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Upper Limit for the Deuteron Electric Dipole Moment from Deuterium Spectroscopy

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Abstract

An upper limit for the deuteron and proton electric dipole moment (edm) are obtained using spectroscopic data. Following Sternheimer [1], the corrections to the deuterium energy levels due to the supposed deuteron electric dipole moment are obtained using second-order perturbation theory. Equating these corrections to the maximum allowed by the appropriate agreement between the theoretic energy levels and experimental spectroscopic values gives an upper limit for the deuteron edm of $8.8 \cdot 10^{-16} e \cdot cm$. Updating similar calculations for hydrogen by Sternheimer gives an upper limit for the proton edm of $1 \cdot 10^{-14} e \cdot cm$.

Contents

1 Introduction

Initially, the existence of an electric dipole moment (edm) on elementary particles, baryons and nuclei was deemed impossible, since mirror symmetry (parity conservation P) and time symmetry (time-reversal invariance T) were assumed [2]. After all, a parity operation ($\vec{r} \rightarrow -\vec{r}$) would change the sign of the edm while leaving the spin direction unchanged. In a similar vein, a time-reversal operation ($t \rightarrow -t$) would reverse the spin direction while leaving the sign of the edm unchanged. Therefore, since an edm must lie along the particle spin [3], both operations produce the same distinct particle with an edm of the opposite sign. Since this particle does not exist, an edm would destroy the assumed symmetry.

When Wu [4] and Christenson *et al.* [5], however, discovered the non-conservation of P in Beta decay and the violation of T in K^0 decay respectively, the notion of a mirror and time symmetry violating edm became viable. The physics community has been searching for electric dipole moments on elementary particles, baryons and nuclei ever since. Even though the present results are all consistent with the nonexistence of the searched for edms, the limits set have had decisive influence on elementary particle physics. Traditional experiments observed how an external electric field affects the supposed edm. Since an electric field accelerates charged particles, only neutral particles could be examined, rendering the neutron standard candidate for edm experiments. As shown in Fig. 1, the upper limit for the neutron edm ($d_{neutron}$) has been narrowed down over the past five decades. The current experimental upper limit is $1.6 \times 10^{-26} e \cdot cm$ [6]. Although the standard model of elementary particles (SM) predicts edms that are much smaller (e.g. $d_{neutron} \sim 10^{-32} e \cdot cm$), other plausible models, such as the supersymmetry model, predict larger edms with values just below the current experimental limits. These models predict the discovery of edms in the near future and could, in contrast with SM, help to explain the particle-antiparticle asymmetry in our universe [7]. As noticed by Sakharov, this asymmetry requires more P and T violation than predicted by SM [8].

The edm of the proton, neutron, deuteron (i.e. a deuterium nucleus) and the Helium-3 nucleus play a complementary role in our quest to explain P and T violation [9]. Although the edms of charged particles cannot be measured directly by traditional methods, a new method using a magnetic storage ring and a radial electric field is proposed to measure the edm of the deuteron [10] [11]. The deuteron is an attractive candidate for this experiment since it is relatively simple and well understood. Furthermore, the sensitivity aimed at by this new method, $10^{-27} e \cdot cm$, will indirectly improve upon the neutron and proton edm by a factor of 60 to 100 and 10^4 respectively.

The aim of this paper is to set a theoretical upper limit for the deuteron edm, since currently no upper limit can be found in literature [6]. Follow-

