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Effect of an Electric Dipole Moment of the Proton on the Energy Levels of the Hydrogen Atom*

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The perturbations of the energy levels of the hydrogen atom by a possible electric dipole moment of the proton, d, have been obtained. The inhomogeneous equation for the first-order perturbation of the wave functions was solved analytically. The shifts of the energy levels are of the second order in d. In particular, there results a decrease of the Lamb shift between the $2S_{\frac{1}{2}}$ and $2P_{\frac{1}{2}}$ levels. By equating this decrease to the maximum allowed by the approximate agreement between the experimental and theoretical values of the Lamb shift, it is concluded that the electric dipole moment of the proton, d, must be less than 1.3×10^{-13} cm times the charge of the electron. Calculations have also been carried out for the shifts of the energy levels of deuterium produced by a possible electric dipole moment of the deuteron.

I. INTRODUCTION

SINCE the discovery of nonconservation of parity in the weak interactions,[1] it has become of interest to investigate the possible existence of an electric dipole moment of the elementary particles. It has been shown that a nonvanishing electric dipole moment for any elementary particle would imply that time-reversal invariance is violated,[2] unless there is an additional degeneracy of the particle states, such as the degeneracy involving magnetic pole conjugation considered by Ramsey.[3] Several years ago, Smith, Purcell, and Ramsey[4] obtained an upper limit for the dipole moment of the neutron d_n by a magnetic resonance method: $d_n < 5\times 10^{-20}$ cm$\times e$, where e is the charge of the electron. Very recently, Berley, Garwin, Gidal, and Lederman[5] have shown that the electric dipole moment of the muon must be less than $\sim 2\times 10^{-15}$ cm$\times e$, by a deflection method which utilizes the longitudinal polarization of muons from pion decay. Feinberg[6] and Salpeter[7] have obtained an upper limit for the dipole moment of the electron d_e from a comparison of the resultant shift of the hydrogen energy levels with the possible experimental and theoretical uncertainties of the Lamb shift.[8] The resulting upper limit for d_e is $d_e < 1\times 10^{-13}$ cm$\times e$.

In the present paper, we have determined the perturbation of the hydrogen energy levels by a possible electric dipole moment of the proton, d. It is found that the presence of a proton dipole moment d would decrease the Lamb shift between the $2S_{\frac{1}{2}}$ and $2P_{\frac{1}{2}}$ levels, in the same manner as a dipole moment of the electron.[6,7] By requiring that the decrease of the calculated Lamb shift be less than 1 Mc/sec, one finds that the proton dipole moment d must be less than 1.3×10^{-13} cm$\times e$.

In Sec. II, we obtain the shifts of the hyperfine levels of the hydrogen atom in the $1S_{\frac{1}{2}}$, $2S_{\frac{1}{2}}$, $2P_{\frac{1}{2}}$, and $2P_{\frac{3}{2}}$ states. The expressions for the energy level shifts are given in terms of certain integrals over the radial parts of the perturbations of the wave functions u_1'. These radial integrals are evaluated in Sec. III, using a method[9] in which the radial perturbations u_1' are obtained analytically,[10] by directly solving the inhomogeneous equation for u_1'. Upon using the values of the radial integrals, one obtains the decrease of the Lamb shift in terms of d, and hence an upper limit on d.

Besides the calculations for hydrogen, we also give in Sec. II the expressions for the level shifts of the deuterium atom produced by a possible dipole moment of the deuteron. In view of the very small upper limit on the neutron dipole moment[4] d_n, a dipole moment of the deuteron d_d would represent essentially the effect of a proton dipole moment d.

II. CALCULATION OF THE ENERGY LEVEL SHIFTS

The energy level shifts due to an electric dipole moment of the proton d are of the second order in d. The required second-order perturbation of the energy E_2 is obtained from the first-order perturbation of the wave function Ψ_1. The basic equation for Ψ_1 is given by

$$(H_0-E_0)\Psi_1=-H_1\Psi_0,\tag{1}$$

where H_0, E_0, and Ψ_0 are the unperturbed Hamiltonian, energy, and wave function, respectively; H_1 is the perturbation due to the dipole moment:

$$H_1=-(A/r^2)\boldsymbol{\sigma}\cdot\hat{r},\tag{2}$$

where H_1 is in Rydberg units; r is the distance from the nucleus in units of the Bohr radius a_{H}; A is a constant

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given by

$$A=2d/(ea_{\mathrm{H}})\,; \tag{3}$$

$\boldsymbol{\sigma}$ is twice the spin vector of the proton (in units $\hbar$); and $\hat{r}$ is a unit vector in the direction of $\mathbf{r}$.

After Ψ_1 is determined from Eq. (1), the level shift E_2 is obtained from the equation

$$E_2=\int \Psi_0{}^* H_1 \Psi_1 dV, \tag{4}$$

where the integration extends over the volume of the atom, and the asterisk (for $\Psi_0{}^*$) denotes the complex conjugate.

In order to solve Eq. (1), we note that this equation involves the following radial equation:

$$\left[-\frac{d^2}{dr^2}+\frac{l(l+1)}{r^2}-\frac{2Z}{r}+\frac{Z^2}{n^2}\right]u_1'=(A/r^2)u_0', \tag{5}$$

where u_1' is r times the radial part of the perturbation Ψ_1, u_0' is r times the radial part of the unperturbed function Ψ_0, and the operator in the square bracket on the left-hand side represents (H_0-E_0) in Rydberg units, provided that r is in units a_{H}. In Eq. (5), l is the azimuthal quantum number of the perturbation, n is the principal quantum number of the unperturbed state ($E_0=-Z^2/n^2$ ry), and we have considered the case of arbitrary Z for the sake of generality. The function u_0' on the right-hand side of (5) is normalized as follows:

