single nuclear level with an excitation energy between 0 and $\sim$200 kev would cause, on account of contributions from $E=2$ to $E=10$ alone, a value of $|E^{(2)}/\delta_c E|=\frac{1}{2}$ if one takes $|V|=(28/2)^{\frac{1}{2}}=3.8$.

The values of $\mathfrak{R}$ which follow from Eqs. (9.4), (9.6) are about 25 for $E=2$, 10 for $E=10$. For higher E the expression for $\mathfrak{R}$ is only applicable to conditions at smaller distances than the nuclear radius $r=a$. It is nevertheless of interest that even for $E=50$ the formulas give $\mathfrak{R}\cong5$.

VI. MONOPOLE EFFECT

The interaction of the electron with the nucleus has been represented in Eq. (2) by H_{01}' which has been replaced schematically by the constant value V through the nuclear interior. Estimates of V^2 have been obtained above by comparison with experiment. The values obtained will now be compared with expectation. In making the comparison the experimental indication of the largeness of effects for $s_{\frac{1}{2}}$ and $p_{\frac{1}{2}}$ will be used as a guide. The Coulomb interaction between an electron and a nuclear proton can be considered as being expanded into spherical harmonics in the usual manner,

$$e^2/|\mathbf{r}-\mathbf{r}_P|=(e^2/r_>)[1+(r_</r_>)P_1(\cos\Theta)+\cdots],$$

where

$$(r_<, r_>)=(r, r_P), \quad (r_P>r)$$
$$=(r_P, r), \quad (r>r_P).$$

The first term in this expansion will be referred to as the monopole term. It can give transitions between an $s_{\frac{1}{2}}$ atomic state of the electron and the continuum of $s_{\frac{1}{2}}$ states; it also gives transitions between $p_{\frac{1}{2}}$ and $p_{\frac{1}{2}}$ states. Both of these types of transitions are of immediate interest because the experimental evidence appears to be pointing to the proportionality of the isotope displacement and the density of the electron probability at the nucleus. The dipole term containing P_1 gives transitions between $s_{\frac{1}{2}}$ and $p_{\frac{1}{2}}$ electronic states and is of interest also. It turns out, however, that the effects of penetration of the electron into the nucleus are not marked for the matrix elements between $s_{\frac{1}{2}}$ and $p_{\frac{1}{2}}$ states on account of a cancellation of effects for the first non-vanishing power of r for the Coulomb field. These effects are not readily distinguishable from those for electron states which do not penetrate to the nucleus and they are very small for the part of the continuum corresponding to ionization. For a Coulomb field the matrix element vanishes with the nuclear radius at ionization. It appears safe to conclude that the $s_{\frac{1}{2}}$, $p_{\frac{1}{2}}$ matrix elements do not have much to do with observed phenomena and that the main effects of interest arise from the monopole term. The effect of the latter depends on whether the nuclear wave function is considered to be an antisymmetrized product of single particle central field functions or a linear combination of such products. Estimates will first be made for wave functions which are antisymmetrized products, i.e., products of two determinants; one for neutrons and one for protons. Since the interaction energy is a sum of operators each of which contains quantities referring to no more than one nucleon, it suffices to consider the excitation of only one proton at a time. The matrix element of the energy is then the same as though the electron were interacting only with that proton. The spherical symmetry of the monopole excludes all transitions involving changes either in the azimuthal or magnetic quantum numbers. Only angular averages of the cross-product proton density enter the result. The calculation is the same in form for the excitation of protons or α-particles since the charge e enters only through the combination $z_N e^2$, where $z_N=1$ for protons or 2 for α-particles.

Interactions of this type are strongly decreased by the orthogonality of wave functions with the same value of the azimuthal quantum number. This orthogonality confines the contributions to the matrix elements to electron positions inside the nucleus. An application of the completeness relation to the sum of squares of matrix elements yields an upper limit on the effective value of this sum. The upper limit appears then in a form containing only the wave function of the ground state. The main result of the transformation is

expressible as

$$\sum_n{}' \left| \int H_{0n}'(r) w(r) dr \right|^2 = \int \left(w - \int w du \right)^2 du, \quad (11)$$

where the accent on the summation sign indicates omission of $n=0$ and

$$du = S^2(r)dr, \quad w(r) = e^2 r^{2\rho} / [2\rho(2\rho+1)], \quad (11.1)$$

while $S(r)/r$ stands for the wave function of the nuclear particle in the ground state. For the lower energies in the continuum the spatial dependence of electronic density can be approximated by $r^{2\rho+2}$. One finds that

$$(V^2)_{\text{eff}} \leqq z_N^2 (e^2/a)^2 / [(4\rho+1)(2\rho+1)^2]. \quad (11.2)$$

The evaluation of the right side was made by approximating S by a constant within the nucleus. This approximation is immaterial in view of the smallness of the whole effect which can be inferred from the fact that the right side of Eq. (11.2) is approximately $z_N^2 (mc^2/17)^2$, for $\rho=0.8$ and $a=1.5\times 10^{-13} A^{\frac{1}{3}}$ cm. The monopole effect for the antisymmetrized product approximation to the nuclear wave function is seen to be very small unless one allows z_N to have a value of about 17. Such a value is difficult to reconcile with the central field approximation which was the starting point of the present estimate.

Larger values for the expected monopole effect are obtained if one considers the possibility of linear combinations of antisymmetrized products of single particle central field functions. For example, let

$$\begin{aligned} \psi &= c_1(\text{I, II}) + c_2(\text{III, IV}), \\ \psi' &= c_1'(\text{I, II}) + c_2'(\text{III, IV}) \end{aligned} \quad (11.3)$$

stand, respectively, for the ground state and perturbing excited state. The symbol (I, II) represents an antisymmetrized product of two single particle wave functions. The notation is similar for (III, IV), the single particle functions I, II, III, IV are mutually orthogonal and are not necessarily central field functions. For a fixed position of the electron the matrix element of the electron-proton electrostatic energy consists of two parts containing, respectively, $c_1^* c_1'$ and $c_2^* c_2'$ as factors. The orthogonality of ψ to ψ' implies $c_1^* c_1' = -c_2^* c_2'$ and the result is expressible therefore in terms of one of these quantities. As an approximation each of the states I, II, III, IV is regarded as localized in a narrow range of values of r centered in the neighborhood of the four values $r_{\text{I}}, \cdots, r_{\text{IV}}$, respectively. This estimate yields

$$\begin{aligned} |V| = |c_1^* c_1'| (2\rho)^{-1} (e^2/a) \\ \times [r_{\text{III}}^{2\rho} + r_{\text{IV}}^{2\rho} - r_{\text{I}}^{2\rho} - r_{\text{II}}^{2\rho}] / a^{2\rho} \cdots. \end{aligned} \quad (11.4)$$