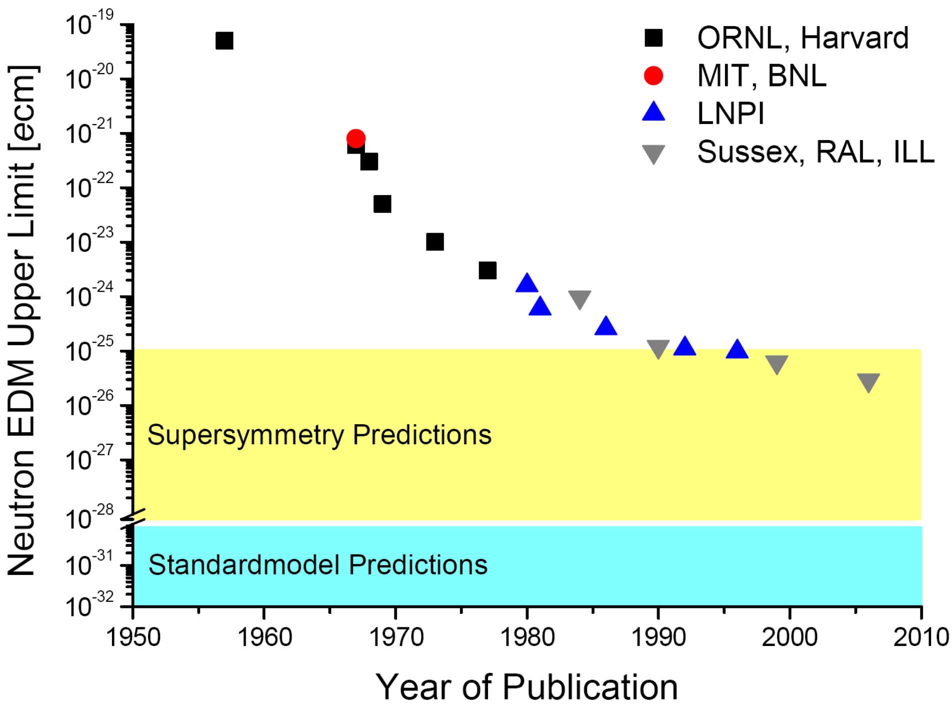

Figure 1: Upper limits for the neutron edm during the past five decades.

ing Sternheimer [1], the perturbations of the $1S\frac{1}{2}$, $2S_{\frac{1}{2}}$ and $2P_{\frac{1}{2}}$ deuterium energy levels by a possible electric dipole moment of the deuteron will be obtained using perturbation theory. Equating this correction to the energy levels to the maximum allowed by the approximate agreement between the experimental and theoretical values of the energy levels will give an upper limit for the deuteron edm. Furthermore, Sternheimers upper limit for the proton edm will be updated using recent proton spectroscopy data.

2 The Procedure: Second-Order Perturbation Theory

The shifts of the deuterium energy levels due to the supposed electric dipole moment of the deuteron are obtained using perturbation theory. Since the first-order correction to the energy E_1 vanishes (Appendix A), the second-order perturbation of the energy E_2 is required. E_2 is obtained from the first-order perturbation of the wave function Ψ_1, which is determined by the following equation:

$$(H_0 - E_0)\Psi_1 = -H_1\Psi_0, \tag{2.1}$$

where H_0, E_0, and Ψ_0 are the unperturbed Hamiltonian, energy and wave function respectively [12]; H_1 is the perturbation due to the electric dipole moment $\vec{d}$:

$$H_1 = -\vec{d} \cdot \vec{E}_e = -\frac{A}{r^2} \vec{\sigma} \cdot \hat{r}, \tag{2.2}$$

where H_1 is in Rydberg units; $\vec{d}$ has magnitude d and is in the direction of the deuteron spin; $\vec{E}_e$ is the electric field of the electron; r is the distance from the nucleus in units of the Bohr radius a_H; A is a dimensionless constant given by

$$A = 2d/(ea_H); \tag{2.3}$$

$\vec{\sigma}$ is the spin vector of the deuteron (in units $\hbar$), which is a spin 1 particle; and $\hat{r}$ is a unit vector in the direction of $\vec{r}$. Eq. (2.1) can be written in Rydberg units as

$$\left[-\frac{\mathrm{d}^2}{\mathrm{d}r^2} + \frac{\hat{L}^2}{r^2} - \frac{2}{r} + \frac{1}{n^2} \right] \Psi_1 = \frac{A}{r^2} \vec{\sigma} \cdot \hat{r} \Psi_0, \tag{2.4}$$

where n is the principal quantum number of the unperturbed state ($E_0 = -\frac{Z^2}{n^2}$ Ry).

After Ψ_1 is determined from Eq. (2.1), the level shift E_2 is obtained from the following equation:

$$E_2 = \int \Psi_0^* H_1 \Psi_1 \mathrm{d}V, \tag{2.5}$$

where the integration extends over the volume of the atom and Ψ_0^* denotes the complex conjugate of Ψ_0 [12].

