which is indeed smaller by a factor α^2 than the matrix element $\langle|S_{\frac{1}{2}}|V|2P_{\frac{1}{2}}\rangle$ which does not vanish in the nonrelativistic limit.

Since the matrix element (A.8) is an off-diagonal perturbation between states which are also split by the Lamb shift, the total splitting is obtained by diagonalizing the 2×2 matrix

$$\begin{pmatrix} V_{2S}{}^{L} & V_{2S,2P}{}^{\text{dipole}} \\ V_{2S,2P}{}^{\text{dipole}} & V_{2P}{}^{L} \end{pmatrix},$$

where $V_{2S}{}^{L}$, $V_{2P}{}^{L}$ are the matrix elements of the Lamb shift operator for the indicated states and $V_{2S,2P}{}^{\text{dipole}}$ is the matrix element (A.8). The eigenvalues of this matrix are

$$E_{\pm}=\tfrac{1}{2}(V_{2S}{}^{L}+V_{2P}{}^{L}) \pm\tfrac{1}{2}[(V_{2S}{}^{L}-V_{2P}{}^{L})^2+4|V_{2S,2P}{}^{\text{dipole}}|^2]^{\frac{1}{2}}. \quad \text{(A.9)}$$

We expect that the dipole moment will be so small that the splitting due to the Lamb shift alone, $V_{2S}{}^{L}-V_{2P}{}^{L}$, is much larger than the dipole matrix element $V_{2S,2P}{}^{\text{dipole}}$ so that these eigenvalues can be approximated by

$$E_{\pm}\simeq\tfrac{1}{2}(V_{2S}{}^{L}+V_{2P}{}^{L})\pm\tfrac{1}{2}(V_{2S}{}^{L}-V_{2P}{}^{L}) \pm|(V_{2S,2P}{}^{\text{dipole}})|^2/(V_{2S}{}^{L}-V_{2P}{}^{L}). \quad \text{(A.10)}$$

The first two terms are just the usual Lamb-shift splitting, so that the change will be

$$2|V_{2S,2P}{}^{\text{dipole}}|^2/(V_{2S}{}^{L}-V_{2P}{}^{L}),$$

which is again proportional to d^2 rather than to d.

This may be compared with the splitting coming from second and higher order perturbations using the nonrelativistic wave functions, which we have calculated exactly in Sec. II, and which is of order

$$|V_{2P,1S}{}^{\text{dipole}}|^2/(E_{2P}-E_{1S}),$$

as can be seen immediately from perturbation theory.

The ratio of these two is approximately

$$\frac{|V_{2S,2P}{}^{\text{dipole}}|^2}{|V_{2P,1S}{}^{\text{dipole}}|^2}\times\left(\frac{E_{2P}-E_{1S}}{E_{2P}-E_{2S}}\right)\simeq\alpha^4\times\frac{1}{\alpha^3}=\alpha, \quad \text{(A.11)}$$

so the relativistic contribution to the splitting is small compared to the nonrelativistic part, even though there is a first-order matrix element with the relativistic wave functions.

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Some Atomic Effects of an Electronic Electric Dipole Moment*

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A parity-violating perturbation, corresponding physically to a permanent electric dipole moment of an electron parallel to its spin, is introduced into the Dirac equation for an electron. For positrons two choices of the relative sign of electric moment and spin are considered. Some numerical consequences of such a perturbation for hydrogenic atoms and for positronium are calculated.

From various experiments carried out previously, rough upper limits are obtained for ξ, the electric dipole moment expressed in units of $e\hbar/mc$: From the numerical value of the Lamb shift, $\xi<0.004$; from the metastability of the $2s$-state in hydrogen, $\xi<0.03$. From the absence of $K\rightarrow L_{\text{I}}$ x-ray transitions in the heaviest atoms, the upper limit for ξ is about 0.005 or, probably, even smaller. From the value of the hyperfine splitting of the positronium ground state, $\xi<0.02$.

1. INTRODUCTION

RECENT experiments[1] on the formation and decay of positronium in the presence of a static external electric field have brought up the question of the possible existence of a small intrinsic electric dipole moment of the electron and positron. In connection with these experiments more complicated possibilities might be of interest, such as parity-violating field-theoretic terms[2] which give some effects in positronium akin to those produced by electric dipole moments but have no effect on single-electron atoms. We shall not consider any such possibilities in this paper but only a small permanent electric point-dipole moment coupled with the spin of individual electrons or positrons. We merely calculate, for future reference, some effects such a dipole moment would have on hydrogenic atoms and on positronium and discuss upper limits on such a moment which are already implied by various experiments which were carried out in the past for other purposes. Some discussion of the effects of such a moment on more complex atomic and molecular systems will be found elsewhere.[3]

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[1] F. E. Obenshain and L. A. Page, Bull. Am. Phys. Soc. Ser. II, 3, 228 (1958).

[2] P. Stehle (unpublished work).

[3] M. Sachs (to be published).