Here $|c_1^* c_1'|$ can be as large as $\frac{1}{2}$ and favorable conditions for a larger $|V|$ than in the previous estimate are obtained by making r_{III}, r_{IV} large in comparison with r_{I}, r_{II}. For such conditions and for $\rho=0.8$ the value of $|V|$ is approximately

$$|V| \cong 0.62 (e^2/a)(r_P/a)^{2\rho}. \quad (11.5)$$

Here r_P stands for a suitably taken mean of r_{III} and r_{IV}. The value of $|V|$ obtainable in this manner is sensitive to the choice of r_P and a. It appears appropriate, therefore, to consider first the range of possible values for these parameters. The value of $a=1.5\times 10^{-13} A^{\frac{1}{3}}$ cm represents the effective nuclear radius for the charge as a whole. The value of the numerical constant 1.5 can be varied by interpreting the theory of α-decay in different ways. This uncertainty is not very important for the present purpose since the right side of Eq. (11.5) is mainly sensitive to the ratio r_P/a. The value of a will be therefore taken as given sufficiently well by the value 1.5 for the constant in the formula for a. In order to have a large value for the right side of Eq. (11.5) one needs a large r_P/a. The question arises as to how large r_P can be in comparison with a. It would appear that one could modify the Coulomb barrier of the Gamow, Condon-Gurney theory at the nuclear boundary without serious consequences on the comparison with experiment. A few protons could be pictured as being somewhat outside the sphere $r=a$, therefore. It appears fair to add to a about 2.8×10^{-13} cm, since the range of nuclear forces is of this order of magnitude. On this basis one has for $A=208$ the value $V \cong mc^2/3.3$ which is still too small. If instead of protons one considers α-particles then one obtains an additional factor 2 for V so that $V \cong mc^2/1.6$. Four such perturbing levels are equivalent to a single one with $V \cong mc^2/0.8$, which is sufficient to explain the odd-even isotope staggering effect on the basis of differences in nuclear level systems in a wide energy range ($30\ mc^2$) but not sufficient for an explanation by differences in level systems between 0 and 5 Mev. For the latter one needs an additional factor of roughly 4. To obtain it one could invoke interactions with larger units than an α-particle or else wave functions of the type

$$\begin{aligned} \psi &= c_1(\text{I}_1, \text{II}_1, \text{III}_1, \text{IV}_1) + c_2(\text{I}_2, \text{II}_2, \text{III}_2, \text{IV}_2), \\ \psi' &= c_1'(\text{I}_1, \text{II}_1, \text{III}_1, \text{IV}_1) + c_2'(\text{I}_2, \text{II}_2, \text{III}_2, \text{IV}_2). \end{aligned} \quad (11.6)$$

It is difficult to exclude such possibilities but there appears to be no binding reason for assuming them. The fact that the packing fraction has a minimum for $A \sim 50$ —which is smaller than any of the mass numbers for which the isotope effect has been observed—could be used as an argument for considering the temporary existence in the nucleus of groups of particles much greater than an α-particle. The large mass of such groups would interfere with the explanation if it depended on the conditions treated by means of Eqs. (11), (11.2) because in this case the effect is caused only by radial fluctuations of charge. The large mass does not interfere, however, under circumstances discussed by means of wave functions such as in Eq. (11.3) with the understanding that I, II, III, IV now apply to the

larger aggregates. While large factors could arise in such a picture it is not proposed here as more than a speculation. It is nevertheless difficult to exclude the presence of an effect depending on low nuclear excitations.

If the monopole effect were estimated only for initial states describable in the central field approximation, i.e., by determinantal wave functions, an upper bound on the expected shift could be set by means of the following consideration. The initial single particle states can be arranged into two classes according to spin direction. The operation of the exclusion principle can be considered separately for the two classes. For each class there is only one particle in an orbital state. There are no matrix elements of the monopole energy between states with different orbital angular momenta L or different magnetic quantum numbers. The exclusion principle does not interfere, therefore, with the contributions from proton states within an occupied shell. If the shells of nuclear particles are supposed temporarily to correspond to different values of L the summation of the squares of matrix elements can be arranged in independent parts, each part corresponding to one of the initial single particle states. A part of the sum belonging to one of the states does not depend on what other states are occupied initially. The whole sum is, therefore, less than the number of protons times contributions such as considered in Eq. (11). If there are several shells for the same L, the sum is decreased because in Eq. (11) all non-diagonal matrix elements are taken into account while the squares of these elements which correspond to the initial and final states being occupied do not occur in the sum for the antisymmetric five function. One may take, therefore, for $Z=80$, the value $80^{\frac{1}{3}}mc^2/17=mc^2/1.9$ as an upper bound for $|V|$ of the monopole effect if the wave function of the initial state is approximated sufficiently well by a determinant having as elements single particle central field functions. It will be noted that this value of $|V|$ is smaller than that indicated by the staggering of the isotopic shift even if one admits the possibility that excitation to higher nuclear energies ($\sim$20 Mev) might be qualitatively different for even and odd isotopes. It will be seen later that the dipole effect cannot account for an appreciable part of the staggering effect. It appears, therefore, that one could perhaps claim the inadequacy of a central field nuclear model if the staggering effect should not be explicable in some other way than as a polarization effect. In the present state of the subject it cannot be claimed that some other explanation will not prove adequate and the mutual exclusiveness of the two possibilities is mentioned only as a matter of record.

The situation just discussed is not changed materially by taking the square of the wave function S^2 in Eq. (11.4) to have the form $(n+1)r^n a^{-n-1}$ and adjusting n to give a maximum of the effect. This generalization introduces an extra factor

$$(n+1)(2\rho+1)^2(4\rho+1)/[(2\rho+n+1)^2(4\rho+n+1)]$$

on the right side of Eq. (11.2). A straightforward calculation for $Z=80$ gives $n=(-1+5^{\frac{1}{2}})\rho-1=0.005$ which is so close to $n=0$ that the difference caused in the expected effect is negligible. The value of V^2 is readily found to be insensitive to n in the range from -0.5 to 1.0, the effects on the upper bound for V^2 being of the order of 10 percent. While the function S has favorable properties for giving a large effect it is not much more favorable than other possibilities which provide for a large range of variations of charge density within the nucleus.

