$\omega=\bar{\omega}_0+d\omega$, where

$$d\omega=(\bar{\omega}_0-\omega_0)Gl/L, \tag{8'}$$

in which

$$G=\frac{\tan b\tau+l/L[\tan b\tau-\cos b\tau+1/(b\tau)]}{2l/L\,\tan b\tau+b\tau+(l/L)^2[\tan b\tau-\cos b\tau+1/(b\tau)]}.$$

For $l/L=1/15$ and for values of $4b\tau$ between 1 and 5, G is between 0.9 and 2.0. If $(\bar{\omega}_0-\omega_0)/2\pi=100$ kc/sec, $d\omega/2\pi$ is between 6 and 12 kc/sec.

Consideration of the velocity distribution of the beam and of the case of a system with three equally-spaced energy levels (helium) is not expected to change the order of magnitude of the above estimate.

PHYSICAL REVIEW VOLUME 112, NUMBER 5 DECEMBER 1, 1958

Effects of an Electric Dipole Moment of the Electron on the Hydrogen Energy Levels*

G. Feinberg
Brookhaven National Laboratory, Upton, New York

(Received July 18, 1958)

The bound states in a Coulomb field of a charged, spin $\frac{1}{2}$, particle with an electric dipole moment are obtained. The nonrelativistic Schrödinger equation for such a particle is solved in closed form. The wave functions are generalizations of the Coulomb wave functions, involving Laguerre polynomials of nonintegral upper index. The accidental degeneracies of the Coulomb energy levels are removed by the dipole interaction. In particular, there will be an additional contribution to the splitting between the $2S_{\frac{1}{2}}$ and $2P_{\frac{1}{2}}$ states coming from the dipole moment. By requiring that this extra energy shift should not destroy the agreement between the theoretical and experimental values of the Lamb shift, it is found that the dipole moment of the electron must be less than 10^{-13} cm times the electron charge. Other effects of the dipole moment on the hydrogen energy levels are discussed.

I. INTRODUCTION

THE possible existence of electric dipole moments for the spin $\frac{1}{2}$ elementary particles has been the subject of some recent theoretical and experimental investigation. Theoretically, it has been shown that the invariance of physical laws under space reflection or time reversal would imply the nonexistence of such moments,[1] provided that there is no more degeneracy of the states of a free spin $\frac{1}{2}$ particle at rest than that given by the two spins and the particle-antiparticle.[2] Experimentally, there is a very accurate measurement of the neutron electric dipole moment through a magnetic resonance method.[3] This indicates that the electric dipole moment of the neutron is less than 5×10^{-20} cm times the electron charge. There do not seem to be any such accurate limits known for the dipole moments of charged particles such as electrons. In view of some recent experiments which have been interpreted as indicating that the positron has a large dipole moment,[4] it seems useful to see what limits for the electron dipole moment are implied by the measurements of the hydrogen energy levels by Lamb and others.[5] In particular, one may expect that the $2S_{\frac{1}{2}}$ and $2P_{\frac{1}{2}}$ states, which are split only by radiative corrections to the Dirac equation, would further be split by the interaction of an electric dipole moment with the Coulomb field, and so the dipole moment must be small enough so as not to spoil the agreement between the experimental value of this splitting and the value predicted by quantum electrodynamics. The dependence of the splitting on the dipole moment will be obtained in Sec. II, where the nonrelativistic Schrödinger equation for a charged particle, with a dipole moment, in a Coulomb field is solved in closed form. The energy levels depend only on the square of the dipole moment, as would be expected from a perturbation calculation. The energy levels and wave functions obtained are used in Sec. III to discuss the limits on the dipole moment of the electron implied by various measurements on the hydrogen atom.

II. WAVE FUNCTIONS FOR A PARTICLE WITH AN ELECTRIC DIPOLE MOMENT IN A COULOMB FIELD

We consider the Schrödinger equation for a nonrelativistic charged particle with an electric dipole

---

* Work performed under the auspices of the U. S. Atomic Energy Commission.