At this point, two preliminary notions are worth mentioning. First, since the unperturbed wave functions can be separated in a radial and an angular part, and since the operator $\vec{\sigma} \cdot \hat{r}$ affects only the angular part, solving Eq. (2.1) will involve the following radial equation:

$$\left[-\frac{\mathrm{d}^2}{\mathrm{d}r^2} + \frac{l(l+1)}{r^2} - \frac{2}{r} + \frac{1}{n^2} \right] u_1' = \frac{A}{r^2} u_0', \tag{2.6}$$

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 l is the azimuthal quantum number of the perturbation.

Second, for the states we are considering (i.e. the $1S_{\frac{1}{2}}$, $2S_{\frac{1}{2}}$ and $2P_{\frac{1}{2}}$ states of the deuterium atom) it will turn out that, 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. After solving analytically the radial perturbations u_1' for $ns \rightarrow p$, $np \rightarrow s$ and $np \rightarrow d$ from Eq.(2.6), one can obtain the following radial integrals

$$E_2' = \int_0^\infty u_0' u_1' H_1' \mathrm{d}r, \tag{2.7}$$

where $H_1' = -A/r^2$ is the radial part of H_1. As will be shown below, these are the only radial integrals necessary for calculating the energy shifts. The values of E_2' for $1s \to p$, $2s \to p$, $2p \to s$ and $2p \to d$, as obtained by Sternheimer in Section 3 [1] using a theorem proven by Feinberg [13] (Appendix B), are as follows:

$$\begin{aligned} E_2'(1s \to p) &= -A^2, & (2.8) \\ E_2'(2s \to p) &= -\frac{1}{8}A^2, & (2.9) \\ E_2'(2p \to s) &= \frac{1}{24}A^2, & (2.10) \\ E_2'(2p \to d) &= -\frac{1}{48}A^2, & (2.11) \end{aligned}$$

where all of the E_2' are in Rydberg units[1].

Before applying the above mentioned procedure (using the two notes) to the $1S_{\frac{1}{2}}$, $2S_{\frac{1}{2}}$ and $2P_{\frac{1}{2}}$ states of the deuterium atom in order to determine E_2 in terms of the radial integrals E_2', we briefly repeat the hyperfine structure interaction. The magnetic moment due to the total electronic angular momentum of deuterium $\vec{J}$ interacts with the magnetic moment due to the nuclear spin of the deuteron $\vec{I}$, resulting in a splitting of the energy levels, called the hyperfine structure [14]. Since the nuclear spin quantum number of the deuteron $I = 1$, the $1S_{\frac{1}{2}}$, $2S_{\frac{1}{2}}$ and $2P_{\frac{1}{2}}$ terms are all split into two levels, $F = \frac{1}{2}$ and $F = \frac{2}{3}$ (see Fig. 2). Here F is the total angular momentum of the atom with $\vec{F} = \vec{I} + \vec{J}$.

3 Calculation of the Energy Level Shifts

3.1 $E_2(1S_{\frac{1}{2}},\ F = \frac{3}{2})$

We are now ready to calculate the second-order corrections to the deuterium energy levels E_2, starting with the $F = \frac{3}{2}$ level of $1S_{\frac{1}{2}}$. The $M_F = \frac{3}{2}$ state will be used, where M_F is the magnetic quantum number pertaining to F, that is, the projection of F along an arbitrary z axis. Since the energy shift E_2 is independent of the state used, one can check the results by repeating the calculations for a different M_F state.

First, using the correct Clebsch-Gordan coefficients to couple both the orbital angular momentum L with the electronic spin S and the resulting total angular momentum J with the nuclear spin I [17], the unperturbed wave function Ψ_0 is found to be

$$\Psi_0 = \Psi_{1s}\eta_{\frac{1}{2}}\chi_1 = \sqrt{\frac{1}{2}}\frac{u_0'}{r}\eta_{\frac{1}{2}}\chi_1 \qquad (3.1)$$

[1]Although calculated for the hydrogen atom, these results also apply to deuterium.