$$\int_0^\infty u_0'^2 dr=1. \tag{6}$$

We will consider in particular the $1S_{\frac{1}{2}}$, $2S_{\frac{1}{2}}$, $2P_{\frac{1}{2}}$, and $2P_{\frac{3}{2}}$ states of the hydrogen atom. As a result of the perturbation H_1, the ns states are excited into p states, and the np states are excited into both s and d states. Following a method used previously,[9] the radial perturbations u_1' for $ns\rightarrow p$, $np\rightarrow s$, and $np\rightarrow d$ will be obtained by directly solving Eq. (5), without any expansion in terms of the excited states of the Hamiltonian H_0. Since the unperturbed functions u_0' are hydrogenic, it turns out that u_1' can be obtained analytically.[10] The solution of Eq. (5) will be discussed in Sec. III. As will be shown below, the various energy shifts involve only the following radial integrals:

$$E_2'=\int_0^\infty u_0' u_1' H_1' dr, \tag{7}$$

where $H_1'=-(A/r^2)$ is the radial part of H_1. The values of E_2' for $1s\rightarrow p$, $2s\rightarrow p$, $2p\rightarrow s$, and $2p\rightarrow d$ (as obtained in Sec. III) are as follows:

$$E_2'(1s\rightarrow p)=-Z^2A^2, \tag{8}$$

$$E_2'(2s\rightarrow p)=-(1/8)Z^2A^2, \tag{9}$$

$$E_2'(2p\rightarrow s)=+(1/24)Z^2A^2, \tag{10}$$

$$E_2'(2p\rightarrow d)=-(1/48)Z^2A^2=-\tfrac{1}{2}E_2'(2p\rightarrow s), \tag{11}$$

where all of the E_2' are in Rydberg units.

Referring to Eqs. (1) and (4), we wish to determine the expressions for E_2 in terms of the radial integrals E_2' for the various hyperfine levels. The $1S_{\frac{1}{2}}$ and $2S_{\frac{1}{2}}$ atomic levels are each split into two levels, $F=0$ and $F=1$, by the hyperfine structure interaction. Here F is the total angular momentum of the atom. We have: $\mathbf{F}=\mathbf{I}+\mathbf{J}$, where $\mathbf{I}$ is the spin of the proton ($\mathbf{I}=\frac{1}{2}\boldsymbol{\sigma}$), and $\mathbf{J}$ is the angular momentum of the electron.

We first take as an example the $2S_{\frac{1}{2}}$ state with $F=1$, $M_F=1$. Here M_F is the magnetic quantum number pertaining to F, i.e., the projection of F along an arbitrary z axis. In all cases, the final result for E_2 must be independent of M_F. This property can be used as a check on the results, by repeating the calculation for a different M_F state. The unperturbed wave function Ψ_0 for $F=1$, $M_F=1$ is given by

$$\Psi_0=\psi_{2s}\chi_{\frac{1}{2}}\eta_{\frac{1}{2}}=2^{-\frac{1}{2}}R_{2s}\chi_{\frac{1}{2}}\eta_{\frac{1}{2}}, \tag{12}$$

where ψ_{2s} is the $2s$ wave function normalized according to

$$\int_0^\infty\int_0^\pi \psi_{2s}{}^2 r^2 dr \sin\theta d\theta=1, \tag{13}$$

where θ is the angle between the radius vector $\mathbf{r}$ and the z axis. Thus $\psi_{2s}=2^{-\frac{1}{2}}R_{2s}$, where $R_{2s}=u_0'/r$, with u_0' normalized according to Eq. (6). In Eq. (12), $\chi_{\frac{1}{2}}$ is the proton spin function with magnetic quantum number $m=\frac{1}{2}$, and $\eta_{\frac{1}{2}}$ is the electron spin function with $m=\frac{1}{2}$.

H_1 can be written as follows:

$$H_1=H_1'[\tfrac{1}{2}(\sigma_x+i\sigma_y)\sin\theta e^{-i\varphi}+\tfrac{1}{2}(\sigma_x-i\sigma_y)\sin\theta e^{i\varphi}+\sigma_z\cos\theta], \tag{14}$$

where φ is the azimuthal angle, and $H_1'=-(A/r^2)$, as defined above [Eq. (7)]. The operator $(\boldsymbol{\sigma}\cdot\hat{r})$ does not act on $\eta_{\frac{1}{2}}$, and we have $\sigma_z\chi_{\frac{1}{2}}=\chi_{\frac{1}{2}}$, $(\sigma_x-i\sigma_y)\chi_{\frac{1}{2}}=2\chi_{-\frac{1}{2}}$, and $(\sigma_x+i\sigma_y)\chi_{\frac{1}{2}}=0$. One thus obtains

$$H_1\Psi_0=H_1'\eta_{\frac{1}{2}}\psi_{2s}(\chi_{\frac{1}{2}}\cos\theta+\chi_{-\frac{1}{2}}\sin\theta e^{i\varphi}). \tag{15}$$

The resulting perturbation Ψ_1 is given by

$$\Psi_1 r=2^{-\frac{1}{2}}u_1'\eta_{\frac{1}{2}}(\chi_{\frac{1}{2}}\cos\theta+\chi_{-\frac{1}{2}}\sin\theta e^{i\varphi}), \tag{16}$$

where u_1' satisfies the following equation [see Eq. (5)]:

$$\left(-\frac{d^2}{dr^2}+\frac{2}{r^2}-\frac{2Z}{r}+\frac{Z^2}{4}\right)u_1'=-H_1'u_0'. \tag{17}$$

From Eq. (16), one obtains

$$H_1\Psi_1 r=2^{-\frac{1}{2}}H_1'u_1'\eta_{\frac{1}{2}}\chi_{\frac{1}{2}}. \tag{18}$$

The resulting energy shift E_2 is given by

$$E_2=\int_0^\infty\int_0^\pi (\Psi_0^*r)H_1\Psi_1 rdr \times\sin\theta d\theta=\int_0^\infty u_0'H_1'u_1'dr. \quad (19)$$