Wherever possible we shall use the notation of Bethe and Salpeter.[4] We introduce an electric dipole moment in a Lorentz-covariant manner into the Dirac equation for a single electron in an electromagnetic field by means of a term analogous to the Pauli anomalous moment term but multiplied by the pseudoscalar Dirac operator γ_5. In covariant notation we put, by analogy with (I, 10.15),

$$\left[\left(p_\mu+\frac{e}{c}A_\mu\right)\gamma_\mu-imc\right]u=-\xi\left(\frac{e\hbar}{4mc^2}\right)\gamma_5\gamma_\mu\gamma_\nu F_{\mu\nu}u. \quad (1)$$

In conventional notation the Dirac equation then reads

$$(H_0+H')u=Eu, \quad H_0=m\beta c^2+\boldsymbol{\alpha}\cdot(c\mathbf{p}+e\mathbf{A})-e\phi, \quad H'=\xi(e\hbar/2mc)\beta[\boldsymbol{\sigma}\cdot\boldsymbol{\mathcal{E}}+i\boldsymbol{\alpha}\cdot\boldsymbol{\mathcal{H}}], \quad (2)$$

where $\boldsymbol{\mathcal{E}}$ and $\boldsymbol{\mathcal{H}}$ are the electric and magnetic field. In the Pauli approximation, which will be sufficiently accurate for part of our calculations, the pseudoscalar perturbation Hamiltonian H', expressed in atomic units, reduces to

$$H'=\xi\alpha(\mathbf{s}\cdot\boldsymbol{\mathcal{E}}+\tfrac{1}{4}i\mathbf{p}\cdot\boldsymbol{\mathcal{H}}+\tfrac{1}{2}\mathbf{s}\times\mathbf{p}\cdot\boldsymbol{\mathcal{H}}), \quad (3)$$

where $\alpha=1/137.04$ is the Sommerfeld fine structure constant and $\mathbf{s}=\frac{1}{2}\boldsymbol{\sigma}^P$ is the Pauli spin-operator. ξ is a dimensionless constant throughout which measures the electric dipole moment in units of the Bohr magneton. We shall assume $\xi\ll1$, i.e., electric dipole moment small compared with e times the Compton wavelength of the electron.

We shall find as rather sensitive, although indirect, tests for the presence of an electric dipole moment some second-order perturbation energy shifts. For hydrogenic atoms these shifts contribute to the Lamb shift and are discussed in Sec. 2. For positronium they contribute to the hyperfine splitting of the ground state and are discussed in Sec. 4. More direct effects of the parity-violating perturbation Eq. (3), the breakdown of the metastability of the $2s$-state in hydrogenic and of equivalent selection rules in the x-ray spectra of heavy atoms, are discussed in Sec. 3. The behavior of an electric dipole moment in the presence of an external static electric field is discussed in Sec. 5.

2. CONTRIBUTIONS TO THE LAMB SHIFT

We consider a hydrogenic atom with charge Z in the absence of any external field, using at first the lowest-order Pauli approximation. The perturbation Hamiltonian H' in Eq. (3) then reduces to

$$H'=-\xi Z\alpha r^{-2}s_r, \quad s_r\equiv r^{-1}\mathbf{r}\cdot\mathbf{s}, \quad (4)$$

in atomic units. We assume this perturbation to be small compared with the fine structure splitting ($\xi\ll1$) and consider matrix elements of H' between the usual stationary states which are simultaneous eigenstates of the operators $\mathbf{k}^2$, $\mathbf{M}^2$, and M_z with quantum numbers (l,j,m), where $\mathbf{M}=\mathbf{k}+\mathbf{s}$ is the total angular momentum. The operator s_r commutes with $\mathbf{M}^2$ and M_z but has odd parity.[5] Its only nonzero matrix elements are

$$\langle l=j\pm\tfrac{1}{2},\, j,\, m|\, s_r\,|\, l=j\mp\tfrac{1}{2},\, j,\, m\rangle=\tfrac{1}{2}. \quad (5)$$

We need next the matrix element of r^{-2} between the radial wave functions for two different atomic states. We shall find it useful to rewrite this radial integral in the following manner. Let χ_{nl} be r times the radial wave function and E_{nl} the corresponding energy eigenvalue for principal and orbital quantum numbers n and l, for an electron in an *arbitrary* central $V(r)$. This function satisfies the equation [in atomic units (a.u.)]

$$\{[2\mu V-d^2/dr^2]+l(l+1)r^{-2}-2\mu E_{nl}\}\chi_{nl}=0, \quad (6)$$

where μ is the reduced mass in units of the electron mass m_e. Multiplying on the left by $\chi_{n'l'}$, integrating over r and subtracting an equivalent expression with nl and $n'l'$ interchanged, we obtain the desired relation

$$[l(l+1)-l'(l'+1)]\int dr\,\chi_{nl}r^{-2}\chi_{n'l'}=2\mu(E_{nl}-E_{n'l'})\int dr\,\chi_{nl}\chi_{n'l'}. \quad (7)$$

For our hydrogenic atom, with $V(r)$ replaced by the Coulomb potential, we then obtain for the only non-zero matrix-elements of H' in Eq. (4)

$$\langle n,l_+,j,m|\,H'\,|\,n',l_-,j,m\rangle=-\xi Z\alpha(2j+1)^{-1}\times(E_n-E_{n'})\int dr\,\chi_{nl_+}\chi_{n'l_-}, \quad (8)$$

where $l_\pm\equiv j\pm\frac{1}{2}$ and we have replaced the reduced mass μ by unity. As expected, our parity-violating perturbation Hamiltonian H' mixes a given unperturbed state with the states of opposite parity and the same values of j and m.