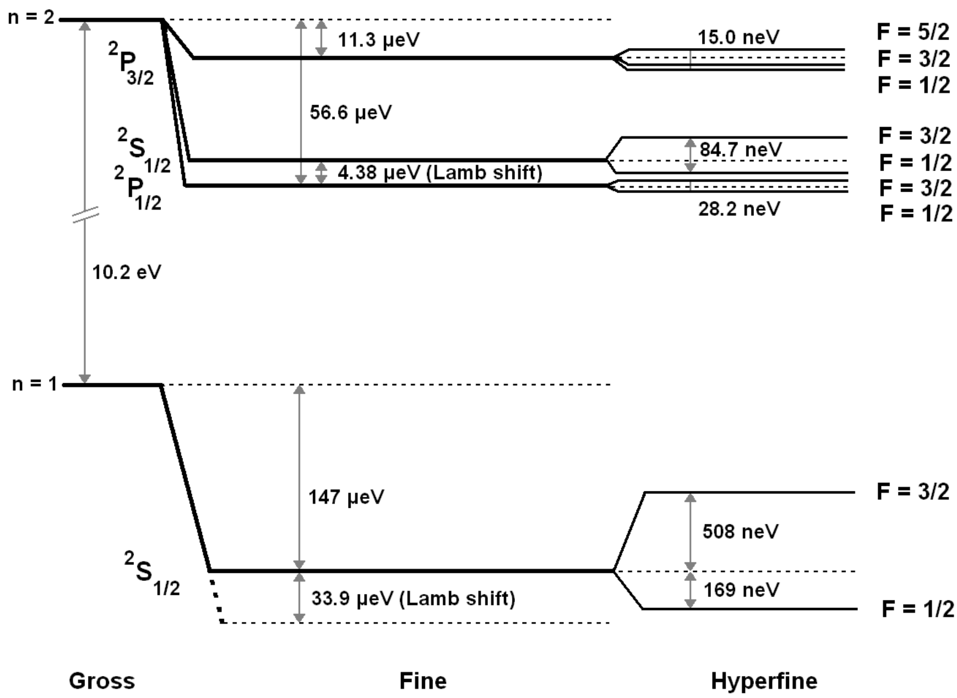

Figure 2: The Hyperfine Energy Levels of Deuterium. Not on scale. Transition energies were calculated using formulas from reference [14] and values of the physical constants from reference [15] and the LBNL Isotopes Project (http://ie.lbl.gov/toi.html), except for the $1S$ Lamb shift [16] and the $2S$ Lamb shift (NIST, http://physics.nist.gov).

where χ_{m_I} is the deuteron spin function with magnetic quantum number $m_I = -1, 0, 1$; η_{m_s} is the electron spin function with magnetic quantum number $m_s = \pm\frac{1}{2}$ and $\Psi_{1s} = \sqrt{\frac{1}{2}}\frac{u_0'}{r}$ is the $1s$ wave function normalized according to

$$\int_0^\infty \int_0^\pi |\Psi_{1s}|^2 r^2 \mathrm{d}r \sin\theta \mathrm{d}\theta \qquad (3.2)$$

where θ is the angle between the radius vector $\vec{r}$ and the z axis [12].

For the next step, that is, determining Ψ_1 from Eq. (2.1), we need to take a closer look at the dot product in the operator $H_1 = -\frac{A}{r^2}\vec{\sigma} \cdot \hat{r}$. The unit vector r in spherical coordinates is given by

$$\begin{pmatrix} \sin\theta\cos\phi \\ \sin\theta\sin\phi \\ \cos\theta \end{pmatrix} \qquad (3.3)$$

whence

$$\vec{\sigma}\cdot\hat{r} = \hat{\sigma}_x \sin\theta\cos\phi + \hat{\sigma}_y \sin\theta\sin\phi + \hat{\sigma}_z\cos\theta \tag{3.4}$$

which can be rewritten as

$$\vec{\sigma}\cdot\hat{r} = \frac{1}{2}\hat{\sigma}_+ \sin\theta e^{-i\phi} + \frac{1}{2}\hat{\sigma}_- \sin\theta e^{i\phi} + \hat{\sigma}_z\cos\theta \tag{3.5}$$

where the ladder operators are given by

$$\hat{\sigma}_\pm = \hat{\sigma}_x \pm i\hat{\sigma}_y. \tag{3.6}$$

Finally, generalising the Pauli spin matrices to a spin 1 system gives

$$\begin{aligned}\vec{\sigma}\cdot\hat{r} &= \frac{1}{\sqrt{2}}\begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 0 & 0 & 0 \end{pmatrix}\sin\theta e^{-i\phi} + \frac{1}{\sqrt{2}}\begin{pmatrix} 0 & 0 & 0 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}\sin\theta e^{i\phi} \\ &\quad + \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}\cos\theta \end{aligned} \tag{3.7}$$

in the basis of $\chi_1, \chi_0, \chi_{-1}$ [12], which are represented by

$$\chi_1 = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}, \ \chi_0 = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}, \ \chi_{-1} = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}. \tag{3.8}$$

