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The electric-dipole moments of an atom
II. The contribution from an electric-dipole moment on the electron with particular reference to the hydrogen atom

P. G. H. SANDARS
Clarendon Laboratory, Oxford
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Abstract. A quantitative calculation is made of the electric-dipole moment on a free one-electron atom which would result from the existence of a non-zero moment on the electron. It is shown that in the non-relativistic approximation the atomic moment is zero, but that relativistic effects allow a non-zero value. For the ground state of hydrogen the atomic moment is found to be $-2Z^2\alpha^2 d_e$, while for the 2s state it is of order d_e/α; d_e is the electron moment and α is the fine-structure constant. The enhancement in the 2s state is closely connected with the near degeneracy of the 2s and 2p states.

1. Introduction

In the first paper in this series (Sandars 1968, to be referred to as S) we examined in some detail the various electric-dipole moments (e.d.m.) that could occur in a free atom as a result of the violation of parity (P) and time-reversal (T) invariances. In this paper we consider a particular model of P and T violation in which an e.d.m. is attributed to the electron. This assumption is of some current interest because some of the models of CP violation which have followed the discovery of the $K_L^0 \to 2\pi$ decay mode (Christenson *et al.* 1963) predict that the electron may have an e.d.m. of the order of $10^{-23}\, e \times$ cm.

Measurements of this precision on the free electron seem to be ruled out by the perturbing effect of the charge and magnetic moment. The best limit on the free electron, $d_e \lesssim 2{\cdot}3 \times 10^{-16}\, e \times$ cm, has been obtained (Rand 1965) using 100 MeV electrons from the Stanford linear accelerator.

In contrast, modern atomic beam techniques allow extremely accurate measurements to be carried out on free neutral atoms. This suggests that one should make one's measurements on suitable atoms and then interpret the results in terms of the e.d.m. of the electron, rather in the way that the anomalous magnetic moment of the electron was discovered.

Unfortunately, there is a basic difficulty in this approach. Schiff (1963) has given a very general theorem which implies that an atom does not have an e.d.m., even if the electron does. The reason for this 'shielding' of the electron e.d.m. will become clear from our analysis in the next section. The purpose of this paper is to emphasize that the shielding argument is essentially non-relativistic and that it no longer holds when the electron is treated relativistically. Thus, when relativistic effects are included it is possible for an e.d.m. on the electron to induce an e.d.m. on the atom as a whole (Sachs and Schwebel 1959, Salpeter 1958). Furthermore, we show that in favourable circumstances the induced moment can be appreciably larger than that of the electron itself.

Because of the importance of this result for the detection of an electronic e.d.m. we carry out the arguments in some detail and in several different ways. However, in this paper we restrict ourselves to the problem of a single electron moving in a central potential with particular reference to the hydrogen atom. Preliminary calculations using the methods devised here (for alkali atoms in their ground states) have been reported (Sandars 1965, 1966). More detailed calculations on these atoms will be given in a subsequent paper.

2. Shielding factors

In this section we consider, in rather general terms, the e.d.m. induced in an atom in a state γ by an e.d.m. on the electron. The induced e.d.m. is rather conveniently expressed

in terms of the shielding factor

$$R(\gamma) = \frac{\text{e.d.m. of atom in state } \gamma}{\text{e.d.m. of free electron}}. \tag{2.1}$$

As we pointed out in the introduction, a correct treatment must be relativistic. Salpeter (1958) showed that an e.d.m. for the electron could be introduced in a Lorentz covariant manner by adding to the normal Dirac Hamiltonian for a single electron

$$H^{\mathrm{A}} = \beta mc^2 + \boldsymbol{\alpha} \,.\, (c\mathbf{p} + e\mathbf{A}) - eV \tag{2.2}$$

the additional perturbation

$$H^{\mathrm{edm}} = -d_{\mathrm{e}}\beta(\boldsymbol{\sigma} \,.\, \mathbf{E} + i\boldsymbol{\alpha} \,.\, \mathbf{H}). \tag{2.3}$$

Here, d_{e} is the e.d.m. of the electron, $\mathbf{E}$ and $\mathbf{H}$ are the total electric and magnetic fields at the electron and $\boldsymbol{\sigma}$, $\boldsymbol{\alpha}$ and β are the usual Dirac matrices.