[1] Lee, Oehme, and Yang, Phys. Rev. **106**, 340 (1957).

[2] The requirement of the lack of degeneracy has been stressed by N. F. Ramsey, Phys. Rev. **109**, 225 (1958). If there exist spin $\frac{1}{2}$ particles with two otherwise degenerate states for each value of the spin, momentum, and charge, and these states have opposite but nonvanishing electric dipole moment, then the definition of space reflection and time reversal may be extended so that these states are transformed into each other under these operations, and the invariance of the Hamiltonian will be maintained. The particles which constitute ordinary matter, i.e., the electron, neutron and proton, presumably cannot be of this type, because such an added degeneracy would change the form of the periodic table and the nuclear shell structure by allowing twice as many particles into each closed shell.

[3] Smith, Purcell, and Ramsey, Phys. Rev. **108**, 120 (1957).

[4] F. E. Obenshain and L. A. Page, Phys. Rev. **112**, 179 (1958).

[5] Triebwasser, Dayhoff, and Lamb, Phys. Rev. **89**, 98 (1953).

d in a Coulomb field $\mathcal{E}=(-Ze/r^2)\hat{r}$. The spin-orbit coupling produced by the magnetic moment of the particle is neglected in this approximation. Therefore, if the dipole moment vanishes, the energy levels are completely determined by the total quantum number n and the degeneracy for a state with given n is $2n^2$. As we shall see, this degeneracy will be split by the dipole interaction so that the energy will depend not only on one principle quantum number, but also on the total angular momentum j, and on another quantum number which indicates which of the 2 states of opposite parity and equal j is predominantly present in the eigenstate.

The Hamiltonian of the system is

$$H=\frac{p^2}{2m}-\frac{Z\alpha}{r}-\frac{Z\alpha d\boldsymbol{\sigma}\cdot\mathbf{r}}{r^3},\quad (\hbar=c=1), \tag{1}$$

where the last term represents the interaction $d\boldsymbol{\sigma}\cdot\mathcal{E}$ of the intrinsic dipole moment with the Coulomb field.

We wish to solve

$$H\Psi=-|E|\Psi, \tag{2}$$

where $-|E|$ is the energy of one of the bound states.

The total angular momentum $\mathbf{J}=\mathbf{L}+\frac{1}{2}\boldsymbol{\sigma}$ commutes with H, so that we can separate the equation by writing

$$\Psi_J(r)=f_J(r)|J,\,l=J-\tfrac{1}{2}\rangle+g_J(r)|J,\,l=J+\tfrac{1}{2}\rangle. \tag{3}$$

Here the functions f_J, g_J depend only on the distance $|\mathbf{r}|$, and the states $|J,l\rangle$ are eigenfunctions of J^2, L^2, and J_z with the indicated quantum numbers. The quantum number for J_z which is inessential, has been omitted. Thus the state $|\frac{1}{2},0\rangle$ would be an $S_{\frac{1}{2}}$ state; $|\frac{3}{2},1\rangle$ a $P_{\frac{3}{2}}$ state, etc. With the usual normalization of J, these states satisfy

$$\boldsymbol{\sigma}\cdot\hat{r}|J,l=J-\tfrac{1}{2}\rangle=|J,\,l=J+\tfrac{1}{2}\rangle. \tag{4}$$

Furthermore,

$$\begin{aligned}
&p^2[f_J(r)|J,l=J-\tfrac{1}{2}\rangle]\\
&\quad=\left[-\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{df_J}{dr}\right)+(J^2-\tfrac{1}{4})f_J\right]|J,l=J-\tfrac{1}{2}\rangle,\\
&p^2[g_J(r)|J,l=J+\tfrac{1}{2}\rangle]\\
&\quad=\left[-\frac{1}{r^2}\frac{d}{dr}\left(\frac{dg_J}{dr}\right)+(J+\tfrac{1}{2})(J+\tfrac{3}{2})g_J\right]|J,l=J+\tfrac{1}{2}\rangle.
\end{aligned} \tag{5}$$