Applying this operator to the unperturbed wave function gives

$$H_1\Psi_0 r = \sqrt{\frac{1}{2}}u_0' H_1' \eta_{\frac{1}{2}}[\sqrt{\frac{1}{2}}\chi_0 \sin\theta e^{i\phi} + \chi_1\cos\theta], \tag{3.9}$$

which can be substituted in Eq. (2.1) to obtain the resulting $1s \rightarrow p$ perturbation Ψ_1:

$$\Psi_1 r = \sqrt{\frac{1}{2}}u_1' \eta_{\frac{1}{2}}[\sqrt{\frac{1}{2}}\chi_0 \sin\theta e^{i\phi} + \chi_1\cos\theta] \tag{3.10}$$

where u_1' satisfies the following radial equation (cf. Eq. (2.6)):

$$\left(-\frac{\mathrm{d}^2}{\mathrm{d}r^2} + \frac{2}{r^2} - \frac{2Z}{r} + \frac{Z^2}{4}\right)u_1' = -H_1' u_0'. \tag{3.11}$$

For the last step one needs to calculate $H_1\Psi_1 r$ from Eq. (3.10):

$$\begin{aligned} H_1\Psi_1 r &= \sqrt{\frac{1}{2}}H_1' u_1' \eta_{\frac{1}{2}}[\sqrt{\frac{1}{2}}(\sqrt{\frac{1}{2}}\chi_1 \sin\theta e^{-i\phi} + \sqrt{\frac{1}{2}}\chi_{-1}\sin\theta e^{i\phi})\sin\theta e^{i\phi} \\ &\quad +(\sqrt{\frac{1}{2}}\chi_0 \sin\theta e^{i\phi} + \chi_1\cos\theta)\cos\theta] \\ &= \sqrt{\frac{1}{2}}H_1' u_1' \eta_{\frac{1}{2}}[\frac{1}{2}\chi_1 \sin^2\theta + \frac{1}{2}\chi_{-1}\sin^2\theta e^{i2\phi} \\ &\quad +\sqrt{\frac{1}{2}}\chi_0 \sin\theta\cos\theta e^{i\phi} + \chi_1\cos^2\theta], \end{aligned} \tag{3.12}$$

whence the resulting energy shift is given by

$$\begin{aligned} E_2 &= \int_0^\infty \int_0^\pi (\Psi_0^* r) H_1 \Psi_1 r \mathrm{d}r \sin\theta \mathrm{d}\theta \\ &= \frac{1}{2}\int_0^\infty \int_0^\pi |\eta_{\frac{1}{2}}|^2 u_0' H_1' u_1' |\chi_1|^2 [\frac{1}{2}\sin^2\theta + \cos^2\theta] \mathrm{d}r \sin\theta \mathrm{d}\theta \\ &= \frac{2}{3} E_2'(1s \to p) = -\frac{2}{3} A^2, \end{aligned} \tag{3.13}$$

where the orthogonality of the deuteron spin functions χ_{m_I} has been used.

3.2 $E_2(1S_{\frac{1}{2}},\ F = \frac{1}{2})$

The same procedure can be employed to determine the energy level shift of the $F = \frac{1}{2}$ level of $1S_{\frac{1}{2}}$, using the $M_F = \frac{1}{2}$ state. The unperturbed wave function Ψ_0 for this state is given by

$$\begin{aligned} \Psi_0 &= \Psi_{1s}[\sqrt{\frac{2}{3}}\eta_{-\frac{1}{2}}\chi_1 - \sqrt{\frac{1}{3}}\eta_{\frac{1}{2}}\chi_0] \\ &= \frac{u_0'}{r}[\sqrt{\frac{1}{3}}\eta_{-\frac{1}{2}}\chi_1 - \sqrt{\frac{1}{6}}\eta_{\frac{1}{2}}\chi_0] \equiv \Psi_0^- + \Psi_0^+. \end{aligned} \tag{3.14}$$

It is convenient to consider the $\eta_{\frac{1}{2}}$ and $\eta_{-\frac{1}{2}}$ terms, denoted by Ψ_0^+ and Ψ_0^- respectively, separately. This is justified by the absence of matrix elements of the operator $\vec{\sigma}\cdot\hat{r}$ connecting these terms.