The radial integral on the right-hand side is just $E_2'(2s\rightarrow p)$, as given by Eq. (9), so that

$$E_2(F=1)=-(1/8)Z^2A^2\text{ ry}. \quad (20)$$

For the $2S_{\frac{1}{2}}$ state $F=0$, the unperturbed wave function Ψ_0 is given by

$$\Psi_0 r=\tfrac{1}{2}u_0'(\chi_{\frac{1}{2}}\eta_{-\frac{1}{2}}-\chi_{-\frac{1}{2}}\eta_{\frac{1}{2}}), \quad (21)$$

where χ_m and η_m are the spin wave functions for the proton and the electron, respectively. By using the same procedure as for the state $F=1$ discussed above, one finds

$$\Psi_1 r=\tfrac{1}{2}u_1'[\eta_{\frac{1}{2}}(-\chi_{\frac{1}{2}}\sin\theta e^{-i\varphi}+\chi_{-\frac{1}{2}}\cos\theta) +\eta_{-\frac{1}{2}}(\chi_{\frac{1}{2}}\cos\theta+\chi_{-\frac{1}{2}}\sin\theta e^{i\varphi})], \quad (22)$$

whence

$$H_1\Psi_1 r=\tfrac{1}{2}H_1'u_1'(\eta_{-\frac{1}{2}}\chi_{\frac{1}{2}}-\eta_{\frac{1}{2}}\chi_{-\frac{1}{2}}), \quad (23)$$

$$E_2=\int_0^\infty\int_0^\pi (\Psi_0^*r)H_1\Psi_1 rdr\sin\theta d\theta =E_2'(2s\rightarrow p)=-(1/8)Z^2A^2\text{ ry}. \quad (24)$$

Thus $E_2(F=1)$ and $E_2(F=0)$ are equal for the $2S_{\frac{1}{2}}$ state. Both levels are shifted downward by the same amount, while the hyperfine splitting is unaffected. The same is, of course, true for any S state, since we have not used the properties of the radial wave functions except to evaluate $E_2'(2s\rightarrow p)$. Thus for the $1S_{\frac{1}{2}}$ state, we have $E_2'(1s\rightarrow p)=-Z^2A^2$; both the $F=1$ and $F=0$ levels are shifted by this amount, and the hfs splitting $\Delta\nu(1s)$ is not affected. As will be discussed in Sec. III, the radial integrals for a given type of angular excitation ($nl\rightarrow l'$) are proportional to $1/n^3$. The shift for the $3S_{\frac{1}{2}}$ state is $-(1/27)Z^2A^2$ ry.

The $2P_{\frac{1}{2}}$ state consists of two levels, $F=1$ and $F=0$. The energy shift for $F=1$ will be determined by means of the magnetic substate $M_F=1$. The unperturbed wave function Ψ_0 for this state is given by

$$\Psi_0=-(1/3)^{\frac{1}{2}}\psi_{2p,0}\eta_{\frac{1}{2}}\chi_{\frac{1}{2}}+(2/3)^{\frac{1}{2}}\psi_{2p,1}\eta_{-\frac{1}{2}}\chi_{\frac{1}{2}}, \quad (25)$$

where $\psi_{2p,m}$ is the normalized $2p$ wave function pertaining to magnetic quantum number m. $\psi_{2p,m}$ is normalized in the same manner as ψ_{2s} [Eq. (13)]:

$$\int_0^\infty\int_0^\pi |\psi_{2p,m}|^2r^2dr\sin\theta d\theta=1. \quad (26)$$

Thus we have

$$\psi_{2p,1}=-(3^{\frac{1}{2}}/2)(u_0'/r)\sin\theta e^{i\varphi}, \quad (27)$$

$$\psi_{2p,0}=(3/2)^{\frac{1}{2}}(u_0'/r)\cos\theta, \quad (28)$$

where u_0' is r times the radial wave function, normalized according to Eq. (6):

$$u_0'=(Z^{\frac{5}{2}}/24^{\frac{1}{2}})r^2\exp(-Zr/2). \quad (29)$$

The $2p$ electron will be excited into both s and d states. In order to obtain these perturbations, it is convenient to consider separately the $\eta_{\frac{1}{2}}$ and $\eta_{-\frac{1}{2}}$ terms of Ψ_0 [Eq. (25)], since the operator $\boldsymbol{\sigma}\cdot\hat{r}$ has no matrix elements connecting these terms, which will be denoted by Ψ_0^+ and Ψ_0^-, respectively. Taking first Ψ_0^+, we have

$$\begin{aligned}H_1\Psi_0^+r&=-2^{-\frac{1}{2}}H_1'\eta_{\frac{1}{2}}u_0'(\chi_{\frac{1}{2}}\cos^2\theta+\chi_{-\frac{1}{2}}\sin\theta\cos\theta e^{i\varphi})\\&=-2^{-\frac{1}{2}}H_1'\eta_{\frac{1}{2}}u_0'\{\tfrac{1}{3}\chi_{\frac{1}{2}}+[\chi_{\frac{1}{2}}(\cos^2\theta-\tfrac{1}{3})\\&\qquad+\chi_{-\frac{1}{2}}\sin\theta\cos\theta e^{i\varphi}]\},\end{aligned} \quad (30)$$

where, in the last expression, the term $\frac{1}{3}\chi_{\frac{1}{2}}$ gives the $2p\rightarrow s$ perturbation, while the square bracket leads to the $2p\rightarrow d$ perturbation.