We now make the important point that the e.d.m. of the electron contributes to the e.d.m. of the atom in two very different ways. The first is simply the projection of the electronic e.d.m. along the total angular momentum of the atom. For a single-electron system the calculation of this part is trivial. The second contribution, the one that makes the whole problem difficult, arises through the interaction of the electronic e.d.m. with the central field of the atom. This interaction is odd under both P and T, and hence, according to our analysis in S, can lead to an e.d.m. of the atom as a whole. The two effects are particular examples of equations (S.3.3) and (S.3.7), respectively.

In terms of the eigenstates and energies of the free atom, the e.d.m. in the particular hyperfine state γ is given by

$$D(\gamma) = d_{\mathrm{e}}\langle\gamma|\beta\sigma_z|\gamma\rangle + \sum_{i\neq\gamma}\frac{d_{\mathrm{e}}}{W_\gamma - W_i} \times (\langle\gamma|-\beta\boldsymbol{\sigma} \,.\, \mathbf{E}_{\mathrm{int}}|i\rangle\langle i|-ez|\gamma\rangle + \langle\gamma|-ez|i\rangle\langle i|-\beta\boldsymbol{\sigma} \,.\, \mathbf{E}_{\mathrm{int}}|\gamma\rangle). \tag{2.4}$$

Provided we neglect the very small effects from the magnetic hyperfine structure, the operators in equations (2.4) contain no reference to the nuclear spin. It follows that the effective operator, which represents the dipole moments (2.4) within a given hyperfine structure multiplet, must be a scalar in nuclear-spin space. Hence, from our analysis in S, we know that all the moments in the multiplet can be expressed in terms of a single constant, the d_{01} of our analysis in S. To find d_{01} it is only necessary to evaluate (2.4) in a single state of the multiplet. For simplicity, this is always taken as the stretched state with $M_I = I$ and $M_J = J$. In this state the nuclear spin is completely uncoupled from the electronic angular momentum. It no longer plays any part in our analysis, and we shall simply omit reference to it. The shielding factor (2.1) now takes the form for the stretched state

$$R = \langle JJ|\beta\sigma_z|JJ\rangle + \sum_{i\neq 0}\frac{1}{W_0 - W_i} \times (\langle JJ|-\beta\boldsymbol{\sigma} \,.\, \mathbf{E}_{\mathrm{int}}|i\rangle\langle i|-ez|JJ\rangle + \langle JJ|-ez|i\rangle\langle i|-\beta\boldsymbol{\sigma} \,.\, \mathbf{E}_{\mathrm{int}}|JJ\rangle). \tag{2.5}$$

For reasons which will quickly become apparent, it is convenient to separate the relativistic and non-relativistic parts of the shielding factor. This can be done most easily by writing

$$\beta\boldsymbol{\sigma} = \boldsymbol{\sigma} + (\beta - 1)\boldsymbol{\sigma} \tag{2.6}$$

where $(\beta - 1)$ is a projection operator which picks out the small component of the Dirac wave function, and hence vanishes in the non-relativistic limit. Using equation (2.6) we can express the shielding factor (2.5) as the sum of four terms

$$R = R_1 + R_2 + R_3 + R_4 \tag{2.7}$$

with

$$R_1 = \langle JJ|\sigma_z|JJ\rangle \tag{2.8}$$

$$R_2 = \sum_i \frac{1}{W_0 - W_i}(\langle JJ|-\boldsymbol{\sigma}\,.\,\mathbf{E}_{\rm int}|i\rangle\langle i|-ez|JJ\rangle + \text{c.c.}) \tag{2.9}$$

$$R_3 = \langle JJ|(\beta-1)\sigma_z|JJ\rangle \tag{2.10}$$

and

$$R_4 = \sum_i \frac{1}{W_0 - W_i}\{\langle JJ|-(\beta-1)\boldsymbol{\sigma}\,.\,\mathbf{E}_{\rm int}|i\rangle\langle i|-ez|JJ\rangle + \text{c.c.}\}. \tag{2.11}$$

We now show that R_1 and R_2 exactly cancel so that in the non-relativistic limit the e.d.m. of the atom is zero. To do this we note that

$$-\boldsymbol{\sigma}\,.\,\mathbf{E}_{\rm int} = -\frac{1}{e}[\boldsymbol{\sigma}\,.\,\nabla, H^0] \tag{2.12}$$

where $H^0 = \beta mc^2 + \boldsymbol{\alpha}.c\mathbf{p} - eV(\mathbf{r})$ is the free-atom Hamiltonian. On inserting (2.12) into (2.9), we obtain

$$R_2 = \sum_i \left(\langle JJ|\frac{1}{e}\boldsymbol{\sigma}\,.\,\nabla\,|i\rangle\langle i|-ez\,|JJ\rangle - \langle JJ|-ez\,|i\rangle\langle i|\frac{1}{e}\boldsymbol{\sigma}\,.\,\nabla\,|JJ\rangle\right). \tag{2.13}$$

The sum over intermediate states spans a complete set so that we can use closure to obtain

$$R_2 = -\langle JJ|[\boldsymbol{\sigma}\,.\,\nabla, z]|JJ\rangle = -\langle JJ|\sigma_z|JJ\rangle = -R_1 \tag{2.14}$$

as desired.