Substituting (1) and (3) into (2) and using (4), (5) and the orthonormality of $|J,\,l=J-\frac{1}{2}\rangle$ and $|J,\,l=J+\frac{1}{2}\rangle$, we get the two equations

$$\begin{aligned}
&\frac{1}{2m}\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{df_J}{dr}\right)+\frac{\alpha Z}{r}f_J-\frac{(J-\frac{1}{2})(J+\frac{1}{2})}{r^2}f_J\\
&\qquad\qquad+\frac{Z\alpha d}{r^2}g_J=|E|f_J,\\
&\frac{1}{2m}\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dg_J}{dr}\right)+\frac{\alpha Z}{r}g_J-\frac{(J+\frac{1}{2})(J+\frac{3}{2})}{r^2}g_J\\
&\qquad\qquad+\frac{Z\alpha d}{r^2}f_J=|E|g_J.
\end{aligned} \tag{6}$$

We introduce the dimensionless variable $\rho=(8m|E|)^{\frac{1}{2}}r$, and let

$$\zeta=2m\alpha Z/8m|E|;\quad k=2mZ\alpha d. \tag{7}$$

Then (we drop the index J)

$$\begin{aligned}
&\frac{1}{\rho^2}\frac{d}{d\rho}\left(\rho^2\frac{df}{d\rho}\right)+\left(\frac{\zeta}{\rho}-\frac{[J+\frac{1}{2}][J-\frac{1}{2}]}{\rho^2}-\frac{1}{4}\right)f+\frac{k}{\rho^2}g=0,\\
&\frac{1}{\rho^2}\frac{d}{d\rho}\left(\rho^2\frac{dg}{d\rho}\right)+\left(\frac{\zeta}{\rho}-\frac{[J+\frac{1}{2}][J+\frac{3}{2}]}{\rho^2}-\frac{1}{4}\right)g+\frac{k}{\rho^2}f=0.
\end{aligned} \tag{8}$$

The similarity of the terms kg/ρ^2 and kf/ρ^2 coming from the dipole moment to the terms $(J-\frac{1}{2})(J+\frac{1}{2})f/\rho^2$ and $(J+\frac{1}{2})(J+\frac{3}{2})g/\rho^2$ coming from the centrifugal potential suggests that we look for solutions of the form

$$g(r)=cf(r). \tag{9}$$

Substitution of this into the Eqs. (8) gives the consistency condition

$$kc-(J-\tfrac{1}{2})(J+\tfrac{1}{2})=\frac{k}{c}-(J+\tfrac{1}{2})(J+\tfrac{3}{2}),$$

or

$$c_{\pm}=\frac{k}{(J+\frac{1}{2})\pm[(J+\frac{1}{2})^2+k^2]^{\frac{1}{2}}}, \tag{10}$$

which is more conveniently written

$$\begin{aligned}
c_{+}&=\frac{k}{J+\frac{1}{2}+[(J+\frac{1}{2})^2+k^2]^{\frac{1}{2}}},\\
c_{-}&=-\frac{\{J+\frac{1}{2}+[(J+\frac{1}{2})^2+k^2]^{\frac{1}{2}}\}}{k}.
\end{aligned} \tag{11}$$

When this condition is satisfied the two Eqs. (8) become identical, and

$$\frac{1}{\rho^2}\frac{d}{d\rho}\left(\rho^2\frac{df}{d\rho}\right)+\left(\frac{\zeta}{\rho}-\frac{1}{4}\right)f-\frac{s_{\pm}(s_{\pm}+1)}{\rho^2}f=0, \tag{12}$$

where

$$s_{\pm}(s_{\pm}+1)=(J+\tfrac{1}{2})^2\mp[(J+\tfrac{1}{2})^2+k^2]^{\frac{1}{2}}. \tag{13}$$