Since it is unlikely that the conditions for approaching the upper bound are realized in nuclei, the monopole effect may be supposed to give rise to appreciable polarization effects only if the central field picture of the nucleus is inadequate. While it is probable that this is true in some sense it is not clear from the previous discussion that the types of modification made use of in Eqs. (11.3), (11.4) are probable. The main reason for an increase in the expected effect by these modifications is the occurrence of matrix elements which are diagonal in single particle states. Furthermore the wave functions in Eq. (11.3) would not give a large effect if it were not for the assumption that two of the single particle states correspond to locations close to the periphery of the nucleus and two other states to locations in the interior. These assumptions are in a sense artificial and have been made above in order to see under what conditions the polarization effect can become comparable with the experimentally observed irregularities in the isotope shift.

VII. DIPOLE EFFECT

In this section the effects of dipole matrix elements are considered and the contributions to the second-order perturbation energy from different parts of the continuum are estimated. The dipole effect arises from the second term in the expansion of $|\mathbf{r}-\mathbf{r}_P|^{-1}$ in terms of Legendre functions.

The needed expressions may be obtained in the following way. The four-component wave functions for the s and $p_{\frac{1}{2}}$ states with magnetic quantum number m can be conveniently represented as

$$\psi_s{}^m=(4\pi)^{-\frac{1}{2}}\begin{pmatrix} f_s[(\mathbf{r}\sigma)/r]S^m \\ -ig_sS^m \end{pmatrix},$$
$$\psi_p{}^m=(4\pi)^{-\frac{1}{2}}\begin{pmatrix} f_pS^m \\ -i[(\mathbf{r}\sigma)/r]g_pS^m \end{pmatrix}, \tag{12}$$

where S^m is a two component spin function with magnetic quantum number m. This spin function is a one-column matrix with two rows and is treated like the spin functions of a single electron in non-relativistic theory which are usually denoted by α and β.

Since one is interested only in averages over all relative orientations of the angular momentum L of a nuclear particle and the angular momentum vector $\mathbf{j}$ of the electron the detailed consideration of individual matrix elements can be avoided. One finds readily by means of Eq. (12) for the $p_{\frac{1}{2}}$ electron that

$$\Sigma_{\mu'}|(s,\mu|x_i/r^3|p,\mu')|^2=(I_{sp}/3)^2, \tag{12.1}$$

where

$$I_{sp}=\int_0^\infty (f_sf_p+g_sg_p)dr=(r^{-2})_{sp}. \tag{12.1a}$$

The x_i denotes either x, y, or z and r is the usual electron-nucleus distance. The magnetic quantum number in the s state is designated by μ, that in the $p_{\frac{1}{2}}$ state by μ' and the sum over all μ' is taken. It will suffice to know the sums occurring in Eq. (12.1) rather than individual matrix elements.

The interaction energy of a nuclear proton with the electron contains the dipole interaction term

$$(e^2r_</r_>^2)\cos\Theta =(e^2r_</r_>^2)[xx_P+yy_P+zz_P]/(rr_P), \tag{12.2}$$

where $r_<$, $r_>$ stand, respectively, for the smaller and greater of the two distances r, r_P. Arguments similar to those used in demonstrations of spectroscopic stability show that the average over the magnetic quantum number M of the nuclear proton of the expression

$$\Sigma_Q|(L,M;s,\mu|(r_</r_>^2)\cos\Theta|L',M';p,\mu')|^2,$$

where Q stands for L', M', μ' can be expressed as the average over M of

$$\Sigma_R|(s,\mu|x/r^3|p,\mu')|^2|(L,M|x_P|L',M')|^2, \tag{12.2a}$$

where R stands for L', M', μ', x, y, z. Using familiar forms for dipole matrix elements[12] the second part of expression (12.2a) for $L'=L+1$ gives rise to

$$\Sigma_S|(L,M|x_P|L+1,M')|^2 =(L+1)(2L+1)^{-1}|(r_P)_{L,L+1}|^2, \tag{12.2b}$$

where S stands for M', x, y, z and $(r_P)_{L,L+1}$ is the matrix element of the proton distance r_P taken between two states having the same magnetic quantum number but different azimuthal quantum numbers L, $L+1$. Substituting Eqs. (12.1) and (12.2b) into Eq. (12.2a) gives

$$(I_{sp}/3)^2\{(L+1)|(r_P)_{L,L+1}|^2 +L|(r_P)_{L,L-1}|^2\}/(2L+1). \tag{12.2c}$$

The integral over r inside the nucleus is negligible and has been omitted. Employing the completeness relation and assuming the nuclear particle to be at $r_P=a$, the surface of the nucleus, expression (12.2c) becomes

$$(\alpha mc^2aI_{sp}/3)^2. \tag{12.3}$$

[12] B. L. van der Waerden, *Die Gruppentheoretische Methode in der Quantenmechanik* (Verlag Julius Springer, Berlin, 1932), p. 78.

The α enters in converting lengths in Eq. (12.2) to $\hbar/mc$. The quantities f_s, g_s and f_p, g_p are the solutions for $k=-1$, $+1$, respectively, of the radial Dirac equations. The choice of signs is such as to make

$$rf=\varphi_1, \quad rg=\varphi_2, \tag{12.3a}$$

where φ_1, φ_2 are Gordon's[8] radial functions.

As in the monopole case, the square root of this will be equated to a constant nuclear perturbing potential, V, integrated over the nucleus. Solving for V one obtains

$$V=\alpha mc^2aI_{sp}\Big/\left[3\int_0^a (f_sf_s'+g_sg_s')r^2dr\right]\cdots. \tag{12.4}$$

In Eq. (12.4) and the following, the prime is used to indicate functions in the continuum when it is desired to distinguish them from the functions for the bound state. To get the expression for V corresponding to the perturbation of a $p_{\frac{1}{2}}$ electron by the continuum of $s_{\frac{1}{2}}$ states, one need only interchange the subscripts s and p in Eq. (12.4).

The approximation used in the monopole case does not apply in this case because

$$f_s/g_s=-f_p/g_p=-[(1-\rho)/(1+\rho)]^{\frac{1}{2}}, \quad (r=0). \tag{12.5}$$

Hence the coefficient of the first power of r in the integrand $f_sf_p+g_sg_p$ is zero and a more exact treatment is required. For convenience the bound electron is assumed to be described by the wave functions for an electron at ionization. This is justified by the strong localization of the integral at small values of r. The shape of the wave function is insensitive to the energy in this region on account of the dominance of potential energy. The functions are taken to be [13,14] the usual Bessel function expressions at ionization. The normalization factor is taken so that

$$rf=(\pi/2)^{\frac{1}{2}}\gamma J_{2\rho}(2(2\gamma r)^{\frac{1}{2}}). \tag{12.6}$$

To facilitate computation, ρ in this section is taken as 0.75 instead of 0.8. From the form of Eq. (12.4) it is seen that the normalization of the s function is immaterial, the comparison being made with the perturbation by the continuum of s states. The solution of the radial equations obtained by Gordon[8] can be written in the following form for the continuum

$$N_s(f_s+i\chi g_s)=N_p[(\rho-i\sigma)/(1-i\gamma/p)](f_p+i\chi g_p) =r^{\rho-1}e^{-ipr}F(\rho+i\sigma+1,2\rho+1,2ipr), \tag{12.7}$$

$$N_p(f_p-i\chi g_p)=-N_s[(\rho+i\sigma)/(1-i\gamma/p)](f_s-i\chi g_s) =r^{\rho-1}e^{-ipr}F(\rho+i\sigma,2\rho+1,2ipr). \tag{12.8}$$

The quantity χ indicates $[(E-1)/(E+1)]^{\frac{1}{2}}$. In these formulas the normalization factors for s and p states are not as yet related to each other. Adjusting normalization to give unit linear density at large r, the connections between (f_s, g_s) and (f_p, g_p) available in

[13] G. Breit, Phys. Rev. 38, 463 (1931).