It is important to emphasize at this point that one cannot carry out an analogous argument for the full relativistic expression (2.5) for the shielding factor. Since $\boldsymbol{\alpha}$ and β do not commute one cannot obtain an expression free from energy denominators. The important role of β in e.d.m. shielding has already been pointed out by Salpeter (1958), who argued that its presence is essential to ensure that the interaction of the e.d.m. with the electromagnetic field transforms correctly under Lorentz transformations. The presence of β is the reason why Schiff's very general theorem on the absence of effects linear in electric dipole moments does not apply here. Schiff (1963) did not consider the problem of relativistic particles with e.d.m.'s.

3. Dirac theory of shielding factors

In order to evaluate the remaining shielding factors R_3 and R_4 one first needs to express them in terms of integrals over radial wave functions. If we consider R_3 first, it has the form

$$R_3 = \langle JJ|(\beta-1)\sigma_z|JJ\rangle \tag{3.1}$$

where $|JJ\rangle$ is a solution of the central-field Dirac equation and can therefore be written in the form

$$|JJ\rangle = \begin{pmatrix} \dfrac{P(r)}{r}\chi(lJJ) \\ \dfrac{iQ(r)}{r}\chi(l'JJ) \end{pmatrix}. \tag{3.2}$$

The angular functions $\chi(lJJ)$ are given by

$$\chi(lJJ) = \sum_m C(l\ \tfrac{1}{2}J;\ J-m, m)\,Y_{J-m}{}^{l}(\theta,\phi)\chi^m \tag{3.3}$$

and the phase of the spherical harmonic is given by Rose (1961). $C(l\ \frac{1}{2}J;\ J-m, m)$ is the familiar Clebsch–Gordan coefficient, and is a spin function with projection m. If $l = J+\frac{1}{2}$ then $l' = J-\frac{1}{2}$, but if $l = J-\frac{1}{2}$ then $l' = J+\frac{1}{2}$. The radial functions $P(r)$ and $Q(r)$ satisfy

the coupled differential equations (atomic units)

$$\frac{d}{dr}\begin{pmatrix} P(r) \\ Q(r) \end{pmatrix} = \begin{pmatrix} -\frac{k}{r} & \alpha\left(W+\frac{1}{\alpha^2}\right)+\alpha V(r) \\ -\alpha\left(W-\frac{1}{\alpha^2}\right)-\alpha V(r) & \frac{k}{r} \end{pmatrix}\begin{pmatrix} P(r) \\ Q(r) \end{pmatrix} \tag{3.4}$$

where W is the energy eigenvalue and k takes the values $\mp(J+\frac{1}{2})$ according to whether $l = J \pm \frac{1}{2}$. In the non-relativistic limit $P(r)$ remains finite, but $Q(r)$ tends to zero.

Using the form

$$(\beta - 1) = \begin{pmatrix} 0 & 0 \\ 0 & -2I \end{pmatrix} \tag{3.5}$$

one can readily express (3.1) in terms of radial integrals

$$R_3 = -2\left\{\frac{J(J+1)-l'(l'+1)}{J+1}+\tfrac{3}{4}\right\}\int_0^\infty \{Q(r)\}^2\, dr. \tag{3.6}$$

The evaluation of R_4 is a harder problem because of the sum over excited states in equation (2.11). However, this sum can be removed by a method which is analogous to that introduced by Sternheimer (1954) for use in non-relativistic calculations involving second-order perturbations. We first write R_4 in the form

$$R_4 = 2\langle JJ|(1-\beta)\boldsymbol{\sigma} \cdot \mathbf{E}_{\text{int}}|p\rangle \tag{3.7}$$

where $|p\rangle$ is a 'perturbed' function defined by

$$|p\rangle = \sum_i \frac{|i\rangle\langle i| - z|JJ\rangle}{W_0 - W_i}. \tag{3.8}$$

Now the functions $|i\rangle$ satisfy the Dirac equation

$$\{H^0 - W_i\}|i\rangle = 0 \tag{3.9}$$

and we can make use of this by multiplying both sides of (3.8) by $W_0 - H^0$ to remove the energy denominators. The sum over states spans a complete set so that on using closure we obtain the following simple inhomogeneous equation for

$$\{W_0 - H^0\}|p\rangle = -z|JJ\rangle. \tag{3.10}$$

Since the non-relativistic equivalent of (3.10) is often referred to as the Sternheimer equation we shall call (3.10) the relativistic Sternheimer equation.