The $2p\rightarrow s$ perturbation $(\Psi_1^+)_s$ is given by

$$(\Psi_1^+)_s r=-(18)^{-\frac{1}{2}}\eta_{\frac{1}{2}}\chi_{\frac{1}{2}}(u_1')_s, \quad (31)$$

where the radial function $(u_1')_s$ satisfies the following equation:

$$\left(-\frac{d^2}{dr^2}-\frac{2Z}{r}+\frac{Z^2}{4}\right)(u_1')_s=-H_1'u_0'. \quad (32)$$

From Eq. (31) one obtains

$$H_1(\Psi_1^+)_s r=-(18)^{-\frac{1}{2}}H_1'(u_1')_s \times\eta_{\frac{1}{2}}(\chi_{\frac{1}{2}}\cos\theta+\chi_{-\frac{1}{2}}\sin\theta e^{i\varphi}). \quad (33)$$

The resulting energy shift due to the $2p\rightarrow s$ perturbation of Ψ_0^+ is given by

$$\begin{aligned}(E_2^+)_s&=\int_0^\infty\int_0^\pi (\Psi_0^+)^*rH_1(\Psi_1^+)_s rdr\sin\theta d\theta\\&=(1/6)E_2'(2p\rightarrow s)\int_0^\pi\cos^2\theta\sin\theta d\theta\\&=(1/9)E_2'(2p\rightarrow s).\end{aligned} \quad (34)$$

The $2p\rightarrow d$ perturbation due to Ψ_0^+ is given by

$$(\Psi_1^+)_d r=-2^{-\frac{1}{2}}(u_1')_d\eta_{\frac{1}{2}}[\chi_{\frac{1}{2}}(\cos^2\theta-\tfrac{1}{3}) +\chi_{-\frac{1}{2}}\sin\theta\cos\theta e^{i\varphi}], \quad (35)$$

where the radial function $(u_1')_d$ is determined by

$$\left(-\frac{d^2}{dr^2}+\frac{6}{r^2}-\frac{2Z}{r}+\frac{Z^2}{4}\right)(u_1')_d=-H_1'u_0', \quad (36)$$

with u_0' given by Eq. (29). From Eq. (35), one obtains

$$H_1(\Psi_1{}^+)_d r = -2^{-\frac{1}{2}} H_1'(u_1')_d \times \eta_{\frac{1}{2}} \left(\tfrac{2}{3}\chi_{\frac{1}{2}} \cos\theta - \tfrac{1}{3}\chi_{-\frac{1}{2}} \sin\theta e^{i\varphi}\right), \tag{37}$$

so that the energy shift is found to be

$$(E_2{}^+)_d = \int_0^\infty \int_0^\pi (\Psi_0{}^+)^* r H_1 (\Psi_1{}^+)_d r dr \times \sin\theta d\theta = (2/9) E_2'(2p \rightarrow d). \tag{38}$$

We shall now consider the $\eta_{-\frac{1}{2}}$ term $\Psi_0{}^-$ of Eq. (25). One obtains

$$H_1 \Psi_0{}^- r = -2^{-\frac{1}{2}} H_1' \eta_{-\frac{1}{2}} u_0' \times \left[\chi_{\frac{1}{2}} \sin\theta \cos\theta e^{i\varphi} + \chi_{-\frac{1}{2}} \sin^2\theta e^{2i\varphi}\right]. \tag{39}$$

The angular functions in the square bracket of the right-hand side are pure d wave functions (with $m=1$ and $m=2$). Thus there is no $2p \rightarrow s$ excitation of $\Psi_0{}^-$. On the other hand, the $2p \rightarrow d$ perturbation is given by

$$(\Psi_1{}^-)_d r = -2^{-\frac{1}{2}} (u_1')_d \eta_{-\frac{1}{2}} \times \left(\chi_{\frac{1}{2}} \sin\theta \cos\theta e^{i\varphi} + \chi_{-\frac{1}{2}} \sin^2\theta e^{2i\varphi}\right), \tag{40}$$

where $(u_1')_d$ is determined by Eq. (36). From Eq. (40), one obtains

$$H_1(\Psi_1{}^-)_d r = -2^{-\frac{1}{2}} H_1'(u_1')_d \eta_{-\frac{1}{2}} \chi_{\frac{1}{2}} \sin\theta e^{i\varphi}. \tag{41}$$

Finally, the $2p \rightarrow d$ energy shift is given by

$$(E_2{}^-)_d = \int_0^\infty \int_0^\pi (\Psi_0{}^-)^* r H_1 (\Psi_1{}^-)_d r dr \sin\theta d\theta = \tfrac{2}{3} E_2'(2p \rightarrow d). \tag{42}$$

From Eqs. (34), (38), and (42), one finds for the total energy shift of the $F=1$ level of $2P_{\frac{1}{2}}$:

$$\begin{aligned} E_2(F=1) &= (E_2{}^+)_s + (E_2{}^+)_d + (E_2{}^-)_d \\ &= (1/9) E_2'(2p \rightarrow s) + (8/9) E_2'(2p \rightarrow d) \\ &= -(1/72) Z^2 A^2 \text{ ry}. \end{aligned} \tag{43}$$

For the $F=0(M_F=0)$ state, Ψ_0 is given by

$$\Psi_0 = \eta_{\frac{1}{2}} \left[3^{-\frac{1}{2}} \psi_{2p,-1} \chi_{\frac{1}{2}} - 6^{-\frac{1}{2}} \psi_{2p,0} \chi_{-\frac{1}{2}}\right] + \eta_{-\frac{1}{2}} \left[-6^{-\frac{1}{2}} \psi_{2p,0} \chi_{\frac{1}{2}} + 3^{-\frac{1}{2}} \psi_{2p,1} \chi_{-\frac{1}{2}}\right]. \tag{44}$$

By proceeding in the same manner as for $F=1$, $M_F=1$, one obtains for the energy shift

$$E_2(F=0) = E_2'(2p \rightarrow s) = +(1/24) Z^2 A^2 \text{ ry}. \tag{45}$$

There is no $2p \rightarrow d$ excitation for the $F=0$ state. This result can be explained on general grounds, by noting that the operator $\boldsymbol{\sigma} \cdot \hat{r}$ commutes with $\mathbf{F}^2$, and hence the perturbation Ψ_1 has the same total angular momentum F as the unperturbed function, namely $F=0$ in the present case. For a $2p \rightarrow d$ perturbation, the electronic part of Ψ_1 would represent a ${}^2D_{\frac{3}{2}}$ or ${}^2D_{\frac{5}{2}}$ state ($J=3/2$ or $5/2$) which can only give rise to $F=1$, 2, and 3, but not $F=0$.