Taking first Ψ_0^-, we have

$$H_1 \Psi_0^- r = H_1' u_0' \eta_{-\frac{1}{2}} (\sqrt{\frac{1}{6}}\chi_0 \sin\theta e^{i\phi} + \sqrt{\frac{1}{3}}\chi_1 \cos\theta). \tag{3.15}$$

The resulting $1s \to p$ perturbation Ψ_1^- is given by

$$\Psi_1^- r = u_1' \eta_{-\frac{1}{2}} (\sqrt{\frac{1}{6}}\chi_0 \sin\theta e^{i\phi} + \sqrt{\frac{1}{3}}\chi_1 \cos\theta) \tag{3.16}$$

where u_1' satisfies the following radial equation:

$$\left(-\frac{\mathrm{d}^2}{\mathrm{d}r^2} + \frac{2}{r^2} - \frac{2Z}{r} + Z^2\right) u_1' = -H_1' u_0'. \tag{3.17}$$

From Eq. (3.16) one obtains

$$\begin{aligned} H_1 \Psi_1^- r &= H_1' u_1' \eta_{-\frac{1}{2}} [\sqrt{\frac{1}{12}}\chi_1 \sin^2\theta + \sqrt{\frac{1}{12}}\chi_{-1} \sin^2\theta e^{i2\phi} \\ &\quad + \sqrt{\frac{1}{6}}\chi_0 \sin\theta\cos\theta e^{i\phi} + \sqrt{\frac{1}{3}}\chi_1 \cos^2\theta]. \end{aligned} \tag{3.18}$$

The resulting energy shift due to the perturbation of Ψ_0^- is given by

$$\begin{aligned} E_2^- &= \int_0^\infty \int_0^\pi (\Psi_0^{-*} r) H_1 \Psi_1^- r \mathrm{d}r \sin\theta \mathrm{d}\theta \\ &= \frac{1}{3} E_2'(1s \to p) \int_0^\pi [\frac{1}{2}\sin^2\theta + \cos^2\theta] \sin\theta \mathrm{d}\theta \\ &= \frac{4}{9} E_2'(1s \to p). \end{aligned} \quad (3.19)$$

Subsequently, taking the Ψ_0^+ term gives

$$H_1 \Psi_0^+ r = -H_1' u_0' \eta_{\frac{1}{2}} (\sqrt{\frac{1}{12}} \chi_1 \sin\theta e^{-i\phi} + \sqrt{\frac{1}{12}} \chi_{-1} \sin\theta e^{i\phi}). \quad (3.20)$$

The resulting $1s \to p$ perturbation Ψ_1^+ is given by

$$\Psi_1^+ r = -u_1' \eta_{\frac{1}{2}} (\sqrt{\frac{1}{12}} \chi_1 \sin\theta e^{-i\phi} + \sqrt{\frac{1}{12}} \chi_{-1} \sin\theta e^{i\phi}) \quad (3.21)$$

where u_1' satisfies the following equation:

$$\left(-\frac{\mathrm{d}^2}{\mathrm{d}r^2} + \frac{2}{r^2} - \frac{2Z}{r} + \frac{Z^2}{4} \right) u_1' = -H_1' u_0'. \quad (3.22)$$

From Eq. (3.21) one obtains

$$\begin{aligned} H_1 \Psi_1^+ r &= -H_1' u_1' \eta_{\frac{1}{2}} [\sqrt{\frac{1}{6}} \chi_0 \sin^2\theta + \sqrt{\frac{1}{12}} \chi_1 \cos\theta \sin\theta e^{-i\phi} \\ &\quad - \sqrt{\frac{1}{12}} \chi_{-1} \cos\theta \sin\theta e^{i\phi}]. \end{aligned} \quad (3.23)$$