Equation (11) is the same as the ordinary radial wave equation for a particle without a dipole moment in a Coulomb field, with $s_\pm$ replacing the angular momentum l. For small k (i.e., small dipole moment) it can be seen by expanding Eq. (12) that

$$\begin{aligned} s_+(s_++1) &\simeq (J-\tfrac{1}{2})(J+\tfrac{1}{2})-\frac{k^2}{2(J+\frac{1}{2})}, \\ s_-(s_-+1) &\simeq (J+\tfrac{1}{2})(J+\tfrac{3}{2})+\frac{k^2}{2(J+\frac{1}{2})}. \end{aligned} \tag{14}$$

Then according to (9), (11), (12), and (14), if the dipole moment is small the two solutions of (10) represent states which contain mostly one or mostly the other of the two states of the hydrogen atom with equal J and different l. In the following we shall sometimes refer to the exact solutions by the quantum numbers of the pure Coulomb states which they approach for small dipole moments.

The normalizable solutions of Eq. (12) are "generalized" Coulomb wave functions of the form

$$f_{n,J,s_\pm}=N_{n,J,s_\pm}e^{-\frac{1}{2}\rho}\rho^{s_\pm}L_n^{2s_\pm+1}(\rho). \tag{15}$$

Here $N_{n,J,s_\pm}$ is a normalization constant, n is a nonnegative integer related to the eigenvalue ζ by

$$n=\zeta-s-1, \tag{16}$$

and $L_n^{2s_\pm+1}(\rho)$ are the associated Laguerre polynomials of the indicated argument as defined in Morse and Feshbach[6]:

$$L_n^{2s_\pm+1}(\rho)=\frac{\Gamma(n+2s_\pm+2)}{\Gamma(n+1)}\frac{e^\rho}{\rho^{2s_\pm+1}}\frac{d^n}{d\rho^n}(e^{-\rho}\rho^{n+2s_\pm+1}). \tag{17}$$

It may be seen from the definition that $L_n^{2s_\pm+1}$ is indeed a polynomial when n is an integer, even if $s_\pm$ is not an integer, in which case $L_n^{2s_\pm+1}$ cannot be expressed as a derivative of the ordinary Laguerre polynomial.

It is apparent from Eqs. (13) and (15) that $f_{n,\frac{1}{2},s_+}$ will behave like a negative irrational power of ρ near the origin. For sufficiently large dipole moments, this implies that the expectation value of the kinetic energy operator for instance, will become undefined, and so the solution (15) will break down. This occurs for the states with $J=\frac{1}{2}$ at $k=\frac{3}{4}$, corresponding to a dipole moment on the order of ea_0 (a_0= Bohr radius). Such a large dipole moment would produce a radical change in the energy levels and we will not consider this possibility here. If the dipole moment is small compared to this critical value, the wave function near the origin is not so singular as to make the expectation values of T and V diverge and the solution (15) is valid.

The energy levels corresponding to the eigenfunctions are obtained by solving Eqs. (7), (16) for E.

$$E_{n,J,s_\pm}=\frac{-Z^2\alpha^2m}{2}\frac{1}{(n+s_\pm+1)^2}. \tag{18}$$

The energy levels are thus given by an expression similar to the Bohr formula, however, $n+s+1$ is not an integer in general. Each value of n, J and each choice of s_+ or s_- will correspond to a different value of the energy, except for special values of k which are all bigger than the critical value, and so are not considered. This has two main consequences about the degeneracy of the levels.

Let us denote by L, the nearest integer to s, so that if the dipole moment vanished $L=s=$ orbital momentum of the state. States which have different values of J, but the same value of $n+L$, which are degenerate in the ordinary hydrogen spectrum when the spin-orbit coupling is neglected, are now no longer degenerate, since $n+s$ will be different for them. An example of such states are the states $n=0$, $J=\frac{1}{2}$, $s=s_-$ and $n=0$, $J=\frac{3}{2}$, $s=s_+$, which go into the $2P_{\frac{1}{2}}$ and $2P_{\frac{3}{2}}$ states when the dipole moment vanishes. Of course, the degeneracy between such states is already removed by the (much larger) fine-structure energy, which has not been included. Thus one effect of the dipole moment would be to change the fine-structure splitting by a small amount, whose magnitude we discuss in the next section.