From Eqs. (43) and (45), it is seen that the $F=1$ level (which lies above $F=0$) is lowered, while the $F=0$ level is raised, and as a result the $2P_{\frac{1}{2}}$ hyperfine splitting $\Delta\nu(2P_{\frac{1}{2}})$ is decreased by an amount $(1/18)Z^2A^2$ ry.

The centroid (weighted average) of the $2P_{\frac{1}{2}}$ levels is not changed by the dipole perturbation, since one finds

$$\textstyle\sum_F (2F+1) E_2(F) = 3E_2(F=1) + E_2(F=0) = 0. \tag{46}$$

On the other hand, as discussed above, the $2S_{\frac{1}{2}}$ levels are shifted downward by $\frac{1}{8}Z^2A^2$ ry. Thus the Lamb shift for hydrogen would be decreased by the presence of an electric dipole moment of the proton. At present, the agreement between the theoretical expression for the Lamb shift[11] and the observed value is to within $\sim\frac{1}{3}$ Mc/sec. If one assumes that any possible discrepancy due to a proton dipole moment d must be less than 1 Mc/sec, one obtains an upper limit for d as follows:

$$\tfrac{1}{8}A^2 < 6.62\times10^{-27}\times10^{6}/(2.18\times10^{-11}) = 3.04\times10^{-10}, \tag{47}$$

so that

$$A < 4.93\times10^{-5},$$

$$d < e(\tfrac{1}{2})(0.529\times10^{-8})(4.93\times10^{-5}) = 1.30\times10^{-13}\text{ cm}\times e. \tag{48}$$

A convenient formula for the upper limit on d from the Lamb shift or the $2P$ hyperfine structure is given by

$$d < 0.46\times10^{-13}\text{ cm}\times e \times (\delta\nu/a)^{\frac{1}{2}}, \tag{49}$$

where $\delta\nu$ is the upper limit on the experimental and theoretical uncertainties of the frequency in Mc/sec, and a is the coefficient of A^2 in the theoretical expression ($a=\frac{1}{8}$ for the Lamb shift; 1/18 for the $2P_{\frac{1}{2}}$ or $2P_{\frac{3}{2}}$ hfs in H).

We will now determine the energy shifts of the ${}^2P_{\frac{3}{2}}$, $F=2$ and $F=1$ hyperfine levels. For the $F=2$ level, E_2 will be obtained by considering the $M_F=2$ state. Ψ_0 is given by

$$\Psi_0 = \Psi_{2p,1} \chi_{\frac{1}{2}} \eta_{\frac{1}{2}}. \tag{50}$$

One obtains

$$H_1 \Psi_0 r = -(3^{\frac{1}{2}}/2) H_1' \eta_{\frac{1}{2}} u_0' \times \left[\chi_{\frac{1}{2}} \sin\theta \cos\theta e^{i\varphi} + \chi_{-\frac{1}{2}} \sin^2\theta e^{2i\varphi}\right], \tag{51}$$

where u_0' is given by Eq. (29). The angular functions in the square bracket are pure d wave functions, showing that there is no $2p \rightarrow s$ excitation for the $F=2$ state. As discussed above for $E_2(F=0,\ 2P_{\frac{1}{2}})$, this result follows from the fact that for a $2p \rightarrow s$ perturbation, the electronic part of Ψ_1 would represent a ${}^2S_{\frac{1}{2}}$ state ($J=1/2$) which cannot give rise to an $F=2$ state.

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The $2p\rightarrow d$ perturbation $(\Psi_1)_d$ is given by

$$(\Psi_1)_d r = -(3^{\frac{1}{2}}/2)(u_1')_d \times\eta_{\frac{1}{2}}(\chi_{\frac{1}{2}}\sin\theta\cos\theta e^{i\varphi}+\chi_{-\frac{1}{2}}\sin^2\theta e^{2i\varphi}), \quad (52)$$

from which one obtains

$$H_1(\Psi_1)_d r = -(3^{\frac{1}{2}}/2)H_1'(u_1')_d\eta_{\frac{1}{2}}\chi_{\frac{1}{2}}\sin\theta e^{i\varphi}. \quad (53)$$

The energy shift is found to be

$$E_2(F=2)=E_2'(2p\rightarrow d)=-(1/48)Z^2A^2\text{ ry}. \quad (54)$$

For the $F=1$ state with $M_F=1$, Ψ_0 is given by

$$\Psi_0=\eta_{\frac{1}{2}}[(3/4)^{\frac{1}{2}}\psi_{2p,1}\chi_{-\frac{1}{2}}-6^{-\frac{1}{2}}\psi_{2p,0}\chi_{\frac{1}{2}}] -(12)^{-\frac{1}{2}}\eta_{-\frac{1}{2}}\psi_{2p,1}\chi_{\frac{1}{2}}. \quad (55)$$

By means of (55), one obtains for the energy shift

$$E_2(F=1)=(8/9)E_2'(2p\rightarrow s) +\tfrac{1}{9}E_2'(2p\rightarrow d)=(5/144)Z^2A^2\text{ ry}. \quad (56)$$

From (54) and (56), one finds that the hyperfine splitting $\Delta\nu(2P_{\frac{3}{2}})$ is decreased by an amount

$$E_2(F=1)-E_2(F=2)=(1/18)Z^2A^2\text{ ry}. \quad (57)$$

This change of $\Delta\nu(2P_{\frac{3}{2}})$ is the same as for the $2P_{\frac{1}{2}}$ state. Also in similarity to $2P_{\frac{1}{2}}$, the centroid of the $2P_{\frac{3}{2}}$ levels is not affected by the perturbation. We have

$$\textstyle\sum_F(2F+1)E_2(F)=5E_2(F=2)+3E_2(F=1)=0. \quad (58)$$

In view of these results for the weighted average of the $2P_{\frac{1}{2}}$ and $2P_{\frac{3}{2}}$ levels, a dipole moment of the proton would have no effect on the fine structure in the $2P$ states, i.e., on the $2P_{\frac{1}{2}}$-$2P_{\frac{3}{2}}$ level separation.