[14] G. Breit and L. A. Wills, Phys. Rev. 44, 470 (1933).

Eqs. (12.7) and (12.8) give

$$f_s=(E^2-\rho^2)^{-\frac{1}{2}}[\gamma f_p+(E-1)g_p], \quad g_s=(E^2-\rho^2)^{-\frac{1}{2}}[\gamma g_p-(E+1)f_p], \tag{12.9}$$

with the help of

$$(f_s^2+g_p^2)/(f_s^2+g_s^2)=(E-\rho)/(E+\rho), \quad (r=0). \tag{12.9a}$$

It will now be shown that

$$I_{sp}=0, \quad (E_s=E_p). \tag{13}$$

Here it is understood that the Coulomb law holds strictly. One can satisfy $E_s=E_p$ exactly either in the discrete or in the continuum. One has the matrix equation of motion which relates matrix elements of the force and momentum by

$$-(Ze^2\mathbf{r}/r^3)_{nm}=(i/\hbar)(E_n-E_m)\mathbf{p}_{nm}, \tag{13.1}$$

where n, m designate energy states in general. Applying this identity to s and $p_{\frac{1}{2}}$ states one sees that the left side of the preceding equation contains as a factor the quantity I_{sp} while on the right there occurs the product of a vanishing energy difference and a finite matrix element of the momentum. It is also possible to demonstrate Eq. (13) by means of Eqs. (12.9) and an identity[15] due to G. E. Brown. However, as will be seen later, consideration of the derivatives of the wave functions with respect to energy indicates that $\partial V/\partial|E_s-E_p|$ is large and possibly infinite at $|E_s-E_p|=0$. It has been verified that I_{sp} increases very rapidly with $|E_s-E_p|$.

Using the first terms in the power series expansions of f and g from Eq. (12.6) and fixing on the normalizing factor for the continuum by means of Eqs. (9) and (9.7), there results from Eq. (12.4)

$$V=0.801z_NI_{sp}/[C(E_p)]^{\frac{1}{2}} \tag{13.2}$$

for an $s_{\frac{1}{2}}$ electron perturbed by the $p_{\frac{1}{2}}$ continuum while for a $p_{\frac{1}{2}}$ electron perturbed by the $s_{\frac{1}{2}}$ continuum,

$$V=2.12z_NI_{ps}/[C(E_s)(E_s-\rho)/(E_s+\rho)]^{\frac{1}{2}}. \tag{13.3}$$

The quantity z_N is the charge on the nuclear particle. Assuming interaction with nuclear alpha-particles as will be done here one has a z_N of 2. Since $C(E)$ is readily calculated one needs only evaluate I_{sp} to find V.

The Bessel function expressions for f and g defined by Eq. (12.6) were used for the wave functions describing the bound electron. Using up to 10 terms in the hypergeometric series occurring in Eqs. (12.7) and (12.8), f_p and g_p for the continuum were calculated to beyond the first maximum of rg_p. Employing a suitable reduction[13] of Dirac's equation the wave functions were extended by means of JWKB solutions. These continuum functions were then conveniently normalized to unit linear density by considering the asymptotic forms. The normalization coefficients were checked by noting that f_p and g_p behaved properly for small r by comparison with $C(E)$. From these values of f_p and g_p, f_s and g_s were calculated by the use of Eqs. (12.9). The integrals I_{sp}, I_{ps} were then evaluated by numerical quadrature with a probable error of about five percent. The values of V from Eqs. (13.2) and (13.3) for $z_N=2$ are given in Table I for various energy combinations. The numerical quadratures used for Table I were made from the nuclear radius a on to ∞. The results are very insensitive to the choice of the lower limit.

Comparing with the calculations of Section V it is seen from Table I that the effective V's for the dipole interaction and $z_N=2$ are relatively small. A calculation based on the relation

$$|E^{(2)}/\delta_cE|=(z_N^2/7100)\int_1|E-E_1|^{-1}(E/p)I_{sp}^2dE \tag{13.4}$$

shows that for $E_1=0.9$ (a single nuclear level at 50 kev) the staggering effect due to the dipole term is about three percent of the top slice volume effect. This figure includes an integration up to $E=100$. If only the range $E=1$ to $E=10$ is taken then the corresponding number is 1.5 percent. This result is comparable with values in Table I and the estimate $V=3.8$ obtained soon after Eq. (10.2). Since this V corresponds to 50 percent of the volume effect on the top slice basis one would estimate for 1.5 percent a V of $3.8/[50/1.5]^{\frac{1}{2}}=0.66$, which is approximately the value in Table I.

The figure 1.5 percent was obtained by quadrature based on the calculation of the integrand. The value three percent which was stated for the effect up to $E=100$ is not considered to be nearly so reliable since the integrand was not evaluated from $E=10$ to $E=100$. The relative smallness of the effects under consideration makes this contribution have only a secondary interest.

Calculations on perturbations of $p_{3/2}$ states by the s continuum have been made. It has been found that as the energy of the s electron is increased the effective V decreases rapidly and that these perturbations are much smaller than those of $p_{\frac{1}{2}}$ states. At $E_s=2$ the effect on the $p_{3/2}$ state is $\sim\frac{1}{2}$ of that on the $p_{\frac{1}{2}}$ state.

As a check on the accuracy of the wave functions for the continuum and to get an indication of $\partial V/\partial E$, $(E=1)$, the energy derivatives of the s-wave functions at $E=1$ were computed by two independent methods (derivations included in Appendix). In the first, the quantity $y=f/g$ was used. One obtains[6]

$$\partial y/\partial E=-(rg)^2\int_0^r r^2(f^2+g^2)dr \tag{14}$$

and

$$\partial g/\partial E=g(r)\int_0^r[y+(E+1+\gamma/r)\partial y/\partial E]dr. \tag{14.1}$$

In the second a Bessel function expansion[16] is employed

[15] G. E. Brown, Proc. Nat. Acad. Sci. **36**, 15 (1950).