The resulting energy shift due to the perturbation of Ψ_0^+ is given by

$$\begin{aligned} E_2^+ &= \int_0^\infty \int_0^\pi (\Psi_0^{+*} r) H_1 \Psi_1^+ r \mathrm{d}r \sin\theta \mathrm{d}\theta \\ &= \frac{1}{6} E_2'(1s \to p) \int_0^\pi \sin^3\theta \mathrm{d}\theta = \frac{2}{9} E_2'(1s \to p). \end{aligned} \quad (3.24)$$

Combining Eq. (3.19) and Eq. (3.24) gives

$$E_2(1S_{\frac{1}{2}}, F = \frac{1}{2}) = E_2^- + E_2^+ = \frac{2}{3} E_2'(1s \to p) = -\frac{2}{3} A^2. \quad (3.25)$$

3.3 $E_2(2S_{\frac{1}{2}}, F = \frac{3}{2}$ & $F = \frac{1}{2})$

The calculation of the energy level shifts for both hyperfine levels of $2S_{\frac{1}{2}}$, $F = \frac{1}{2}$ and $F = \frac{3}{2}$, is almost completely analogous to the previous two subsections, except for the different value of n (i.e., 2 instead of 1) which affects only radial equation (2.6) (cf. Eq. (3.11), Eq. (3.17) and Eq. (3.22)). As a consequence, $E_2'(1s \to p)$ should be substituted by $E_2'(2s \to p)$ to obtain

$$E_2(2S_{\frac{1}{2}}, F = \frac{1}{2}) = E_2(2S_{\frac{1}{2}}, F = \frac{3}{2}) = \frac{2}{3} E_2'(2s \to p) = -\frac{1}{12} A^2. \quad (3.26)$$

3.4 $E_2(2P_{\frac{1}{2}},\ F = \frac{3}{2})$

For the $F = \frac{3}{2}$, $M_F = \frac{3}{2}$ state of $2P_{\frac{1}{2}}$, the unperturbed wave function Ψ_0 is given by

$$\Psi_0 = \sqrt{\frac{2}{3}}\Psi_{2p,1}\eta_{-\frac{1}{2}}\chi_1 - \sqrt{\frac{1}{3}}\Psi_{2p,0}\eta_{\frac{1}{2}}\chi_1 \tag{3.27}$$

where Ψ_{2p,m_l} is the $2p$ wave function pertaining to magnetic quantum number m_l, normalized according to

$$\int_0^\infty\int_0^\pi |\Psi_{2p,m_l}|^2 r^2 \mathrm{d}r \sin\theta \mathrm{d}\theta = 1. \tag{3.28}$$

Thus we have [12]

$$\Psi_{2p,1} = -\frac{\sqrt{3}}{2}\frac{u_0'}{r}\sin\theta e^{i\phi}, \tag{3.29}$$

$$\Psi_{2p,0} = \sqrt{\frac{3}{2}}\frac{u_0'}{r}\cos\theta, \tag{3.30}$$

$$\Psi_{2p,-1} = \frac{\sqrt{3}}{2}\frac{u_0'}{r}\sin\theta e^{-i\phi} \tag{3.31}$$

where the last equation will not be needed until the next subsection. Hence, Eq. (3.27) becomes

$$\Psi_0 = -\sqrt{\frac{1}{2}}\frac{u_0'}{r}\eta_{-\frac{1}{2}}\chi_1\sin\theta e^{i\phi} - \sqrt{\frac{1}{2}}\frac{u_0'}{r}\eta_{\frac{1}{2}}\chi_1\cos\theta \equiv \Psi_0^- + \Psi_0^+. \tag{3.32}$$

Taking first Ψ_0^-, one obtains

$$H_1\Psi_0^- r = -\sqrt{\frac{1}{2}}H_1'u_0'\eta_{-\frac{1}{2}}\left(\sqrt{\frac{1}{2}}\chi_0\sin^2\theta e^{i2\phi} + \chi_1\cos\theta\sin\theta e^{i\phi}\right) \tag{3.33}$$

which gives the following $2p \rightarrow d$ perturbation Ψ_1^-:

$$\Psi_1^- r = -\sqrt{\frac{1}{2}}u_1'\eta_{-\frac{1}{2}}\left(\sqrt{\frac{1}{2}}\chi_0\sin^2\theta e^{i2\phi} + \chi_1\cos\theta\sin\theta e^{i\phi}\right) \tag{3.34}$$

where u_1' satisfies

$$\left(-\frac{\mathrm{d}^2}{\mathrm{d}r^2} + \frac{6}{r^2} - \frac{2Z}{r} + \frac{Z^2}{4}\right)(u_1')_d = -H_1'u_0'. \tag{3.35}$$