We have also calculated the effect of an electric dipole moment of the deuteron on the atomic energy levels of deuterium. Since the dipole moment of the neutron has been shown to be very small ($d_n<5\times10^{-20}$ cm$\times e$),[4] we expect that a possible dipole moment of the deuteron d_d represents essentially the effect of a dipole moment of the proton d (unless $d_d\lesssim10^{-19}$ cm$\times e$). However, the value of d_d need not be identical with d, because of possible effects of the motion of the proton inside the deuteron. In the following, it will be assumed that the dipole moment is given by $d_d\mathbf{I}$, where $\mathbf{I}$ is the spin of the deuteron.

For deuterium, the radial integrals $E_2'(nl\rightarrow l')$ are the same as for hydrogen, except for the replacement of A by A_d, where $A_d\equiv2d_d/(ea_{\text{H}})$. Accordingly the radial integrals will be denoted by $E_{2D}'(nl\rightarrow l')$. The coefficients of the integrals are, of course, different from those for hydrogen, because of the deuteron spin $I=1$. The results are as follows:

$$1S_{\frac{1}{2}}:\quad E_2(F=\tfrac{1}{2})=E_2(F=\tfrac{3}{2}) =\tfrac{2}{3}E_{2D}'(1s\rightarrow p)=-\tfrac{2}{3}A_d^2, \quad (59)$$

$$2S_{\frac{1}{2}}:\quad E_2(F=\tfrac{1}{2})=E_2(F=\tfrac{3}{2}) =\tfrac{2}{3}E_{2D}'(2s\rightarrow p)=-\tfrac{1}{12}A_d^2, \quad (60)$$

$$2P_{\frac{1}{2}}:\quad E_2(F=\tfrac{3}{2})=\tfrac{1}{9}E_{2D}'(2p\rightarrow s) +(5/9)E_{2D}'(2p\rightarrow d)=-(1/144)A_d^2, \quad (61)$$

$$2P_{\frac{1}{2}}:\quad E_2(F=\tfrac{1}{2})=(4/9)E_{2D}'(2p\rightarrow s) +(2/9)E_{2D}'(2p\rightarrow d)=+(1/72)A_d^2, \quad (62)$$

$$2P_{\frac{3}{2}}:\quad E_2(F=\tfrac{5}{2})=\tfrac{3}{5}E_{2D}'(2p\rightarrow d)=-(1/80)A_d^2, \quad (63)$$

$$2P_{\frac{3}{2}}:\quad E_2(F=\tfrac{3}{2})=(5/9)E_{2D}'(2p\rightarrow s) +(17/45)E_{2D}'(2p\rightarrow d)=+(11/720)A_d^2, \quad (64)$$

$$2P_{\frac{3}{2}}:\quad E_2(F=\tfrac{1}{2})=(2/9)E_{2D}'(2p\rightarrow s) +\tfrac{1}{9}E_{2D}'(2p\rightarrow d)=+(1/144)A_d^2, \quad (65)$$

where all of the values are in Rydberg units.

As for hydrogen, there is no effect on the $S_{\frac{1}{2}}$ state hyperfine splittings. The centroids of the $2P_{\frac{1}{2}}$ and $2P_{\frac{3}{2}}$ levels are again unchanged by the perturbation, so that there is also no effect on the fine structure. The decrease of the Lamb shift is $(1/12)A_d^2$ ry. The hyperfine splittings for $2P_{\frac{1}{2}}$ and $2P_{\frac{3}{2}}$ are both affected by the perturbation, similarly to the result for hydrogen. For $2P_{\frac{1}{2}}$, the splitting $E(F=3/2)-E(F=\frac{1}{2})$ is decreased by $(1/48)A_d^2$ ry.

It is of interest that the present perturbation method can also be applied to obtain the energy shifts of the hydrogen atom due to a possible electric dipole moment of the electron d_e. These level shifts have been recently derived by Feinberg[6] and by Salpeter,[7] and have been used to set an upper limit of 10^{-13} cm$\times e$ on the electron dipole moment.

The perturbation of the Hamiltonian is given by

$$H_{1e}=-(A_e/r^2)\boldsymbol{\sigma}_e\cdot\hat{r}, \quad (66)$$

where $A_e=2Zd_e/(ea_{\text{H}})$, $\boldsymbol{\sigma}_e$ is twice the spin vector of the electron (in units $\hbar$). Obviously H_{1e} has the same form as H_1. The factor $-(A_e/r^2)$ will be denoted by H_{1e}'.

For the $2S_{\frac{1}{2}}$ state with $M_J=\frac{1}{2}$, the unperturbed function Ψ_0 is given by

$$\Psi_0=\psi_{2s}\eta_{\frac{1}{2}}. \quad (67)$$

We have

$$H_{1e}\Psi_0 r=2^{-\frac{1}{2}}H_{1e}'u_0'(\eta_{\frac{1}{2}}\cos\theta+\eta_{-\frac{1}{2}}\sin\theta e^{i\varphi}), \quad (68)$$

where u_0' is r times the normalized radial $2s$ function. From (68), one obtains the following perturbation Ψ_1:

$$\Psi_1 r=2^{-\frac{1}{2}}u_{1e}'(\eta_{\frac{1}{2}}\cos\theta+\eta_{-\frac{1}{2}}\sin\theta e^{i\varphi}), \quad (69)$$

where u_{1e}' is determined by the equation obtained from (17) by replacing H_1' by H_{1e}'. Thus $u_{1e}'=u_1'(A_e/A)=u_1'(Zd_e/d)$, where u_1' is the solution of (17). Here and in the following, we label the radial perturbations pertaining to the electron dipole moment by the additional subscript e. The corresponding radial integrals will be denoted by $E_{2e}'(nl\rightarrow l')$.