It is important to note that our nonrelativistic matrix element (8) vanishes between the two degenerate fine structure components with $n=n'$. These two states are still degenerate in the relativistic Dirac theory and are split only by the Lamb shift by an energy of order $(Z\alpha)^2\alpha$ times the energy difference to states of different principal quantum number n'. If we were to consider the Lamb shift as due to a phenomenological extra potential of order $(Z\alpha)^2\alpha$, then Eq. (7) shows that the nonrelativistic matrix-element of H' for $n=n'$ would be an order of $(Z\alpha)^2\alpha$ smaller than for $n\neq n'$. In fact we shall show that the correct relativistic matrix element for $n=n'$, even disregarding the Lamb shift, is smaller than for $n\neq n'$ only by a factor of order $(Z\alpha)^2$. The term with $n=n'$ thus contributes only a fraction of the order

[4] H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Springer Verlag, Berlin and Academic Press, Inc., Heidelberg-New York, 1958); hereafter referred to as I. Equation $(n.m)$ in this reference will be referred to as (I, $n.m$).

[5] For further details, see E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, Cambridge, 1953).

of $Z^2\alpha$ to the second-order perturbation energy due to H'. In evaluating this perturbation energy for reasonably small values of Z we are then justified in using the nonrelativistic approximation which replaces the contribution from $n=n'$ by zero. However, in evaluating the (square of) mixing into a given state of wave functions of the opposite parity, due to H', we shall see that the term with $n=n'$ contributes an order of α^{-2} more than the terms with $n\neq n'$ and we shall have to evaluate the matrix element relativistically.

We can now evaluate the second-order perturbation energy ΔE due to H' for a state $(n,l_\pm,j,m)$, using the nonrelativistic matrix-element (8), a sum rule and Eq. (6):

$$\Delta E_{n,l_\pm,j}=\sum_{n'}|\langle n,l_\pm,j|H'|n',l_\mp,j\rangle|^2(E_n-E_{n'})^{-1}$$

$$=(\xi Z\alpha/2j+1)^2\int dr\,\chi_{nl_\pm}[E_n+\tfrac{1}{2}d^2/dr^2$$

$$+Zr^{-1}-\tfrac{1}{2}l_\mp(l_\mp+1)r^{-2}]\chi_{nl_\pm}.$$

Using Eq. (6) again, this expression reduces to a multiple of the expectation value of r^{-2} [see (I, 3.25)] and we get

$$\Delta E_{n,l_\pm,j}=\pm Z^4\xi^2n^{-3}(2j+1)^{-1}(l_\pm+\tfrac{1}{2})^{-1}\alpha^2\text{ ry}. \quad (9)$$

The difference ΔE_{LS} between this energy shift for the $2s_{\frac{1}{2}}$- and the $2p_{\frac{1}{2}}$-state, i.e., the second-order perturbation contribution of H' to the observed Lamb shift for $n=2$, is then

$$\Delta E_{LS}=-(Z^4\xi^2/6)\alpha^2\text{ ry}$$

$$=-Z^4\xi^2\times 2.9\times 10^4\text{ Mc/sec}. \quad (10)$$

The contribution of H' to the $2p_{\frac{3}{2}}$-$2p_{\frac{1}{2}}$ energy difference is $\frac{3}{8}$ of ΔE_{LS}. In reducing H' given in Eq. (3) to the expression (4) we have omitted the interaction of the electric dipole moment with the virtual radiation field. This interaction, calculated in second-order perturbation theory in close analogy with the ordinary Lamb shift, also gives a contribution to ΔE_{LS}. However, as will be discussed briefly in Sec. 4, this contribution (with divergent integrals cut off at momenta of order $m_e c$) is an order of α smaller than Eq. (10) and we omit it.

The difference[6] between the experimentally observed and the theoretically calculated (with $\xi=0$) Lamb shift is about (-0.26 ± 0.25) Mc/sec for $Z=1$ and (-17 ± 8) Mc/sec for $Z=2$. The stated probable errors do not include an estimate of the field-theoretic terms of order $Z^6\alpha^5$ ry, which have not been calculated yet. Such terms could be as large as $\pm 0.2Z^6$ Mc/sec and, if negative, would remove most of the remaining discrepancy mentioned above both for $Z=1$ and 2. If positive, these terms would enhance the discrepancy, but this discrepancy would have a somewhat stronger Z dependence than a correction term of form (10), due to any electric dipole moment. The value of ΔE_{LS} in Eq. (10) is thus most probably less than about -0.5 Mc/sec, giving an upper limit of about 4×10^{-3} for ξ.

[6] E. Lipworth and R. Novick, Phys. Rev. **108**, 1434 (1957).

3. PURITY OF THE $2s_{\frac{1}{2}}$-STATE IN HYDROGENIC ATOMS

One striking effect of the perturbation H' is the mixing in of small amounts of states of the opposite parity (and same j) for any given state $njlm$. Let R^2 be the sum of the integrated squares of the mixed-in wave functions of opposite parity (with the unperturbed wave function normalized to unity). For a non-Coulombic potential with no orbital degeneracy, the small ratio R would be of the order of $\xi\alpha$. In some non-hydrogenic atoms where two states of opposite parity and different principal quantum numbers accidentally have very similar energy eigenvalues, such as the $3d$- and $4p$-states in Al ($Z=13$), the numerical value of R might be enhanced considerably. We shall not consider such cases but only the states $njlm$ of hydrogenic atoms in the absence of any external electric fields: The mixing in of states with $n\neq n'$ would again only give a ratio R of the order of $\xi\alpha$. We have seen that the nonrelativistic matrix-element of H' between the two states with the same n and j values vanishes. We shall show that the relativistic matrix-element does not vanish exactly and that the mixing ratio between the two almost-degenerate fine structure components is of order ξ. We therefore consider only this mixing and neglect contributions from states with $n\neq n'$.