Now $|p\rangle$ will contain a part with angular momentum J and also a part with angular momentum not equal to J. As $\boldsymbol{\sigma}.\mathbf{E}_{\text{int}}$ is a scalar only the angular momentum J part will contribute to (3.7). The desired perturbed function can readily be seen to have the form

$$|p\rangle = \begin{pmatrix} \frac{P'(r)}{r}\chi(l'JJ) \\ \frac{iQ(r)}{r}\chi(lJJ) \end{pmatrix} \tag{3.11}$$

where l and l' have the same values as in the unperturbed function defined in equation (3.2). This ensures that $|JJ\rangle$ and $|p\rangle$ have opposite parity.

We can obtain the equations satisfied by the perturbed radial functions $P'(r)$ and $Q'(r)$ by multiplying both sides of equation (3.10) by $(\chi^*(l'JJ)\ \chi(lJJ))$ and carrying out the angular

integrals. Using

$$\int \chi^*(l'JJ)\chi(lJJ)\frac{z}{r}d\Omega = \int \chi^*(lJJ)\chi(l'JJ)\frac{z}{r}d\Omega = -\frac{1}{2J+2} \tag{3.12}$$

we obtain the coupled equations

$$\begin{aligned}\left(\frac{d}{dr}-\frac{k}{r}\right)P'(r)-\left\{\alpha\left(W_0+\frac{1}{\alpha^2}\right)+\alpha V(r)\right\}Q'(r) &= -\frac{\alpha}{2J+2}rQ(r)\\ \left(\frac{d}{dr}+\frac{k}{r}\right)Q'(r)+\left\{\alpha\left(W_0-\frac{1}{\alpha^2}\right)+\alpha V(r)\right\}P'(r) &= \frac{\alpha}{2J+2}rP(r)\end{aligned} \tag{3.13}$$

where we have used the fact that the Dirac quantum number for the perturbed state (3.11) is just $-k$.

On using (3.5) and the angular integrals

$$\int \chi^*(lJJ)\frac{\boldsymbol{\sigma}\cdot\mathbf{r}}{r}\chi(l'JJ)\,d\Omega = \int \chi^*(l'JJ)\frac{\boldsymbol{\sigma}\cdot\mathbf{r}}{r}\chi(lJJ)\,d\Omega = -1 \tag{3.14}$$

we can express (3.7) in the form

$$R_4 = 4\int_0^\infty Q(r)Q'(r)\frac{\partial}{\partial r}V(r)\,dr \tag{3.15}$$

where we have used

$$\mathbf{E}_{\text{int}} = -\frac{\mathbf{r}}{r}\frac{\partial}{\partial r}V(r). \tag{3.16}$$

4. v^2/c^2 theory of shielding factors

Very often it is inconvenient to use a complete relativistic Dirac theory of the shielding factor and preferable to work in the framework of the Schrödinger equation with relativistic effects included as a series of additional operators representing an expansion in powers v^2/c^2.

The most elegant way of finding these additional operators is by means of the Foldy–Wouthuysen transformation. One writes the relativistic Hamiltonian in the form

$$H_{\text{rel}} = \beta mc^2 + \Omega_0 + \Omega_e \tag{4.1}$$

where Ω_0 and Ω_e are operators which, respectively, do and do not connect the large and small components of the Dirac wave function. One can then show that the appropriate Schrödinger equation to first order in v^2/c^2 is (Rose 1961)

$$H_{\text{nr}} = mc^2 + \Omega_e + \frac{1}{2mc^2}\Omega_0{}^2 - \frac{1}{8m^2c^4}[\Omega_0,[\Omega_0,\Omega_e]]. \tag{4.2}$$