Equation (69) gives

$$H_{1e}\Psi_1 r=2^{-\frac{1}{2}}H_{1e}u_{1e}'\eta_{\frac{1}{2}}, \quad (70)$$

whence

$$E_2(2S_{\frac{1}{2}})=\int_0^\infty\int_0^\pi (\Psi_0{}^*r)H_{1e}\Psi_1 r dr \sin\theta d\theta$$

$$=E_{2e}'(2s\rightarrow p)=-(1/8)Z^2A_e{}^2 \text{ ry}. \quad (71)$$

For the $2P_{\frac{1}{2}}$ state with $M_J=\frac{1}{2}$, Ψ_0 is given by

$$\Psi_0=-(1/3)^{\frac{1}{2}}\psi_{2p,0}\eta_{\frac{1}{2}}+(2/3)^{\frac{1}{2}}\psi_{2p,1}\eta_{-\frac{1}{2}}. \quad (72)$$

We have

$$H_{1e}\Psi_0 r=-2^{-\frac{1}{2}}H_{1e}'u_0'\eta_{\frac{1}{2}}, \quad (73)$$

where u_0' is given by Eq. (29). One thus obtains for the perturbation Ψ_1:

$$\Psi_1 r=-2^{-\frac{1}{2}}(u_{1e}')_s\eta_{\frac{1}{2}}, \quad (74)$$

where $(u_{1e}')_s\equiv(Zd_e/d)(u_1')_s$. Equation (74) gives

$$H_{1e}\Psi_1 r=-2^{-\frac{1}{2}}H_{1e}'(u_{1e}')_s(\eta_{\frac{1}{2}}\cos\theta+\eta_{-\frac{1}{2}}\sin\theta e^{i\varphi}). \quad (75)$$

The resulting energy shift is given by

$$E_2(2P_{\frac{1}{2}})=E_{2e}'(2p\rightarrow s)=+(1/24)Z^2A_e{}^2 \text{ ry}. \quad (76)$$

For the $2P_{\frac{3}{2}}$ level with $M_J=3/2$, Ψ_0 is given by

$$\Psi_0=\psi_{2p,1}\eta_{\frac{1}{2}}, \quad (77)$$

whence

$$H_{1e}\Psi_0 r=-(3^{\frac{1}{2}}/2)H_{1e}'u_0' \times(\eta_{\frac{1}{2}}\sin\theta\cos\theta e^{i\varphi}+\eta_{-\frac{1}{2}}\sin^2\theta e^{i\varphi}). \quad (78)$$

The resulting perturbation Ψ_1 is given by

$$\Psi_1 r=-(3^{\frac{1}{2}}/2)(u_{1e}')_d \times(\eta_{\frac{1}{2}}\sin\theta\cos\theta e^{i\varphi}+\eta_{-\frac{1}{2}}\sin^2\theta e^{2i\varphi}), \quad (79)$$

where $(u_{1e}')_d\equiv(Zd_e/d)(u_1')_d$. We have

$$H_{1e}\Psi_1 r=-(3^{\frac{1}{2}}/2)H_{1e}'(u_{1e}')_d\eta_{\frac{1}{2}}\sin\theta e^{i\varphi}, \quad (80)$$

so that

$$E_2(2P_{\frac{3}{2}})=E_{2e}'(2p\rightarrow d)=-(1/48)Z^2A_e{}^2 \text{ ry}. \quad (81)$$

The results (71), (76), and (81) are in agreement with those obtained by Feinberg[6] and by Salpeter.[7] For comparison with Feinberg's expressions, we note that his k corresponds to A_e [$k=2d_eZ/(ea_H)$]. The reduction of the Lamb shift due to an electron dipole moment d_e is $(1/6)Z^2A_e{}^2$ ry, as compared to $(1/8)Z^2A^2$ ry for a proton dipole moment d. Thus the upper limit for d_e obtained by Feinberg[6] is slightly smaller [by a factor $(4/3)^{\frac{1}{2}}=1.15$] than the limit for d of Eq. (48).

III. THE RADIAL PARTS OF THE PERTURBATION u_1'

In this section, the radial parts of the perturbation due to the proton dipole moment will be obtained. The $1s\rightarrow p$ perturbation $u_1'(1s\rightarrow p)$ will be considered first. As discussed in Sec. II [Eq. (5)], $u_1'(1s\rightarrow p)$ is determined by the equation

$$\left(-\frac{d}{dr^2}+\frac{2}{r^2}-\frac{2Z}{r}+Z^2\right)u_1'(1s\rightarrow p)=(A/r^2)u_0'(1s), \quad (82)$$

where the unperturbed function $u_0'(1s)$ is given by

$$u_0'(1s)=2Z^{\frac{3}{2}}re^{-Zr}. \quad (83)$$

It can be easily verified that the solution of (82) is

$$u_1'(1s\rightarrow p)=Z^{\frac{3}{2}}Are^{-Zr}, \quad (84)$$

from which one obtains

$$E_2'(1s\rightarrow p)=\int_0^\infty u_0'(1s)(-A/r^2) \times u_1'(1s\rightarrow p)dr=-Z^2A^2. \quad (85)$$

The $2s\rightarrow p$ perturbation $u_1'(2s\rightarrow p)$ is determined by

$$\left(-\frac{d^2}{dr^2}+\frac{2}{r^2}-\frac{2Z}{r}+\frac{Z^2}{4}\right)u_1'(2s\rightarrow p)=(A/r^2)u_0'(2s), \quad (86)$$

where

$$u_0'(2s)=2^{-\frac{1}{2}}Z^{\frac{3}{2}}e^{-Zr/2}(r-\tfrac{1}{2}Zr^2). \quad (87)$$