We consider fixed values of n, j, and m and denote the Dirac wave functions in a Coulomb potential with $l_\pm=j\pm\frac{1}{2}$ by u_+ and u_-. We can write these Dirac spinors in partitioned form as

$$u_\pm=r^{-1}[\chi_{2\pm}(r)\eta_{jl\pm};\quad -i\chi_{1\pm}(r)\eta_{jl\mp}],$$

where the χ_2 and χ_1 are the "large" and "small" normalized radial components, respectively, and the η are Pauli-spinor and orbital wave functions. With H' defined in Eq. (2) and using Eq. (5) we then get, in the absence of any external electromagnetic field

$$\langle n,j,l_+,m|H'|n,j,l_-,m\rangle$$

$$=-\tfrac{1}{2}\xi Z\alpha\int_0^\infty dr\,r^{-2}(\chi_{2+}\chi_{2-}-\chi_{1+}\chi_{1-}). \quad (11)$$

Before evaluating the integrals in Eq. (11) explicitly, we digress a moment: If we had omitted the Dirac operator β in the definition Eq. (2) of H', the only effect on Eq. (11) would be a change of sign of the term $\chi_{1+}\chi_{1-}$. One can show as follows that the integral in Eq. (11) with this changed sign would vanish: In our present notation the exact quadratic Dirac equation

[see (I, 12.9)] reads

$$[2H_0+l_\pm(l_\pm+1)r^{-2}]\chi_{2\pm}=-Z\alpha r^{-2}\chi_{1\pm},$$
$$[2H_0+l_\mp(l_\mp+1)r^{-2}]\chi_{1\pm}=+Z\alpha r^{-2}\chi_{2\pm}, \quad (12)$$

where $H_0=2W+e\phi+\alpha^2(W+e\phi)^2+\partial^2/\partial r^2$ and $-W$ is the binding energy which is the same for both states even in the Dirac theory. After some cross-multiplying, integrating, and subtracting, one obtains the two relations

$$-\int_0^\infty dr\, r^{-2}\chi_{2+}\chi_{2-}=Z\alpha(2j+1)^{-1}\times\int_0^\infty dr\, r^{-2}(\chi_{2-}\chi_{1+}-\chi_{2+}\chi_{1-})=+\int_0^\infty dr\, r^{-2}\chi_{1+}\chi_{1-}. \quad (13)$$

The matrix element of H' modified by the omission of β in Eq. (2) would thus vanish, but this omission would destroy the Lorentz invariance of the Hamiltonian which is presumably unacceptable (even if one might be prepared to admit the parity-violating H' altogether).

We return now to the matrix element Eq. (11). As Eq. (13) shows, the square bracket in (11) contributes simply twice as much as either term in it. For small $Z\alpha$, we have as a simple approximation for the "small component" χ_1, using (I, 14.12),

$$\chi_{1\pm}=\tfrac{1}{2}\alpha[d/dr\pm(j+\tfrac{1}{2})r^{-1}]\chi_\pm\equiv\tfrac{1}{2}\alpha(D_\pm\chi_\pm),$$

where $\chi_\pm$ are the normalized radial Schrödinger wave functions for $l_\pm=j\pm\frac{1}{2}$. In this approximation then

$$4\langle l_+|H'|l_-\rangle=\xi Z\alpha^3\int_0^\infty dr(D_+\chi_+)r^{-2}(D_-\chi_-), \quad (14)$$

where we have omitted the fixed labels n, j, and m. The most interesting case is $n=2$, $j=\frac{1}{2}$, since this mixing between the $2s_{\frac{1}{2}}$ and $2p_{\frac{1}{2}}$ wave functions destroys the metastability of the $2s_{\frac{1}{2}}$-state. Equations (14) and (I, 3.18) then gives, in this approximation for small $Z\alpha$,

$$\langle 2s_{\frac{1}{2}}|H'|2p_{\frac{1}{2}}\rangle=\xi Z^5\alpha^3/8\sqrt{3}. \quad (15)$$

Using the exact Dirac wave functions (I, 14.40) and (I, 14.41), the integrals in Eq. (11) for $n=2$, $j=\frac{1}{2}$ can also be evaluated exactly and give, with $\gamma\equiv(1-Z^2\alpha^2)^{\frac{1}{2}}$,

$$\langle 2s_{\frac{1}{2}}|H'|2p_{\frac{1}{2}}\rangle=\xi Z^3\alpha(\gamma-1)/[2\gamma(2\gamma-1)(\gamma+1)(2\gamma+1)^{\frac{1}{2}}]. \quad (16)$$

Equation (15) is the first nonzero term in the expansion of Eq. (16) in powers of $Z\alpha$.