The second change in degeneracy is that states with equal J, different n, and equal $(n+L)$, which are degenerate in the Dirac theory without radiative corrections, are no longer degenerate if a dipole moment is present because $n+s$ will be different. Thus a dipole moment would contribute a small amount to the Lamb shift of the $2S_{\frac{1}{2}}$ and $2P_{\frac{1}{2}}$ states of hydrogen like atoms.

We summarize the results of this section by writing the normalized wave functions for the bound states,

$$\Psi_{n,J,s_+}=N_{n,J,s_+}e^{-\rho/2}\rho^{s_+}L_n^{2s_++1}(\rho)\left[|J,l=J-\tfrac{1}{2}\rangle+\frac{k}{J+\frac{1}{2}+[(J+\frac{1}{2})^2+k^2]^{\frac{1}{2}}}|J,l=J+\tfrac{1}{2}\rangle\right], \tag{19}$$

where

$$N_{n,J,s_+}^2=\left[\frac{2Z}{(n+s_++1)a_0}\right]^3\frac{n!}{2(n+s_++1)[\Gamma(n+2s_++2)]^3}\times\frac{\{J+\frac{1}{2}+[(J+\frac{1}{2})^2+k^2]^{\frac{1}{2}}\}^2}{\{J+\frac{1}{2}+[(J+\frac{1}{2})^2+k^2]^{\frac{1}{2}}\}^2+k^2},$$

and

$$\Psi_{n,J,s_-}=N_{n,J,s_-}e^{-\rho/2}\rho^{s_-}L_n^{2s_-+1}(\rho)\times\left[\frac{-k}{J+\frac{1}{2}+[(J+\frac{1}{2})^2+k^2]^{\frac{1}{2}}}|J,l=J-\tfrac{1}{2}\rangle+|J,l=J+\tfrac{1}{2}\rangle\right], \tag{20}$$

---

[6] P. M. Morse and H. Feshbach, *Method of Theoretical Physics* (McGraw-Hill Book Company, Inc., New York, 1953), p. 784.

where

$$N_{n,J,s_-}{}^2=\left[\frac{2Z}{(n+s_-+1)a_0}\right]^3\frac{n!}{2(n+s_-+1)[\Gamma(n+2s_-+2)]^3}\times\frac{\{J+\frac{1}{2}+[(J+\frac{1}{2})^2+k^2]^{\frac{1}{2}}\}^2}{\{J+\frac{1}{2}+[(J+\frac{1}{2})^2+k^2]^{\frac{1}{2}}\}^2+k^2}.$$

The corresponding energies are given in Eq. (18).