In finding the expansion of the shielding factor by means of the Foldy–Wouthuysen transformation, it is convenient to consider the atom to be placed in a small uniform electric field E_{ext} in the z direction. We are now interested in the v^2/c^2 expansion of

$$H' = -d_e(\beta-1)\boldsymbol{\sigma}\cdot\mathbf{E} \tag{4.3}$$

where E is the total field $E_{\text{int}}+E_{\text{ext}}$ at the electron. Since the Hamiltonian (4.3) is an even operator and vanishes in the non-relativistic limit, the only term which we need to consider is

$$H_{\text{nr}}' = -\frac{1}{8m^2c^4}[\boldsymbol{\alpha}\cdot c\mathbf{p},[\boldsymbol{\alpha}\cdot c\mathbf{p},-d_e(\beta-1)\boldsymbol{\sigma}\cdot\mathbf{E}]]. \tag{4.4}$$

After some manipulation this reduces to

$$H_{\rm nr}' = -\frac{d_{\rm e}}{2m^2c^2}[\boldsymbol{\sigma}\,.\,\nabla\ \boldsymbol{\sigma}\,.\,\mathbf{E}\ \boldsymbol{\sigma}\,.\,\nabla]. \tag{4.5}$$

On writing

$$\boldsymbol{\sigma}\,.\,\mathbf{E} = -[\boldsymbol{\sigma}\,.\,\nabla, V] \tag{4.6}$$

we obtain the alternative form

$$H_{\rm nr}' = \frac{d_{\rm e}}{mc^2}\left(\boldsymbol{\sigma}\,.\,\nabla V\frac{p^2}{2m} - \frac{p^2}{2m}V\boldsymbol{\sigma}\,.\,\nabla\right). \tag{4.7}$$

The first-order perturbation energy due to (4.7) is

$$W_{\rm nr}' = \frac{d_{\rm e}}{mc^2}\langle\psi|\boldsymbol{\sigma}\,.\,\nabla\frac{p^2}{2m} - \frac{p^2}{2m}V\boldsymbol{\sigma}\,.\,\nabla|\psi\rangle \tag{4.8}$$

where $|\psi\rangle$ is the wave function of the atom in the electric field. $|\psi\rangle$ satisfies a Schrödinger equation

$$\left(\frac{p^2}{2m} - eV\right)|\psi\rangle = W_{\rm nr}|\psi\rangle. \tag{4.9}$$

We can make use of this to write the energy (4.8) in the form

$$W_{\rm nr}' = \frac{d_{\rm e}W_{\rm nr}}{mc^2}\langle\psi|[\boldsymbol{\sigma}\,.\,\nabla, V]|\psi\rangle + \frac{ed_{\rm e}}{mc^2}\langle\psi|[\boldsymbol{\sigma}\,.\,\nabla, V^2]|\psi\rangle. \tag{4.10}$$

But the first term in (4.10) is zero because it can be rewritten

$$-\frac{d_{\rm e}W_{\rm nr}}{emc^2}\langle\psi|[\boldsymbol{\sigma}-\nabla, \frac{p^2}{2m} - eV]|\psi\rangle = 0. \tag{4.11}$$

We are, therefore, left with the very simple result

$$W_{\rm nr}' = \frac{ed_{\rm e}}{mc^2}\langle\psi|[\boldsymbol{\sigma}\,.\,\nabla, V^2]|\psi\rangle. \tag{4.12}$$

The simplicity is, of course, somewhat deceptive, since to get the atomic e.d.m. we are interested in that part of (4.12) which is linear in the small external electric field, and this is contained both in the operator and the wave function. By methods similar to those used in § 2, we can identify two shielding factors $R_{\rm a}$ and $R_{\rm b}$ which are given by (atomic units)

$$R_{\rm a} = -2\alpha^2\langle\psi_{JJ}|[\boldsymbol{\sigma}\,.\,\nabla, V(r)^2]|\psi_{\rm p}\rangle \tag{4.13}$$

and

$$R_{\rm b} = 2\alpha^2\langle\psi_{JJ}|[\boldsymbol{\sigma}\,.\,\nabla, zV(r)]|\psi_{JJ}\rangle. \tag{4.14}$$

Here ψ_{JJ} is the stretched-state wave function in the absence of the electric field. $\psi_{\rm p}$ is a 'perturbed' function analogous to that used in the previous sections. It satisfies the non-relativistic Sternheimer equation

$$\{W_{\rm nr} - \tfrac{1}{2}p^2 + V(r)\}\psi_{\rm p} = z\psi_{JJ}. \tag{4.15}$$

Since ψ_{JJ} is the solution of a central-field Schrödinger equation it will take the form $\{R(r)/r\}\chi(lJJ)$. It is simple to show that the part of $\psi_{\rm p}$ which contributes to the shielding factor must have the same values of the total angular momentum, and hence can be written $\{R'(r)/r\}\chi(l'JJ)$. To ensure that the parity of $\psi_{\rm p}$ is opposite to that of ψ_{JJ}, l' and l must be related in the way described at the beginning of § 3. By carrying out the angular separation on the Sternheimer equation (4.15) using equation (3.12) we find that $R'(r)$ satisfies the

inhomogeneous radial equation

$$\left\{W_{\rm nr}+\frac{1}{2}\frac{d^2}{dr^2}-\frac{l'(l'+1)}{2r^2}+V(r)\right\}R'(r)=-\frac{r}{2J+2}R(r). \tag{4.16}$$