[16] Yost, Wheeler, and Breit, Phys. Rev. **49**, 174 (1936) employed a similar expansion in the calculation of Coulomb wave functions.

and there results

$$\partial(rf)/\partial E=[(r/3\gamma)-(1/2)]rf + [(2r/3)+(r^2/3\gamma)]d(rf)/dr \quad (14.2)$$

and

$$\partial(rg)/\partial E=[(2r^2/3\gamma)+(5r/3)+(1/2\gamma)-(2\rho^2/3\gamma)]rf - (r/6\gamma)d(rf)/dr. \quad (14.3)$$

The normalization is such that

$$\partial(y, g, f)/\partial E=0, \quad r=0. \quad (14.4)$$

Applying Eqs. (13.2) and (13.3) to the energy derivative of I_{sp} the presence of such factors as $2r^2/3\gamma$ in Eq. (14.3) causes the integrand to diverge at large r. While screening may keep the result finite it appears that the curve of V *vs.* E starts off with a steep slope. This may be of importance in estimating the magnitude of the dipole polarization effect for low lying nuclear energy levels.

An upper bound can be set on the expected dipole effect by means of the f sum rule, if the nuclear excitation energy of the perturbing levels is decided on. According to the f sum rule the sum of the f values is equal to the number of protons. One has for any energy range the inequality

$$\Sigma|r_{nm}|^2<(3/4\pi)(\hbar/mc)|c/\nu_{nm}|(m/M)Z$$

where the sum on the left is taken over the energy range that is under consideration. Account is here taken of the fact that in the f sum there occurs a cancellation of effects owing to omission of transitions between occupied states. The f sum rule consideration may be expected to be of significance mainly for excitations corresponding to an average condition rather than one of exceptionally low excitation. Taking 20 Mev, somewhat arbitrarily, for the excitation energy and $Z=80$ one finds from the previous equation

$$\langle|r_{nm}|\rangle<1.56\times10^{-12}\text{ cm}$$

which may be compared with $a=0.89\times10^{-12}$ cm, the value used in the calculations in this section. The ratio of the two is 1.75.

It should be mentioned that all of the values used here are overestimates because of the omission of the factor

$$(Z_1M_2-Z_2M_1)/[Z_1(M_1+M_2)],$$

which has to be included as a correction for the motion of the residual nuclear mass M_2 having charge Z_2e when one considers the effective dipole moment due to charge Z_1e with mass M_1. With a view toward the application in Section VIII, all the protons will be combined into (Z_1, M_1) and all neutrons into (Z_2, M_2) giving a correction factor of $128/208=0.61$ to the effective matrix element V for Pb^{208}. Since the value of $\langle|r_{nm}|\rangle$ was obtained on the basis of protons rather than alpha-particles there is a further factor $\frac{1}{2}$ for V. Combining these factors one has a net factor $1.75\times0.61\times0.5=0.52$. These estimates indicate that the whole effect will not be more than $(0.52)^2\times3$ percent$=0.8$ percent of the theoretically expected effect on the top slice method. If the mean excitation energy were taken as 2.5 Mev so as to correspond to the calculation in which contributions of the second-order perturbation energy have been summed from $E=1$ to $E=10$ the effect would be increased by a factor 8 on account of the effect of the energy ratio on $\langle r^2\rangle$. It would be decreased because the value 1.5 percent rather than three percent was obtained in the estimate by numerical quadrature from $E=1$ to $E=10$. One would obtain at most $4\times0.8=3.2$ percent of the top slice volume effect expected on the $A^{\frac{1}{3}}$ nuclear radius approximation. The nature of this estimate is such as to exaggerate the expected value of the frequency shift except for the probable overestimate of the volume effect.

VIII. DISCUSSION

Extensive experimental material on the isotope shift of Hg, Pb, and Pt is available through the work of Schüler, Kopfermann and many other investigators. The staggering of the term values of odd isotopes in Hg, Pb, and Pt is in such a direction as though the nuclei of the odd isotopes exerted relatively more attraction on the electron than the even ones. This fact is in agreement with expectation since the odd isotopes are less stable and since they have a larger density of nuclear levels close to the ground state. Quantitative comparison in Hg is difficult because of differences in the indications concerning the magnitude of the staggering effect as obtained from different lines. It is convenient in this connection to express the comparison in terms of a unit of isotope displacement which will be referred to as an isotopic unit. This unit will be defined as one-half the separation between term values of the nearest pair of even isotopes if one is discussing the term value of an odd one. Figure 15 of Schueler and Keyston[17] indicates for λ2536 a polarization effect of about one-third of an isotopic unit for Hg^{201} and about 0.9 for Hg^{199}. For λ6072($7\,^3S_1-8\,^1P_1$) the staggering of Hg^{199} and that of Hg^{201} is about 0.6 isotopic unit. For λ6716($7\,^1S_0-8\,^1P_1$) the staggering is according to the same figure of Schueler and Keyston about 0.75 and 0.55 isotopic unit for these two isotopes.

It appears possible that for λ2537 there has been some interference among the components of the hyperfine structure pattern inasmuch as the separation between isotopes 198 and 200 is appreciably smaller for this line than between 200 and 202 while the interval between the centroid of the pattern of isotope 199 and 198 is anomalously small. The well-known difficulties of hyperfine structure measurements on an isotopic mixture make one doubtful concerning the reality of some of the discrepancies. Additional experiments especially with the now available separated isotopes

[17] H. Schueler and J. E. Keyston, Zeits. f. Physik. **72**, 423 (1931).

TABLE I. Values of equivalent interaction energy matrix element V for various excitation energies E_s, E_p of the electron. Only $p_{\frac{1}{2}}$ electrons covered here.

E_s $[mc^2]$	E_p $[mc^2]$	I_{sp}, I_{ps} $[(\hbar/mc)^{-2}]$	V $[mc^2]$
1	1	0	0
1	2	1.92	0.61
1	6	3.4	0.47
1	10	3.8	0.36
2	1	0.38	0.48
6	1	1.10	0.46
10	1	1.31	0.35

would be helpful in providing a more certain basis for theoretical speculation. There is a possibility that some of the discrepancies are the result of a difference in the staggering effect caused by differences in the behavior of different terms with respect to the participation of perturbations by $s_{\frac{1}{2}}$ and $p_{\frac{1}{2}}$ continua. It is also not clear theoretically that this participation of continua will produce similar effects for different isotopes.