The presence of the perturbation H' alters the wave function of the $2s_{\frac{1}{2}}$-state to

$$u_{2s_{\frac{1}{2}}}+Ru_{2p_{\frac{1}{2}}},\quad R=\langle s|H'|p\rangle/\Delta W,$$

where ΔW is the energy separation between the $2s_{\frac{1}{2}}$- and $2p_{\frac{1}{2}}$-states. In the absence of a magnetic field, ΔW is simply the Lamb shift $(7.76\alpha^3Z^4/6\pi)$ a.u.$\approx 1000Z^4$ Mc/sec, and (for $Z\alpha\ll 1$)

$$R=0.18Z\xi. \quad (17)$$

The half-life t_p of the $2p_{\frac{1}{2}}$-state is 1.6×10^{-9} sec for $Z=1$, 1.0×10^{-10} sec for $Z=2$. The half-life t_s of the metastable $2s_{\frac{1}{2}}$-state in the absence of an external electric field and without our parity-violating term H' is 0.7 sec for $Z=1$ and 2.2×10^{-3} sec for $Z=2$. For $\xi\gtrsim10^{-3}$, the presence of H' considerably shortens the life of the $2s_{\frac{1}{2}}$-state to $t_s\approx R^{-2}t_p$. The value of t_s has never been measured directly, but in the course of various microwave experiments on the metastable state in H, D, and He^+ lower limits on t_s have been obtained as a by-product. In Lamb shift experiments[6] for He^+, for instance, t_s for $Z=2$ is bigger than at least 10^{-6} sec, so that $R^2<10^{-4}$ and $|\xi|<0.03$. In hyperfine structure experiments[7] on H and D, the line-width of the $2s_{\frac{1}{2}}$-states give a lower limit of about 3×10^{-5} sec for t_s for $Z=2$, i.e., $R^2<5\times10^{-5}$. The same hyperfine structure experiments also yield a more sensitive, although more indirect, test for the presence of our perturbation Hamiltonian: With a fraction R^2 of the state in $2p_{\frac{1}{2}}$-form, the theoretical value of the hyperfine splitting energy has to be multiplied by a factor $(1-2R^2/3)$. This factor is absent in the nondegenerate $1s$ ground-state. The experimental and theoretical ratios of hyperfine splitting in the $2s$- and $1s$-states in H and D agree to about 1 or 2 ppm (parts per million), so that $R^2<2\times10^{-6}$ for $Z=1$ and $|\xi|\gtrsim0.008$. In principle, direct measurements of the lifetime of the $2s_{\frac{1}{2}}$-states could furnish quite a sensitive test for the presence of H': In the presence of an external magnetic field the $2s_{\frac{1}{2}}$-$2p_{\frac{1}{2}}$ energy separation for one of the m values is decreased and for a suitably chosen magnetic field the mixing ratio R for $Z=2$, for instance, can be increased to about 2ξ or more. If lifetimes up to about 10^{-3} sec could be detected (and stray electric fields kept to a small fraction of a volt/cm) one could detect values of $|\xi|$ as small as 0.0002, say.

The mixing ratio R according to Eq. (17) increases with increasing Z, but accurate experiments cannot be carried out on hydrogenic atoms of large Z and for non-hydrogenic atoms there is no orbital degeneracy and the mixing ratio R is not large. Nevertheless, x-ray experiments on neutral atoms of very large Z again provide a sensitive and very direct test for ξ. Although there is no true orbital degeneracy and no metastable states, the energy separation between the $L_{\rm I}$ and $L_{\rm II}$ shells (a $2s_{\frac{1}{2}}$- or a $2p_{\frac{1}{2}}$-hole) is relatively small for very large Z and single-photon radiative transitions[8] between the K shell and $L_{\rm I}$ shell (jump of a $1s$ hole to a $2s$ hole)

[7] Heberle, Kusch, and Reich, Phys. Rev. **101**, 612 (1956); **104**, 1585 (1956).

[8] The two-photon radiative transition has a non-negligible probability for large Z but, of course, does not lead to monoenergetic x-rays.

are still strictly forbidden in the absence of any parity-violating perturbation Hamiltonian. In the presence of our perturbation H' this selection rule breaks down and the ratio between the intensities for a K-$L_{\rm I}$ to a K-$L_{\rm II}$ ($1s_{\frac{1}{2}}$-$2p_{\frac{1}{2}}$) transition is simply equal to R^2, the square of our mixing ratio. For U ($Z=92$), for instance, the experimental energy separation ΔW between $L_{\rm I}$ and $L_{\rm II}$ is only 30 a.u. and the matrix-element Eq. (16), using hydrogenic Dirac wave functions, is about 760 a.u. and the mixing ratio R is about 26ξ. Screening corrections for this matrix-element are probably appreciable even for Z as large as 92, but our factor of 26 for R/ξ is probably in error by less than a factor of two. The forbidden K-$L_{\rm I}$ line for heavy elements would probably have been detected already if R^2 were as large as 10^{-2}, say, which gives an upper limit for $|\xi|$ of the order of 0.005. A careful analysis of previous experiments on the "wings" of K-$L_{\rm II}$ lines might already be able to decrease our upper limits for R^2 and ξ considerably. The ratio R/ξ increases rapidly with increasing Z and a high-dispersion specific search for this forbidden K-$L_{\rm I}$ x-ray line in the transuranic elements (or in U) would provide a particularly sensitive test for ξ.