We can now readily express the shielding factors $R_{\rm a}$ and $R_{\rm b}$ in terms of radial integrals. We find

$$R_{\rm a}=2\alpha^2\int R(r)R'(r)\frac{\partial}{\partial r}V^2(r)\,dr \tag{4.17}$$

and

$$R_{\rm b}=2\alpha^2\left\{(-1)^{l-J+\frac{1}{2}}\frac{J}{l+\frac{1}{2}}\int R(r)^2V(r)\,dr+\frac{1}{2J+2}\int R(r)^2r\frac{\partial}{\partial r}V(r)\,dr\right\}. \tag{4.18}$$

It is worth noting at this point, that we could have obtained the v^2/c^2 expansion of the shielding factors in a somewhat different way by considering the Foldy–Wouthuysen transformation directly on the complete e.d.m. perturbation $-\beta\, d_{\rm e}\boldsymbol{\sigma}.\mathbf{E}$. The analysis in this case is much more complicated, but by tedious manipulation one can establish that both approaches yield the same result; as indeed they must.

5. Relativistic theory of shielding in ground state of hydrogen

In this section we carry out a relativistic calculation of the shielding factor in the ground state of atomic hydrogen using the methods outlined in § 3.

The radial Dirac wave functions for the ground state of hydrogen take the form (atomic units) (Rose 1961)

$$\begin{aligned}P(r)&=\frac{(2Z)^{\gamma+\frac{1}{2}}}{\{2\Gamma(2\gamma+1)\}^{1/2}}(1+\gamma)^{1/2}r^{\gamma}\,{\rm e}^{-Zr}\\ Q(r)&=-\frac{(2Z)^{\gamma+\frac{1}{2}}}{\{2\Gamma(2\gamma+1)\}^{1/2}}(1-\gamma)^{1/2}r^{\gamma}\,{\rm e}^{-Zr}.\end{aligned} \tag{5.1}$$

The associated energy is

$$W=\frac{\gamma}{\alpha^2}. \tag{5.2}$$

Here $\gamma=(1-Z^2\alpha^2)^{1/2}$, Z being the charge on the nucleus.

For the ground state $k=-1$, $J=\frac{1}{2}$, and $V(r)=Z/r$ so that the relativistic Sternheimer equation (3.13) takes the form

$$\begin{aligned}\left(\frac{d}{dr}+\frac{1}{r}\right)P'(r)-\left(\frac{\gamma+1}{\alpha}+\alpha\frac{Z}{r}\right)Q'(r)&=+\frac{Z\alpha}{1+\gamma}Mr^{\gamma+1}\,{\rm e}^{-Zr}\\ \left(\frac{d}{dr}-\frac{1}{r}\right)Q'(r)+\left(\frac{\gamma-1}{\alpha}+\frac{\alpha Z}{r}\right)P'(r)&=Mr^{\gamma+1}\,{\rm e}^{-Zr}\end{aligned} \tag{5.3}$$

with

$$M=\frac{\alpha(2Z)^{\gamma+\frac{1}{2}}(1+\gamma)^{1/2}}{3\{2\Gamma(2\gamma+1)\}^{1/2}}. \tag{5.4}$$

In order to solve (5.3) we try a power series solution of the form

$$\begin{aligned}P'(r)&=(ar^{\gamma}+br^{\gamma+1}+cr^{\gamma+2})\,{\rm e}^{-Zr}\\ Q'(r)&=(a'r^{\gamma}+b'r^{\gamma+1}+c'r^{\gamma+2})\,{\rm e}^{-Zr}.\end{aligned} \tag{5.5}$$

On substituting this into (5.3) and equating powers of r, we obtain a series of equations which the constants in (5.5) must satisfy. The solution to these equations is found to be

$$\begin{aligned} a &= -\frac{M(2\gamma+1)\alpha}{4Z}, & b &= -\frac{M\alpha}{2(1-\gamma)}, & c &= -\frac{M\gamma}{2Z\alpha} \\ a' &= -\frac{M(2\gamma+1)\alpha^2}{4(1-\gamma)}, & b' &= -\frac{M}{2Z}, & c' &= \frac{M\gamma}{2(1+\gamma)}. \end{aligned} \tag{5.6}$$