There is some indication in the work of Schueler and Keyston on λ2537 that the separation between Hg^{202} and Hg^{200} is larger than that between Hg^{204} and Hg^{202} or that between Hg^{200} and Hg^{198}. For the other lines in their Fig. 15, however, the phenomenon does not appear as clearly. Differences in the behavior of even isotopes are not excluded by the polarization effect explanation but it appears premature to speculate on this point also.

For Pb the observations of Schueler and Jones,[18] Rose and Granath,[19] Kopfermann[20] again show decided staggering of odd isotopes with respect to the even ones. Here only one odd isotope (207) is present. Taking the mean of results obtained from 11 lines measured by Rose and Granath, one obtains for $[(207)-(206)]/[(208)-(207)] \cong 0.59 \pm 0.06$ where 0.06 is the probable error. Here (206) means the term value of Pb^{206}, (207) the centroid of term values of Pb^{207}. This speaks for a specific staggering effect of 0.26 of an isotopic unit which is somewhat smaller than the value assumed in making estimates of V. There is again considerable variation of the $[(206)-(207)]/[(207)-(208)]$ ratio between different lines. It may be premature to claim too much on the basis of this fact since some variation would result as a consequence of experimental error. Different effectiveness of the $s_{\frac{1}{2}}$, $p_{\frac{1}{2}}$ continua for different terms would not be in contradiction with such a variation, however. There are observations on only three even isotopes of Pb. The spacing between Pb^{204} and Pb^{206} is somewhat smaller than that between Pb^{206} and Pb^{208} according to Schueler and Jones[18] and according to observations of Watson and Anderson,[21] and Manning.[22] This fact may possibly be related to the supposed closing of a stable shell[3] of 126 neutrons in Pb^{208}. The stable shell can be expected to be less polarizable and the addition of the 126th neutron could lead, therefore, to a larger than usual apparent volume effect.

For Pt ($Z=78$) there are measurements of Jaeckel and Kopfermann,[23] Jaeckel,[24] and by Tolansky and Lee.[25] The ratio $[(194)-(195)]/[(195)-(196)]$ is 0.82 for λ5369 and 0.5 for λ5391. There is no apparent reason for considering the staggering to be greater than 0.5 of an isotopic unit and it may be much smaller since a smaller value is indicated by λ5369 for which the whole pattern is more open. The displacements between the even isotopes are approximately equal to each other with possibly a tendency for the ratio $[(194)-(196)]/[(196)-(198)]$ to be slightly less than unity.

The observations of Schueler and Schmidt[26] and of Brix and Kopfermann[2] on Sm ($Z=62$) show a large anomaly for the even isotopes. A related phenomenon is present in Nd according to Klinkenberg.[27] Explanations of this phenomenon have been discussed by Schueler and Schmidt, Klinkenberg, Feather,[28] and by Brix and Kopfermann. Klinkenberg brought out the fact that the specially large separation occurs between isotopes with a number of neutrons $N=88$ and $N=90$ for both $Z=62$ and $Z=60$. Feather points out that the new assignment of α-activity to Sm^{152} is not in striking contradiction to expectation from the occurrence of α-activities for radioactive elements with $Z=84$. He further points out that for Sm the isotopes 144, 148, 150 can be considered as tightly bound while 152, 154 are regarded as loosely bound. The volume of Sm^{152} and of Sm^{154} should be anomalously great, therefore. Similarly according to Feather the volume of Nd^{150} may be expected to be anomalously great because Nd^{150} is loosely bound. On the other hand, Brix and Kopfermann suspect connection between the shape of these nuclei and the quadrupole moment of Eu. As has been mentioned in the Introduction, the explanation of Brix and Kopfermann cannot be maintained in its original form if the nuclei in question have a spin O because the charge distribution is then spherically symmetric. A connection with the occurrence of quadrupole moments for neighboring nuclei may, nevertheless, exist as has been also discussed in the Introduction.

If the anomalies in Sm and Nd are to be explained as polarization effects of the nucleus, then it seems necessary to suppose that neutron shells with $N=90$ are especially tightly bound in the sense of having smaller polarization effects for $N=90$ than $N=88$. Such a view does not fit in especially well with Feather's evidence

[18] H. Schueler and E. G. Jones, Zeits. f. Physik **75**, 563 (1932).
[19] J. L. Rose and L. P. Granath, Phys. Rev. **40**, 760 (1932).
[20] H. Kopfermann, Zeits. f. Physik **75**, 363 (1932).
[21] W. W. Watson and C. E. Anderson (private communication); Manning, Anderson and Watson, Phys. Rev. **78**, 417 (1950).
[22] T. E. Manning, Phys. Rev. **76**, 464A (1949).
[23] B. Jaeckel and H. Kopfermann, Zeits. f. Physik **99**, 492 (1936).
[24] B. Jaeckel, Zeits. f. Physik **100**, 513 (1936).
[25] S. Tolansky and E. Lee, Proc. Roy. Soc. **A158**, 110 (1937).
[26] H. Schueler and Th. Schmidt, Zeits. f. Physik **92**, 148 (1934).
[27] P. F. A. Klinkenberg, Physica **11**, 327 (1945).
[28] N. Feather, Nature **162**, 412 (1948).

which indicates loose binding in Sm for $N=90$, 92 and Nd for $N=90$. The conflict between the views is perhaps not a decided one because looseness of binding in Feather's sense has to do with the energy available for α-emission which is not simply related to relative polarizability of isotopes. The latter depends not only on binding but also on the character of the wave function as in Eq. (11.3). No definite claim can be made for the polarization picture on the basis of the isotope shift in Nd and Sm. The anomalies in these shifts can be explained more easily on the nuclear volume picture, as has been pointed out by Feather.

Returning to the general subject of orders of magnitude of the polarization needed for the explanation of the isotope effect, it is of interest that Goldhaber and Teller[29] consider it likely that the (γ,n) reactions indicate the possibility of exciting nuclear "dipole vibrations" of an exceptionally strong type. In their picture the neutrons move in a direction opposite to that of the protons. Such a vibration corresponds to a larger effective charge z_N than is needed in order to make the dipole terms important for the isotope shift.

The expectation of Goldhaber and Teller that there should be resonance absorption for γ-rays by C^{12} and Cu^{63}, has not been confirmed by the experiments of Gaerttner and Yeater.[30] On the other hand, Lawson and Perlman[31] obtain results for the total cross section which fit Goldhaber and Teller's view. Kubitschek and Dancoff[32] find in a study of a large number of elements that there is evidence in γ-ray capture of frequent emission of γ-rays carrying nearly the whole available energy. These observations appear to speak against a purely statistical treatment of the distribution of nuclear energy levels and the possibility of large matrix elements for the higher energy γ-transitions. This evidence regarding nuclear polarization is not in contradiction with the thesis of Teller-Goldhaber. The experiments of Gaerttner and Yeater do not necessarily exclude the general features of the Teller-Goldhaber view. A strong damping of resonance absorption by (γ,n) processes can reduce the effect and the "rest-strahlen" type of vibration is perhaps not taking place in as extreme a manner as originally proposed. Without more definite evidence it appears only fair to draw attention to the relationship which the supposed nuclear dipole vibrations can conceivably have to the odd-even staggering phenomenon.