III. LIMITS ON THE ELECTRON DIPOLE MOMENT

In order to compare the energy levels of the charged dipole with the observed hydrogen levels, it is necessary to include, as a perturbation on the Hamiltonian (1), the relativistic and Lamb shift interactions. This can be done by standard perturbation theory, using the wave functions (19) and (20) for the unperturbed states. There are two problems which arise when this is done. First, the states $\Psi_{n,J=\frac{1}{2},s_+}$ which go over into the s states as $k\to 0$ will contain some admixture of p state when k is not zero, as can be seen from (19). Because of this, the expectation value of the usual fine structure operator $(1/r)(dV/dr)\boldsymbol{\sigma}\cdot\mathbf{L}$, in these states, will diverge. This difficulty can be avoided by using a fine-structure operator corrected at short distances for the effect of the Coulomb field, as discussed in Bethe and Salpeter.[7] When this is done it is found that for states which were not accidentally degenerate for $k=0$, the energy is just the sum of the usual relativistic and Lamb-shift corrections, calculated for hydrogenic wave functions, and the dipole energy of Eq. (18) expanded to order k.[2] The corrections to this are smaller by factors of α or higher. For states such as $2S_{\frac{1}{2}}$ and $2P_{\frac{1}{2}}$ which are degenerate for $k=0$, one has the additional problem that the perturbing effect of the Lamb shift is much larger than the energy splitting due to the dipole, at least for small k. It can be shown here also that the energy shift is the sum of the Lamb-shift and relativistic corrections computed for hydrogenic wave functions and the dipole energy evaluated to order k^2, with corrections that are higher order in α. Thus the main additional effect of the dipole on the energies is given by Eq. (18) expanded to order k^2, and it is this quantity which will be compared with experiment. However, the wave functions (19), (20) will not be a good approximation for the $2S_{\frac{1}{2}}$ and $2P_{\frac{1}{2}}$ even to first order in k.

Let us consider the states with the following quantum numbers:

$$n=1,\quad J=\tfrac{1}{2},\quad s=s_+,$$
$$n=0,\quad J=\tfrac{1}{2},\quad s=s_-,$$
$$n=0,\quad J=\tfrac{3}{2},\quad s=s_+,$$

which go into the $2S_{\frac{1}{2}}$, $2P_{\frac{1}{2}}$, and $2P_{\frac{3}{2}}$ states, respectively, as $k\to 0$.

$$\begin{aligned}E^{2S\frac{1}{2}}&=-\frac{Z^2\alpha^2m}{2}\frac{1}{(2+s_+[J=\frac{1}{2}])^2},\\E^{2P\frac{1}{2}}&=-\frac{Z^2\alpha^2m}{2}\frac{1}{(1+s_-[J=\frac{1}{2}])^2},\\E^{2P\frac{3}{2}}&=-\frac{Z^2\alpha^2m}{2}\frac{1}{(1+s_+[J=\frac{3}{2}])^2}.\end{aligned}\qquad(21)$$

Using Eq. (13) and expanding in powers of k^2, we get

$$\begin{aligned}E^{2S\frac{1}{2}}&=-\tfrac{1}{8}Z^2\alpha^2m[1+\tfrac{1}{2}k^2+O(k^4)],\\E^{2P\frac{1}{2}}&=-\tfrac{1}{8}Z^2\alpha^2m[1-\tfrac{1}{6}k^2+O(k^4)],\\E^{2P\frac{3}{2}}&=-\tfrac{1}{8}Z^2\alpha^2m[1+\tfrac{1}{12}k^2+O(k^4)].\end{aligned}\qquad(22)$$

We write $d=\lambda/m$, so that λ measures the dipole moment in electron Compton wavelengths, and $k=2Z\alpha\lambda$. Then

$$\begin{aligned}E^{2S\frac{1}{2}}&=-E_0-\tfrac{1}{4}Z^4\alpha^4m\lambda^2+O(\lambda^4),\\E^{2P\frac{1}{2}}&=-E_0+\tfrac{1}{12}Z^4\alpha^4m\lambda^2+O(\lambda^4),\\E^{2P\frac{3}{2}}&=-E_0-(1/24)Z^4\alpha^4m\lambda^2+O(\lambda^4),\end{aligned}\qquad(23)$$

where $E_0=-\frac{1}{8}Z^2\alpha^2m$.

Note that the energy of the $2S_{\frac{1}{2}}$ state is lowered while that of the $2P_{\frac{1}{2}}$ state is increased, which effect is opposite to the Lamb shift.

The energy difference between the $2S_{\frac{1}{2}}$ and $2P_{\frac{1}{2}}$ states, neglecting terms of order λ^4 and higher, is

$$E^{2S\frac{1}{2}}-E^{2P\frac{1}{2}}=-\tfrac{1}{3}Z^4\alpha^4m\lambda^2.\qquad(24)$$

This corresponds to a frequency shift of the corresponding line of $10^{11}\ \lambda^2$(cycles/sec) in hydrogen.