The radial integrals needed to obtain R_3 and R_4 from equations (3.6) and (3.15) can now be evaluated. We find

$$R_3 = \frac{1-\gamma}{3} \tag{5.7}$$

and

$$R_4 = -\tfrac{1}{3}Z^2\alpha^2 \frac{8\gamma+5}{(2\gamma-1)(\gamma+1)}. \tag{5.8}$$

The total shielding factor which is the sum of (5.7) and (5.8) is

$$R = -\frac{2Z^2\alpha^2}{2\gamma-1}. \tag{5.9}$$

In the non-relativistic limit when $\gamma \to 1$ the dominant term is given by

$$R = -2Z^2\alpha^2 \tag{5.10}$$

6. v^2/c^2 theory of shielding in the ground state of hydrogen

We now calculate the lowest order in the v^2/c^2 expansion of the shielding factor in the hydrogen ground state using the results of § 4.

The radial wave function for the ground state is given by

$$R(r) = 2Z^{3/2}r\,\mathrm{e}^{-Zr}. \tag{6.1}$$

On substituting this into the expression (4.18) for R_b and carrying out the integrals we find

$$R_b = \tfrac{4}{3}Z^2\alpha^2. \tag{6.2}$$

In order to calculate R_a, equation (4.17), we have to solve the non-relativistic Sternheimer equation

$$\left(-\frac{Z^2}{2}+\frac{1}{2}\frac{d^2}{dr^2}-\frac{1}{r^2}+\frac{Z}{r}\right)R'(r) = -\tfrac{2}{3}Z^{3/2}r^2\,\mathrm{e}^{-Zr}. \tag{6.3}$$

The solution is readily found to be

$$R'(r) = \frac{Z^{1/2}}{3}\left(r^3+\frac{2r^2}{Z}\right)\mathrm{e}^{-Zr}. \tag{6.4}$$

Evaluating the integrals in (4.17) we find

$$R_a = -\tfrac{10}{3}Z^2\alpha^2 \tag{6.5}$$

so that the total shielding factor is

$$R = R_a + R_b = -2Z^2\alpha^2 \tag{6.6}$$

in agreement with the dominant term obtained from the exact relativistic theory.

7. Shielding in the metastable 2s state of hydrogen

We now consider the shielding in the 2s metastable state of hydrogen. The situation here differs from the ground state in that the $2p_{1/2}$ state lies extremely close in energy, the two being separated only by the Lamb shift of about 3×10^{-6} ev.

It is rather instructive to see explicitly in this case how the atomic e.d.m. becomes zero in the non-relativistic limit. The contribution to the atomic e.d.m. induced by the interaction of the electronic e.d.m. with the central field of the atom is given by

$$D' = \sum_n \frac{d_e \langle 2s_{1/2,1/2}| (\boldsymbol{\sigma}.\mathbf{r}/r^3)\, Z|np_{1/2,1/2}\rangle \langle np_{1/2,1/2}|z|2s_{1/2,1/2}\rangle}{W_{2s_{1/2}} - W_{np_{1/2}}} + \text{c.c.} \tag{7.1}$$

At first sight the dominant contribution will come from the $2p_{1/2}$ state in (7.1) on account of its small energy denominator. This does not happen because the non-relativistic matrix element

$$\int R_{2s}(r) R_{2p}(r) \frac{1}{r^2}\, dr = 0 \tag{7.2}$$

and the $2p_{1/2}$ state does not contribute at all. The contribution from higher p states can be found by means of the Sternheimer method. We define the function

$$\left| \frac{R'(r)}{r} \chi(l = 1, \tfrac{1}{2}\tfrac{1}{2}) \right\rangle = \sum_{n \neq 2} \frac{|np_{1/2,1/2}\rangle \langle np_{1/2,1/2}|z|2s_{1/2,1/2}\rangle}{W_{2s_{1/2}} - W_{np_{1/2}}} \tag{7.3}$$

where the sum excludes the $2p_{1/2}$ state. One can readily find the appropriate inhomogeneous equation satisfied by $R'(r)$ and solve it. We obtain

$$R'(r) = \frac{1}{3}\left(\frac{Z}{2}\right)^{3/2} \left(r^4 - \frac{30}{Z^3} r^2\right) e^{-\frac{1}{2}Zr}. \tag{7.4}$$

On substituting this back into (7.1) we obtain

$$D' = -2d_e \int R'(r) R_{2s}(r) \frac{1}{r^2}\, dr = -d_e \tag{7.5}$$

as expected.