The discussion at the end of Section VII on the dipole effect made use of the f sum rule consideration. The occurrence of the vibrations of Goldhaber-Teller at high energies makes the larger of the two estimates ($\sim$three percent) improbable because this estimate assumed a concentration of contributions to the second-order perturbation energy from the 2.5-Mev nuclear excitation region, while experiment and the theory of Teller-Goldhaber speak for the concentration of a large part of the f sum at much higher energies. The experimental situation for the heavier elements discussed by Goldhaber and Teller is not quite clear however and the present argument is not certain before the f sum contributions in nuclei are more thoroughly known.

While the manuscript of the present paper was being prepared there appeared a new and very thorough theoretical discussion of the experimental material by Crawford and Schawlow.[33] They employ the point of view that the features of hyperfine structure originating in the coupling of electrons to the nuclear spin may be used to determine the normalization of the electronic wave function close to the nucleus. This is done much more carefully by Crawford and Schawlow than prebiously and the results are, furthermore, more significant because of the availability of direct measurements of nuclear magnetic moments. Crawford and Schawlow conclude that the ratios of the isotopic shift for different spectroscopic terms are in fair agreement with the volume effect theory. The $A^{\frac{1}{3}}$ law gives, however, an expected isotope shift corresponding to the addition of two neutrons which is too large by a factor of about 2 if the protons are assumed to be uniformly distributed through the nuclear volume. Crawford and Schawlow suggest that the explanation for the smallness of the observed effect might lie in nuclear shell structure along the lines proposed by Mayer,[3] Feenberg and Hammack,[34] and Nordheim.[35] A partial cause of the effect may be nuclear polarization. High electronic excitations do not distinguish markedly between details of the nuclear level systems and would be expected to cause effects varying approximately regularly with the neutron number N.

The nuclear shell structure has to do with comparatively high stability when a certain number of nucleons of the same type exists in the nucleus. The effects are reasonably pronounced on a scale of the binding energy of the last neutron. This fact does not necessarily imply, however, a significant consequence of shell structure regarding the volume effect because the stability of shells is not a marked phenomenon on the scale of the whole nuclear binding energy. For an α-particle compared with a deuteron there would indeed be a strong effect. In the heavier nuclei, however, the conditions can hardly be expected to be as clear cut.

The probable implication of the existence of shell structure is that a certain quota of nucleons has been admitted to available quantum numbers. Such a condition does not have to go with spatial rigidity of the shell. The degree to which shell structure is of im-

[29] M. Goldhaber and E. Teller, Phys. Rev. **74**, 1046 (1948).
[30] E. R. Gaerttner and M. L. Yeater, Phys. Rev. **76**, 363 (1949).
[31] J. J. Lawson and M. L. Perlman, Phys. Rev. **74**, 1190 (1948).
[32] H. E. Kubitschek and S. M. Dancoff, Phys. Rev. **76**, 531 (1949).
[33] M. F. Crawford and A. L. Schawlow, Phys. Rev. **76**, 1310 (1949). The views expressed in this reference are further supported by Schawlow, Hume, and Crawford, Phys. Rev. **76**, 1876 (1949).
[34] E. Feenberg and K. C. Hammack, Phys. Rev. **75**, 1877 (1949).
[35] L. W. Nordheim, Phys. Rev. **75**, 1894 (1949).

portance for the volume effect appears, therefore, to be uncertain.

It should be pointed out that in the present paper the estimates of the ratio of the polarization effect to the volume effect have been made on the basis of a volume effect corresponding to the $A^{\frac{1}{3}}$ law and the top slice (protons on the outside) picture. According to the Crawford-Schawlow reductions and the supposition that the nuclear spin part of the hyperfine structure gives a sufficiently good calibration of the wave function close to the nucleus one has to conclude that the observed isotope effect corresponding to the addition of two neutrons is smaller than the one used in the present paper, as has been previously mentioned. It will also be recalled that the estimates of the staggering effect have been made on the basis of low lying nuclear levels which emphasize contributions from the low energy part of the electronic continuum. So far as an evaluation of the importance of these contributions is concerned, it is immaterial whether the smallness of the effect of *two* neutrons is caused by polarization or by static charge distribution conditions. In either case the relative importance of the theoretically expected effects for odd-even staggering can be considered as having been conservatively presented in the discussion of experimental material since one could claim that it is at least twice as great on account of the too large unit of isotopic displacement which has been used.

The smallness of the observed shift corresponding to the addition of two neutrons increases the probability that nuclear monopole effects contribute to the staggering phenomenon. Instead of $|V|=3.8$ at the end of Section V it would suffice to have $|V|=3.8/\sqrt{2}=2.7$. The equivalent $|V|=1/0.8$ estimated for α-particles in connection with Eq. (11.4) taking into account four levels can be increased to $|V|=2.7$ either by increasing z from 2 to ~ 4 or by using more levels. When it is considered that the discussion of the experimental material does not call for as high a value as $\frac{1}{2}$ for $|\delta E^{(2)}/\delta_c E|$ and that the estimates in the present paper exaggerate the volume effect by employing the top slice cut-off rather than the uniform charge density model it appears possible that the monopole effect can account for the observed staggering.

In order to bring the dipole effect up to the observed values for the staggering one would have to increase the charge z_N by a factor of $\sim(40/3)^{\frac{1}{2}}=3.6$ corresponding to a staggering effect of 40 percent of the regular and to a top slice volume effect of twice the regular isotope shift. The corresponding $z_N\sim 7.2$. Such a value of z_N cannot be used without considering the $Z_1M_2-Z_2M_1$ factor and the sum rule considerations at the end of Section VII. The factor 2 between the volume effect theory and observation changes the 3.2 percent which has been obtained by the f sum rule consideration with the main excitation energy at 2.5 Mev into ~ 6 percent. The discussion of the paper of Goldhaber and Teller which has been attempted indicates, however, that even this number is probably an overestimate of the effect. At this point the writers would like to express their indebtedness to Professor E. Teller for a helpful discussion of the GT paper so often referred to and for pointing out the apparent absence of the "dipole type" vibrations at lower frequencies.