It is known[7] that the measured value of the $2S_{\frac{1}{2}}-2P_{\frac{1}{2}}$ splitting in hydrogen agrees with the theoretical calculation to about $\frac{1}{3}\times 10^6$ cycles/sec. It seems reasonable to require that the shift due to the electric dipole moment should be less than 10^6 cycles/sec. This then gives

$$\lambda<3\times 10^{-3},\qquad(25)$$

or the electric dipole moment of the electron must be less than 3×10^{-3} times its Compton wavelength multiplied by e. According to the *TCP* theorem,[1] a similar result holds for the positron.

There are several other effects of an electron dipole moment on the properties of hydrogen which do not lead to more accurate limits than the above, which will be mentioned briefly.[8]

1. There is an addition to the fine-structure splitting between the $2P_{\frac{1}{2}}$ and $2P_{\frac{3}{2}}$ states. From Eq. (23), we see that

$$E^{2P\frac{1}{2}}-E^{2P\frac{3}{2}}=\tfrac{1}{8}\alpha^4m\lambda^2.\qquad(26)$$

---

[7] H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Academic Press, Inc., New York, 1957), p. 60.

[8] I would like to thank Dr. G. Breit for interesting discussions on the possibility of using the lifetime of the 2S state at a test of the admixture of P state.

The experimental formula for this splitting is in agreement with the fine-structure formula including radiative corrections[7] to within about 10^6 cycles/sec. The requirement that the dipole splitting be less than this then implies $\lambda < 10^{-2}$.

2. If the relativistic form of the electric dipole interaction $\gamma_4\gamma_5\sigma_{\mu\nu}F_{\mu\nu}$ is used, it is seen that there will also be an interaction of the electric dipole moment with the magnetic field produced by the proton magnetic moment, of the form

$$V = de\boldsymbol{\alpha}\cdot\mathbf{H}. \tag{27}$$

This interaction will lead to a hyperfine splitting in the s states of hydrogen which would add to that produced by the usual interaction $\mu e\boldsymbol{\sigma}\cdot\mathbf{H}$. In the $1S$ state this splitting will be very small, since it is of second order both in the electron dipole moment and the proton magnetic moment, and is furthermore a relativistic effect because of the odd operator $\boldsymbol{\alpha}\cdot\mathbf{H}$. The ratio of the dipole splitting to the Fermi splitting in the $1S$ state will be about $\alpha^4(m/m_p)\lambda^2$, which gives no limit on λ of any interest.

We conclude that the electric dipole moment of the electron is less than 10^{-13} cm times the electron charge.

ACKNOWLEDGMENTS

I would like to thank Dr. M. Schwartz, Dr. T. D. Lee, Dr. G. C. Wick, Dr. J. Weneser, Dr. N. Kroll, and Dr. G. Breit for many stimulating discussions.

APPENDIX

According to Eqs. (13) and (18), the energy levels depend only on the square of the dipole moment parameter k. It might have been expected that because the $2S_{\frac{1}{2}}$ and $2P_{\frac{1}{2}}$ states are degenerate in the nonrelativistic theory and have opposite parity, the dipole interaction would have a matrix element between them which would give a splitting in first order, as for example happens when an external electric field is applied to the hydrogen atom. The reason that this does not happen is because of a peculiar property of the nonrelativistic hydrogen wave functions, which we now derive.[9]

Let $\Psi^{2S_{\frac{1}{2}}}$, $\Psi^{2P_{\frac{1}{2}}}$ be the nonrelativistic wave functions for the $2S_{\frac{1}{2}}$ and $2P_{\frac{1}{2}}$ states (i.e., the eigenstates with the indicated quantum numbers of $H = p^2/2m - Z\alpha/r$).