4. POSITRONIUM

Once we are prepared to accept the parity-violating perturbation H' in Eq. (2) for an electron, it is not clear how we should require this term to transform under charge conjugation. We therefore shall consider separately two cases in which the term H' for a positron has the same and opposite sign, respectively, than H' for an electron. In positronium the Coulomb field vector seen by the electron and positron are equal and parallel. The perturbation Hamiltonian in Pauli approximation equivalent to Eq. (4) is then

$$H_c'=-\xi Z\alpha r^{-2}\times\begin{cases} S_r\equiv s_{1r}+s_{2r} & \text{for case (i)} \\ s_{1r}-s_{2r} & \text{for case (ii)}, \end{cases} \tag{18}$$

where $\mathbf{s}_1$, $\mathbf{s}_2$ are the electron and positron spin and $\mathbf{S}=\mathbf{s}_1+\mathbf{s}_2$ is the total spin. We need the matrix-elements of H' between the unperturbed positronium eigenstates of $\mathbf{k}^2$, $\mathbf{S}^2$, $\mathbf{M}^2$, and M_z, with quantum numbers l, $S=0$ (singlet) or 1 (triplet), $J=|l-S|$ to $l+S$, and m ($\mathbf{M}=\mathbf{k}+\mathbf{S}$ is the total angular momentum). The operator S_r connects a state l, S, J, m only with states $l\pm1$, S, J, m and has zero matrix-elements for $S=0$. The operator $(s_{1r}-s_{2r})$ connects l, $S=0$, J, m with $l\pm1$, $S=1$, J, m.

We evaluate explicitly the second-order perturbation energy due to H' only for the ground state of positronium, i.e., for the $S=0$ and $S=1$ levels with $n=1$ and $l=0$. Since $l=0$ the operator S_r (or $s_{1r}-s_{2r}$) connects the ground state only to states with $l=1$. We again use the relation (7) with reduced mass $\mu=\frac{1}{2}$, sum rules and (I, 3.25) as in the derivation of Eq. (9) for hydrogen. One factor needed in our derivation is the expectation value

$$3\langle S_r^2\rangle_{l=0,\ J=S}=\langle\mathbf{S}^2\rangle=S(S+1),$$
$$3\langle(s_{1r}-s_{2r})^2\rangle_{l=0,\ J=S}=\langle 2(\mathbf{s}_1^2+\mathbf{s}_2^2)-\mathbf{S}^2\rangle$$
$$=\tfrac{3}{2}-S(S+1). \tag{19}$$

We call ΔE_c the second-order perturbation energy for $S=1$ minus that for $S=0$ (for the ground state, $n=1$), i.e., the contribution of the perturbation H' to the hyperfine splitting of the positronium ground state. Our final result is

$$\Delta E_c=\mp\tfrac{1}{6}\xi^2\alpha^2\ \text{ry}, \tag{20}$$

where the minus and plus signs refer to cases (i) and (ii), respectively, in Eq. (18).

We now have to consider also the interactions H_1' and H_2' of the electric dipole moment of the electron and positron with the virtual radiation field. H_1' is simply given by Eq. (2) [or, in Pauli approximation, by Eq. (3)] with $\mathfrak{E}$ and $\mathfrak{H}$ replaced by the usual summation of electric and magnetic field of plane waves multiplied by photon creation and annihilation operators. The term involving $\mathfrak{E}$ behaves essentially like ξ times the ordinary magnetic dipole radiation term and the one involving $\mathfrak{H}$ somewhat like $(\xi k/2mc)$ times the ordinary total radiation term ($\mathbf{k}$ is photon momentum), except that the photon polarization direction $\mathbf{e}$ is replaced by $\mathbf{e}\times\mathbf{k}/k$. For a two-electron system or for positronium, H_1' and H_2' taken together in second-order perturbation theory then contribute corrections of relative order ξ^2 to the ordinary Breit interaction.

The spin-spin interaction part of the Breit interaction, H_5 in Eq. (I, 39.14), can be thought of as coming from the magnetic dipole radiation term. Explicit calculations show that this term in Pauli approximation is simply multiplied by $(1\mp\xi^2)$, the upper and lower signs referring to cases (i) and (ii), respectively, in Eq. (18). The corresponding term (I, 23.4) in positronium is multiplied by the same factor, adding another ξ^2-correction term $\Delta E_{\rm Br}$ besides ΔE_c to the hyperfine splitting in the positronium ground state

$$\Delta E_{\rm Br}=\mp\tfrac{2}{3}\xi^2\alpha^2\ \text{ry}. \tag{21}$$

To lowest order in α there is no corresponding ξ^2-correction to the "pair annihilation term," Eq. (I, 23.5). The perturbations H_1' and H_2' also result in terms akin to the Lamb shift, which involve divergent integrals. If momentum cutoffs of order mc are applied, the result is of order $\xi^2\alpha^3$ ry, which we neglect. It should also be pointed out that cross-terms between H_1' (or H_2') and the ordinary radiation interaction, which would have been linear in ξ, vanish from symmetry considerations.

Adding Eqs. (20) and (21) we have

$$\Delta E=\mp(5/6)\xi^2\alpha^2\ \text{ry}=\mp(5/7)\xi^2\Delta W, \tag{22}$$

where the minus sign refers to case (i), plus sign to case (ii) and ΔW is the lowest order hyperfine splitting

in the positronium ground state, Eq. (23.6). The experimental[9] hyperfine splitting agrees with the theoretical calculations (assuming $\xi=0$) to within the combined experimental and theoretical errors of about 1 part in 4000. This yields an upper limit of about 0.02 for $|\xi|$. This upper limit is not as sensitive as those obtained in previous sections from single-electron atoms but it tests, to some extent, any field-theoretic two-electron terms which might give effects akin to those of an electric dipole moment only in many-electron atoms or in positronium.