We now turn our attention to the lowest terms in the v^2/c^2 expansion using the results of § 4. The dominant contribution now comes from the $2p_{1/2}$ state and has the form

$$R = \frac{4\alpha^2 \langle 2s_{1/2,1/2}| (\boldsymbol{\sigma}.\mathbf{r}/r^4)\, Z^2 |2p_{1/2,1/2}\rangle \langle 2p_{1/2,1/2}|z|2s_{1/2,1/2}\rangle}{W_{2s_{1/2}} - W_{2p_{1/2}}} \tag{7.6}$$

where $W_{2s_{1/2}} - W_{2p_{1/2}}$ is the Lamb shift energy. The integrals can readily be evaluated and we obtain

$$R = \frac{Z^4\alpha^2}{2(W_{2s_{1/2}} - W_{2p_{1/2}})}. \tag{7.7}$$

(7.7) agrees with the result obtained by Salpeter (1958) using a somewhat different method.

The important point to note here is that the nearly degenerate state $2p_{1/2}$ does not contribute to the non-relativistic shielding but does contribute to the relativistic terms. Indeed because of the small denominator (7.7) is rather large, for example

$$R \sim 120 \tag{7.8}$$

for hydrogen with $Z = 1$. Thus, in a favourable situation the e.d.m. of the atom can be appreciably bigger than that of the electron. This enhancement effect in the $2s_{1/2}$ state of hydrogen was pointed out by Salpeter (1958).

8. Discussion

In this paper we have discussed in some detail the e.d.m. which a single-electron atom would have if the free electron possessed one. We find, as expected, that in the non-relativistic approximation the atomic moment is zero. But we also find that relativistic effects do allow the atom to have a non-zero moment.

For the ground state of hydrogen the atomic moment is very much smaller than that on the electron, but for the metastable 2s state it is two orders of magnitude larger. This enhancement is connected with the near degeneracy of the 2s and 2p states.

These results for hydrogen do not lead to any useful experiments. The shielding in the ground state is too severe for useful results to be obtained while the measurement of a dipole moment in the 2s state is not feasible since it decays rapidly in applied electric field.

The results derived here are useful because they can be applied to other atoms such as the alkalis which are of considerable experimental interest. In this respect, the calculations on hydrogen form a very useful check on the validity of our ideas and on the correctness of our results.

Preliminary calculations on the alkali ground states using the methods outlined here have already been reported. Their importance lies in the discovery that in the heavy alkalis the atomic e.d.m. may be appreciably larger than the electronic one. This enhancement factor combined with the enormous sensitivity of current atomic beam methods (Angel *et al.* 1967, Stein *et al.* 1967) has allowed the reduction of the limit on the e.d.m. of the free electron from a value $2 \times 10^{-16}\ e \times \text{cm}$ to its present value of $2 \times 10^{-23}\ e \times \text{cm}$.

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References

ANGEL, J. R. P., SANDARS, P. G. H., and TINKER, M. H., 1967, *Phys. Lett.*, **25A,** 160–1.
CHRISTENSON, J. H., CRONIN, J. W., FITCH, V. L., and TURLEY, R., 1964, *Phys. Rev. Lett.*, **13,** 138–40.
RAND, R. E., 1965, *Phys. Rev.*, **140,** B1605–10.
ROSE, M. E., 1961, *Relativistic Electron Theory* (New York: John Wiley).
SACHS, M., and SCHWEBEL, S. L., 1959, *Ann. Phys., N.Y.*, **6,** 244–60.
SALPETER, E. E., 1958, *Phys. Rev.*, **112,** 1642–48.
SANDARS, P. G. H., 1965, *Phys. Lett.*, **14,** 194–6.
—— 1966, *Phys. Lett.*, **22,** 290–1.
—— 1968, *J. Phys.* B (*Proc. Phys. Soc.*), [2], **1,** 499–510.
SCHIFF, L. I., 1963, *Phys. Rev.*, **132,** 2194–200.
STEIN, T. S., CARRICO, J. P., LIPWORTH, E., and WEISSKOPF, M. C., 1967, *Phys. Rev. Lett.*, **19,** 741–3.
STERNHEIMER, R. M., 1954, *Phys. Rev.*, **96,** 951–68.