$$\begin{aligned} \Psi^{2S_{\frac{1}{2}}} &= R_{2S}(r)\,|J=\tfrac{1}{2}, l=0\rangle, \\ \Psi^{2P_{\frac{1}{2}}} &= R_{2P}(r)\,|J=\tfrac{1}{2}, l=1\rangle, \end{aligned} \tag{A.1}$$

where R_{2S} and R_{2P} are the radial wave functions for the states, and $|J=\frac{1}{2}, l=0\rangle$, $|J=\frac{1}{2}, l=1\rangle$ are the angular momentum eigenstates introduced previously. The matrix element of the dipole interaction between these states is proportional to

$$M = \int \frac{R_{2S}(r)R_{2P}(r)}{r^2}\langle J=\tfrac{1}{2}, l=0\,|\,\boldsymbol{\sigma}\cdot\hat{r}\,|\,J=\tfrac{1}{2}, l=1\rangle d^3r. \tag{A.2}$$

Upon using Eq. (4), this becomes

$$M = \int R_{2S}(r)R_{2P}(r)dr. \tag{A.3}$$

The following theorem may be proven for the radial wave functions of the nonrelativistic Schrödinger equation for any central potential:

$$\int R_1(r)R_2(r)r^2dr(E_1-E_2) + [l_2(l_2+1) - l_1(l_1+1)] \times \int R_1(r)R_2(r)dr = 0, \tag{A.4}$$

where R_1, R_2 are the radial wave functions for two states with energy E_1, E_2 and orbital angular momentum l_1, l_2. This result follows directly from the two radial wave equations

$$\begin{aligned} \frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR_1}{dr}\right) + 2m(E_1-V)R_1 - \frac{l_1(l_1+1)}{r^2}R_1 &= 0, \\ \frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR_2}{dr}\right) + 2m(E_2-V)R_2 - \frac{l_2(l_2+1)}{r^2}R_2 &= 0. \end{aligned} \tag{A.5}$$

If $l_1 = l_2$, Eq. (A.4) is just the ordinary orthogonality condition on the radial wave functions for states of different energy. If however $l_1 \neq l_2$ but $E_1 = E_2$, as is the case for the $2S_{\frac{1}{2}}$ and $2P_{\frac{1}{2}}$ states, then Eq. (A.4) implies

$$\int R_1(r)R_2(r)dr = 0, \tag{A.6}$$

so that $M = 0$, and therefore there is no first-order splitting due to the dipole interaction.

This vanishing of the first-order matrix element of the dipole operator no longer holds if we use the relativistic expression for the dipole interaction,

$$V = dZ\alpha\gamma_4\gamma_5\sigma_{\mu\nu}F_{\mu\nu}, \tag{A.7}$$

and use the Dirac wave functions for the $2S$ and $2P$ states. However, since the matrix element must vanish in the nonrelativistic limit, it will be proportional to some power of $\langle v/c\rangle = \alpha$. An explicit evaluation of the matrix element for hydrogen gives

$$\begin{aligned} \langle 2S_{\frac{1}{2}}|\,V\,|2P_{\frac{1}{2}}\rangle &= \frac{1}{4\sqrt{3}}\frac{d\alpha}{a_0^2}\times\alpha^2 \\ &= \frac{1}{4\sqrt{3}}\frac{d\alpha}{a_0^2}\left\langle\frac{v}{c}\right\rangle^2, \end{aligned} \tag{A.8}$$

---

[9] This point has been noted in private communications to the author by Dr. M. Schwartz, Dr. N. Kroll, and Dr. J. Weneser.

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.

PHYSICAL REVIEW VOLUME 112, NUMBER 5 DECEMBER 1, 1958

Some Atomic Effects of an Electronic Electric Dipole Moment*

E. E. SALPETER
Newman Laboratory of Nuclear Studies, Cornell University, Ithaca, New York

(Received August 4, 1958)

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]

---

* Supported in part by the joint program of the Office of Naval Research and the U. S. Atomic Energy Commission.

[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).