The irregularities in the spacings of the even isotopes of Pb having been briefly mentioned. A tentative explanation of these has been previously attempted.[36] At the time the "magic numbers" for nuclear particles were not known and the conditions of stability of nuclear particles were reasoned about from the viewpoint of Gamow's picture of a potential valley. Since Pb^{208} is decidedly stable it was supposed that it was located near the bottom of the valley and that, therefore, the step from Pb^{206} to Pb^{208} should contribute less to stability than the step from Pb^{204} to Pb^{206}. Accordingly, the nuclear radius was expected to increase somewhat more in the 206 to 208 step than in the one from 204 to 206 in apparent agreement with observation.

From general arguments of stability the polarization picture would lead to the opposite result for such changes in the energy. A decrease in the binding energy of the last neutron in the 206–208 step may be expected to give a larger attraction of the electron by the nucleus as though the nuclear radius increased by an anomalously small step. According to the table at the end of the second volume of the book by Rosenfeld[37] the binding energy per nuclear particle in Mev for these isotopes is 7.825 for 204, 7.827 for 206, and 7.819 for 208. According to these numbers Pb^{208} is relatively more loosely bound, in spite of the closure of the magic number shell consisting of 126 neutrons. In this case the volume effect explanation agrees better with the irregularity of level spacing than the polarization picture. On the other hand, the binding energy per nucleon is 7.820 Mev for Pb^{207} according to the same table. Here the volume picture suggests on anomalously large radius and the corresponding volume anomaly might be expected to have a direction opposite to that observed. While the (208–206)/(206–204) ratios speak against the direct applicability of the polarization view it is hardly justifiable to employ binding energies per nucleon as the deciding criterion since the protons rather than neutrons are instrumental in the process and since a tighter neutron configuration does not necessarily imply a stiffer arrangement of protons. Experiments on the isotope shift of Pb^{210} would be helpful and improved knowledge of binding energies of the isotopes of Pt, Hg and other elements showing the spectroscopic isotope shift would contribute also.

The example of Pb^{207} shows that the binding energy per nuclear particle, which is practically as large for this isotope as for Pb^{208}, cannot be used as the only

[36] G. Breit, Phys. Rev. **46**, 319(L) (1934).

[37] L. Rosenfeld, *Nuclear Forces* (Interscience Publishers, Inc., New York, 1948).

criterion either on the volume effect theory or from the polarization viewpoint. The agreement of the direction of the (208–206)–(206–204) difference with that expected from binding energies and a naive application of the volume effect theory does not exclude the possibility that the difference is in part due to the availability of excited states in Pb^{206} which might contribute to larger polarization of this nucleus than that of Pb^{208} and which might conceivably have its origin in the fact that shell closes for 126 neutrons. A study of the level systems of these isotopes will have to be made in order to reach a decision concerning the relative importance of these effects. At present it appears to be impossible to exclude the combined operation of the two possible causes of the anomaly in this as well as in the cases of isotopes under discussion below. It may be of interest also that the masses of the even Pt isotopes as listed by Mattauch are 198.044, 196.039, 194.039 indicating a greater instability of the 198 isotope than that of the other two. The observed isotope shift is greater for the 198–196 interval than for that between 196 and 194. Here again the volume effect explanation fits the facts more naturally. The errors listed by Mattauch are of the order of the differences under discussion, however. The situation is similar for the 150–148 spacing in Nd as has been discussed in relation to the Sm phenomenon.

Summarizing, it appears that the dipole effect is probably too small to be of real interest, that the monopole effect possibly can be made large enough if the departures from the central field approximation to nuclear wave functions are assumed to be sufficiently drastic; the even-odd isotope shift staggering fits the monopole calculations rather naturally especially if it is supposed that differences in densities of perturbing energy levels in the region of a few Mev are not compensated for as the nuclear excitation is increased to 10 or 20 Mev; irregularities in positions of even isotopes are not necessarily in contradiction with the polarization view but do not fit it especially naturally. There is a possibility that the small value of the observed isotope shift is in part caused by a partial cancellation of the volume effect by that of the polarization.

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APPENDIX

Using $y=f/g$ and combining the two Dirac radial equations one obtains[6]

$$(E+1+\gamma/r)y^2+(E-1+\gamma/r)+dy/dr+2y/r=0. \quad \text{(A1)}$$

Differentiating with respect to E and solving for $\partial y/\partial E$ one gets Eq. (14). Equation (14.1) results from the similar treatment of the radial equation containing $\partial g/\partial r$. The normalization convention is that f_s and g_s have been divided by $[C(E)]^{\frac{1}{2}}$ so that the first power of r is energy independent.

While the second method is limited to $E=1$, it gives precise values at all r and is somewhat more convenient than the preceding method for large r. Substituting $rf=F$, $rg=G$, and $r=z^2/8\gamma$, the radial equations may be rewritten

$$\begin{aligned}&[(d/dz)+(2/z)]F+[(2\gamma/z)+z(E-1)/4\gamma]G=0,\\&[(d/dz)-(2/z)]G-[(2\gamma/z)+z(E+1)/4\gamma]F=0.\end{aligned} \quad \text{(A2)}$$

It is from this form of the Dirac equations that Eq. (12.6) may be obtained. Expanding F in powers of $(E-1)$,

$$F=F^{(0)}+(E-1)F^{(1)}+\cdots \quad \text{(A3)}$$

and letting[16]

$$\begin{aligned}&F^{(0)}=\gamma J_v(z), \quad v=2\rho,\\&L\equiv d^2/dz^2+1/z+1-v^2/z^2\end{aligned} \quad \text{(A4)}$$

one finds

$$LF^{(1)}=(1/2\gamma-\gamma-z^2/8\gamma)J_v+(z/4\gamma)dJ_v/dz. \quad \text{(A5)}$$

Using

$$L[z^pJ_v(z)]=z^p\{2pdJ_v/zdz+p^2J_v/z^2\} \quad \text{(A6)}$$

and

$$L[z^qdJ_v(z)/dz]=z^q\{(q-1)^2dJ_v/z^2dz+[2v^2(q-1)/z^3-2q/z]J_v\}, \quad \text{(A7)}$$

it is found that

$$F^{(1)}(z)=[(z^2/24\gamma)-(\gamma/2)]J_{2\rho}+[(z\gamma/3)+(z^3/48\gamma)]dJ_{2\rho}/dz. \quad \text{(A8)}$$

Similarly,

$$G^{(1)}(z)=[(z^4/96\gamma^2)+(5z^2/24)+(1/2)-(2\rho^2/3)]J_{2\rho}-(z/12)dJ_{2\rho}/dz. \quad \text{(A9)}$$

Equations (14.2) and (14.3) follow directly from these.