The situation is very similar, although the calculations slightly lengthier, for the excited states $n\gtrless 2$ of positronium to that for the ground state, i.e., corrections of relative order ξ^2 are obtained to the fine and hyperfine structure splitting energies. The (squared) mixing ratio R^2 between states of opposite parity is simply of order $\xi^2\alpha^2$. The contribution to R^2 from states of the same principal quantum number n is not any larger than $\xi^2\alpha^2$ in positronium, unlike hydrogen, since the hyperfine structure ensures energy separations of order α^2 ry (instead of α^3 ry) between all states with the same n value.

5. EXTERNAL ELECTRIC FIELDS

We consider now the effects of an external homogeneous electric field F (in atomic units) in the z direction. For a single electron we now have, besides the ordinary Stark effect operator H_{St}, a perturbation H_F' representing the direct interaction between the electric dipole moment and the external field,

$$H_{\mathrm{St}}=-Fr\cos\theta, \quad H_F'=\xi\alpha F s_z. \tag{23}$$

We shall obtain terms linear in ξ not only from the direct term H_F' taken in first order, but also from the combination in second-order perturbation theory of H_{St} and H', the operator linear in ξ involving only the Coulomb potential and given in Eq. (4).

We consider first the ground state of a hydrogenic atom with charge Z. Using the fact that the operator s_r couples s states only to p states, and using Eq. (7) and a sum rule, we can write the second-order term ΔE_2 which is linear in ξ in the form

$$2\sum_k (E_0-E_k)^{-1}\langle H_{\mathrm{St}}\rangle_{0k}\langle H'\rangle_{k0}=-2\langle Fr\cos\theta\xi Z\alpha s_r\rangle_{00}.$$

Using the explicit definition (4) of s_r, the fact that the orbital part of the ground-state wave function is spherically symmetrical and the expectation value (I, 3.20) for r, we have

$$\begin{aligned}&\Delta E_2=-2\xi Z\alpha F\langle r\cos^2\theta\rangle_{00}\langle s_z\rangle_{00},\\ &\Delta E\equiv\langle H_F'\rangle_{00}+\Delta E_2=0.\end{aligned} \tag{24}$$

Equation (24) demonstrates that the second-order term involving H' and H_{St} exactly cancels the direct term of order $\xi\alpha F$ for the hydrogen ground state, if one uses nonrelativistic matrix elements. Explicit calculations for the positronium ground state lead to similar results: The direct term alone would lead to an energy splitting of order $\xi\alpha F$ for the triplet states if case (i) holds and to a mixing of order $\xi\alpha F/\Delta W$ between the singlet and triplet $m=0$ states if case (ii) holds. In both cases the direct term is canceled exactly by the second-order term when evaluated in nonrelativistic approximation.

The fact that terms linear in the small parameter ξ vanish in nonrelativistic approximation can also be demonstrated more generally as follows. Let H_0 be the nonrelativistic Hamiltonian for a hydrogen (or positronium) atom in an arbitrary external electrostatic field, in the absence of any terms involving ξ, and let H_ξ be the terms involving ξ. For hydrogen, in atomic units,

$$H_0=\tfrac{1}{2}p^2-\phi(\mathbf{r}), \quad H_\xi=-\xi\alpha\mathbf{s}\cdot\boldsymbol{\nabla}\phi=\xi\alpha\mathbf{s}\cdot[\mathbf{p},H_0]. \tag{25}$$

$\phi(\mathbf{r})$ is the total electrostatic potential, Coulomb plus external. The Pauli spin operator $\mathbf{s}$ commutes with the nonrelativistic Hamiltonian H_0. It then follows from Eq. (25) that the expectation value of H_ξ over any eigenstate of H_0 vanishes, as does the matrix element of H_ξ between two degenerate eigenstates of H_0. An equivalent argument holds for positronium.

I have not carried out detailed relativistic calculations for the Stark effect in the presence of an electric dipole moment, but some statements can be made without extensive calculations. As we have seen, the second-order terms which involve the nonrelativistic matrix elements between states of different principal quantum numbers cancel the direct terms of order $\xi\alpha F$. The relativistic corrections to these matrix elements must be smaller than $\xi\alpha F$ by at least one power of α (probably by α^2 or more). Thus the most interesting terms are the second-order ones which involve the relativistic matrix elements of H' between states of the same principal quantum number (which are discussed in Sec. 3 and vanish in nonrelativistic approximation). For the states with $n=2$ and $j=\frac{1}{2}$ in hydrogen, the calculation is particularly simple: The mixing between the $s_{\frac{1}{2}}$ and $p_{\frac{1}{2}}$ states due to the ordinary Stark effect operator H_{St} is given by (I, 55.7) and the matrix-element of H' by our Eq. (15). If the ordinary Stark effect of order F is small compared with the Lamb shift ($F\ll 500$ volts/cm for H) we get a splitting of the levels with equal and opposite m, due to our parity-violating interaction, which is linear in the field-strength F. This splitting is given by

$$\Delta E=\pm(3\pi/7.76)\xi F m \text{ atomic units}, \tag{26}$$

where the plus sign refers to $2p_{\frac{1}{2}}$, the minus sign to $2s_{\frac{1}{2}}$. Thus, for such weak electric fields, the "electric Zeeman" splitting is actually larger than $\xi\alpha F$, i.e., of order ξF. However, for F large compared with the Lamb shift this "electric Zeeman" effect becomes field-independent and is given by $\xi(\alpha^3/8\sqrt{3})m$; i.e., the splitting between $m=\pm\frac{1}{2}$ is about $\xi\times 185$ Mc/sec.