The solution of Eq. (86) is found to be

$$u_1'(2s\rightarrow p)=8^{-\frac{1}{2}}Z^{\frac{3}{2}}Are^{-Zr/2}+a_{2p}r^2e^{-Zr/2}, \quad (88)$$

where a_{2p} is an arbitrary coefficient. The term in a_{2p} represents an arbitrary admixture of $2p$ function, which arises from the $2s$-$2p$ degeneracy. This term does not contribute to E_2', by virtue of a property of the nonrelativistic hydrogenic radial wave functions, which has been noticed recently by Feinberg[6] and others. This property is as follows:

$$\int_0^\infty u_0'(n,l)(1/r^2)u_0'(n,l')dr=0, \quad (89)$$

where $u_0'(n,l)$ and $u_0'(n,l')$ are any two radial wave functions pertaining to degenerate energy levels with the same n but different l; e.g., $2s$ and $2p$; $3s$, $3p$, and $3d$.

From (87) and (88) one obtains

$$E_2'(2s\rightarrow p)=\int_0^\infty u_0'(2s)(-A/r^2) \times u_1'(2s\rightarrow p)dr=-(1/8)Z^2A^2. \quad (90)$$

For the $2p\rightarrow s$ perturbation, $u_1'(2p\rightarrow s)$, the following equation holds:

$$\left(-\frac{d^2}{dr^2}-\frac{2Z}{r}+\frac{Z^2}{4}\right)u_1'(2p\rightarrow s)=(A/r^2)u_0'(2p), \quad (91)$$

where $u_0'(2p)$ is given by (29). The solution of Eq. (91) is

$$u_1'(2p\rightarrow s)=-\tfrac{1}{2}(24)^{-\frac{1}{2}}Z^{\frac{5}{2}}Ar^2e^{-Zr/2}+a_{2s}e^{-Zr/2}(r-\tfrac{1}{2}Zr^2), \quad (92)$$

where a_{2s} is an arbitrary coefficient. The a_{2s} term represents an arbitrary amount of $2s$ function which, however, does not contribute to E_2', as discussed above [Eq. (89)].

From (29) and (92), one finds

$$E_2'(2p\rightarrow s)=+(1/24)Z^2A^2. \quad (93)$$

The $2p\rightarrow d$ perturbation $u_1'(2p\rightarrow d)$ is determined by

$$\left(-\frac{d^2}{dr^2}+\frac{6}{r^2}-\frac{2Z}{r}+\frac{Z^2}{4}\right)u_1'(2p\rightarrow d)=\left(\frac{A}{r^2}\right)u_0'(2p). \quad (94)$$

The solution of (94) is given by

$$u_1'(2p\rightarrow d)=\tfrac{1}{4}(24)^{-\frac{1}{2}}AZ^{\frac{5}{2}}r^2e^{-Zr/2}, \quad (95)$$

whence

$$E_2'(2p\rightarrow d)=-(1/48)Z^2A^2. \quad (96)$$

Calculations have also been carried out for the $3s\rightarrow p$, $3p\rightarrow s$, and $3p\rightarrow d$ perturbations of the $3s$ and $3p$ states. The results are as follows:

$$E_2'(3s\rightarrow p)=-(1/27)Z^2A^2, \quad (97)$$

$$E_2'(3p\rightarrow s)=+(1/81)Z^2A^2, \quad (98)$$

$$E_2'(3p\rightarrow d)=-(1/162)Z^2A^2. \quad (99)$$

By comparing these values with those obtained above for $n=1$ and $n=2$, one finds that for a given type of angular excitation $nl\rightarrow l'$, $E_2'(nl\rightarrow l')$ decreases as $1/n^3$ with increasing n. Although this property has not been proved for arbitrary n, it seems very probable that it holds true in general.

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Excited State Wave Functions, Excitation Energies, and Oscillator Strengths for Ne$(2p^53s)$*

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Solutions of the Hartree-Fock equations for the ^3P and ^1P terms of neon $(2p^63s)$ have been obtained. Wave functions are tabulated and results of computations of excitation energies and oscillator strengths are presented. The former fall within 10% of experimental values. It is found that enlarging the size of the "invariant core" used to compute the excited state wave functions has only a small effect on the predicted energies. The predicted oscillator strength of the 736 A transition is 0.11, which is in reasonable agreement with available experimental data considering the large uncertainties in the measurements. The computed diamagnetic susceptibility of the ground state is -7.4×10^{-6} cm^{-3} mole, in good agreement with experiment.

1. INTRODUCTION

RECENT interest in investigations of the solid rare gases has made the computation of numerical wave functions for the low-lying excited states of the free-atomic rare gases seem useful.[1] We have calculated LS-coupled wave functions for the ^3P and ^1P terms of neon in the $2p^53s$ configuration using the Hartree-Fock equations.[2] Spin-orbit interaction and electrostatic energies are computed for use in intermediate coupling. Theoretical values of other parameters of interest, namely, dipole matrix elements, polarizability, oscillator strengths, and diamagnetic susceptibility are also calculated. The numerical work was carried out on an IBM type 650 data-processing machine using a program written by Piper[3] for the iteration of the Hartree-Fock equations.

In part 2(a) the Fock equations are written for $2p^53s$ $(^3P,^1P)$ neon, and in part 2(b) their numerical solution is discussed and tables of wave functions given. Part 3 is devoted to the computation of excitation energies and term splittings (including comparison with a $1s^22s^2$ "invariant core" calculation), a comparison with other work, and an estimation of computational errors. In part 4 oscillator strengths, polarizability,

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[1] For a computation of excited state wave functions for argon see R. S. Knox, Phys. Rev. **110**, 375 (1958).

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