[9] Weinstein, Deutsch, and Brown, Phys. Rev. **98**, 223 (1955); Hughes, Marder, and Wu, Phys. Rev. **106**, 934 (1957).

For the excited states of positronium the second-order coupling of H_{St} and H' with fixed n cannot (unlike in hydrogen) produce any effects much larger than $\xi\alpha F$, since all fine structure components in positronium are split by an order of α^2 ry (rather than by α^3 ry). Neglecting any accidental near-degeneracies, all energy splittings and mixing ratios between singlet and triplet states, linear in ξ, are expected to be at most of order $\xi\alpha F$ (probably smaller than this for $F\gg\alpha^2$ ry). I have not evaluated these effects in detail but give, for future reference, the ordinary Stark effect plus fine structure pattern (for $n=2$ and $\xi=0$), on which any ξ terms are merely small perturbations.

For the $n=2$ states in positronium, the spin-dependent parts of the fine structure operators in Pauli approximation (including the pair annihilation term) can be reduced (see[10] I, Sec. 23α) to the form

$$H_{FS}=\{(40\delta_{S1}-30\delta_{S0})\delta_{l0}+\delta_{S1}\delta_{l1} \times[4+6\mathbf{S}\cdot\mathbf{k}-3(\mathbf{S}\cdot\mathbf{k})^2]\}(\alpha^2/480)\text{ ry}. \quad (27)$$

We consider now strong enough fields so that the Stark effect is large compared with the fine structure ($F\gg5000$ volts/cm, say). In zero order the spatial wave functions are the usual ones in parabolic coordinates with quantum numbers (n_1,n_2,m_l). The states $(0, 0, \pm1)$ are unshifted and the wave functions equal $u_{s,m_l=\pm1}$. The states (1,0,0) and (0,1,0) have energies $+6F$ and $-6F$ and wave functions $(u_s\pm u_p)/\sqrt{2}$, where u_s and u_p are the spatial functions for $n=2$, $l=0$ or 1 and $m_l=0$. The components of this Stark triplet are now split by H_{FS}, considered as a perturbation, as follows (S is still a good quantum number, l and J are not). For the (1,0,0) and (0,1,0) states: The triplet states ($S=1$) lie higher than the singlet ($S=0$) state by $[(34/15)+(m^2/10)](\alpha^2/32)$ ry. For the (0,0,1) states: The two states with $m=\pm2$ (triplet states only) are degenerate and raised by $(7/480)\alpha^2$ ry. The two singlet states with $m=\pm1$ are unshifted, the two triplet states with $m=\pm1$ are degenerate and raised by $(\alpha^2/480)$ ry. For $m=0$ there are two triplet states (with $m_s=-m_l=\pm1$), lowered by $-(\alpha^2/96)$ ry and $-(11\alpha^2/480)$ ry.

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[10] The coefficient of the last term in square brackets in Eq. (I, 23.3) should read -3 instead of $-\frac{3}{2}$.

Note added in proof.—In the experiments by F. E. Obenshain and L. A. Page [Phys. Rev. **112**, 179 (1958)] published so far an electric field F of about 15 kv/cm seems to have effects similar to those produced by a magnetic field of about 2 kilogauss. Expressed in atomic units such an electric field is more than ten times weaker than the corresponding magnetic field and the Stark effect splitting is slightly larger than the fine structure and hyperfine structure splittings for $n=2$ states in positronium. If we attempt to explain these results in terms of singlet-triplet mixing for $n=2$ states due to a static electric dipole moment of both the electron and positron we find that the direct term H_F' and the indirect effect of H', discussed in Sec. 5 of the present paper, are of the same order of magnitude. To obtain the rather appreciable singlet-triplet mixing implied by the experiment we would require a value of about ten for our dimensionless parameter ξ. Such a large value is clearly out of the question even if it applied only to positronium and not to other atoms since we have seen in Sec. 4 that positronium ground-state experiments give $\xi<0.02$.

If one still wanted to explain the Obenshain-Page experiments in terms of some parity-violating electric moment-like perturbation one would be forced to hypothesize a term more complicated than our Eq. (3). Such an interaction would have to include an additional position, field or velocity dependence in such a way that there is no cancellation in the Pauli-approximation matrix element between $2s$ and $2p$ so that the matrix element of order $\xi\alpha^3$ in our Eq. (15) would be replaced by one of order $\xi\alpha$. If one were bold enough to assume such an interaction, the Obenshain-Page experiments might require values for ξ of not much more than 10^{-3} which would not be incompatible with our Sec. 5. However, even such an interaction would have to be postulated to exist only for positronium and not for single electron atoms since the experiments on the lifetimes of $2s$ states in hydrogen or ionized helium, discussed in our Sec. 3, would require $\xi<10^{-6}$ for such an interaction in hydrogenic atoms. Finally, it should be noted that, if such an interaction in positronium were responsible for the Obenshain-Page effect, this effect should saturate at electric field strengths of about 5 or 10 kv/cm. The effect would depend on field strength only through the amount of $2s$-$2p$ mixing and for 10 kv/cm this mixing is already very close to the maximum value contained in the Stark effect states labeled (1, 0, 0) and (0, 1, 0) in our Sec. 5.