From Eq. (3.34) one obtains

$$\begin{aligned} H_1\Psi_1^- r &= -\sqrt{\frac{1}{2}}u_1'\eta_{-\frac{1}{2}}[-\frac{1}{2}\chi_1\sin^3\theta e^{i\phi} + \frac{1}{2}\chi_{-1}\sin^3\theta e^{i3\phi} \\ &\quad + \sqrt{\frac{1}{2}}\chi_0\sin^2\theta\cos\theta e^{i2\phi} + \chi_1\sin\theta e^{i\phi}]. \end{aligned} \tag{3.36}$$

The resulting energy shift due to the perturbation of Ψ_0^- is given by

$$\begin{aligned} E_2^- &= \int_0^\infty \int_0^\pi (\Psi_0^{-*} r) H_1 \Psi_1^- r \mathrm{d}r \sin\theta \mathrm{d}\theta \\ &= \frac{1}{4} E_2'(2p \rightarrow d) \int_{-1}^{1} [1-\cos^4\theta] \mathrm{d}\cos\theta \ = \frac{2}{5} E_2'(2p \rightarrow d). \quad (3.37) \end{aligned}$$

Taking the Ψ_0^+ term gives

$$\begin{aligned} H_1 \Psi_0^+ r &= -H_1' \sqrt{\frac{1}{2}} u_0' \eta_{\frac{1}{2}} [\{ \sqrt{\frac{1}{2}} \chi_0 \sin\theta \cos\theta e^{i\phi} \\ &\qquad + \chi_1 (\cos^2\theta - \frac{1}{3}) \} + \frac{1}{3} \chi_1] \qquad (3.38) \end{aligned}$$

where the term $\frac{1}{3}\chi_1$ gives the $2p \rightarrow s$ perturbation, while the term between accolades leads to the $2p \rightarrow d$ perturbation.

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

$$(\Psi_1^+)_s = -\sqrt{\frac{1}{18}} (u_1')_s \eta_{\frac{1}{2}} \chi_1 \qquad (3.39)$$

where $(u_1')_s$ is given by

$$\left(-\frac{\mathrm{d}^2}{\mathrm{d}r^2} - \frac{2Z}{r} + \frac{Z^2}{4} \right) (u_1')_s = -H_1' u_0'. \qquad (3.40)$$

From Eq. (3.39) one obtains

$$H_1 (\Psi_1^+)_s r = -H_1' \sqrt{\frac{1}{18}} (u_1')_s \eta_{\frac{1}{2}} (\sqrt{\frac{1}{2}} \chi_0 \sin\theta e^{i\phi} + \chi_1 \cos\theta). \qquad (3.41)$$

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

$$\begin{aligned} (E_2^+)_s &= \int_0^\infty \int_0^\pi (\Psi_0^{+*}) H_1 (\Psi_1^+)_s r \mathrm{d}r \sin\theta \mathrm{d}\theta \\ &= \frac{1}{6} E_2'(2p \rightarrow s) \int_{-1}^{1} \cos^2\theta \mathrm{d}\cos\theta = \frac{1}{9} E_2'(2p \rightarrow s). \qquad (3.42) \end{aligned}$$

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

$$(\Psi_1^+)_d r = -\sqrt{\frac{1}{2}} (u_1')_d \eta_{\frac{1}{2}} [\sqrt{\frac{1}{2}} \chi_0 \sin\theta \cos\theta e^{i\phi} + \chi_1 (\cos^2\theta - \frac{1}{3})] \qquad (3.43)$$

where $(u_1')_d$ is determined by

$$\left(-\frac{\mathrm{d}^2}{\mathrm{d}r^2} + \frac{6}{r^2} - \frac{2Z}{r} + \frac{Z^2}{4} \right) (u_1')_d = -H_1' u_0'. \qquad (3.44)$$

From Eq. (3.43) one obtains

$$
\begin{aligned}
H_1(\Psi_1^+)_d r &= -H_1'\sqrt{\frac{1}{2}}(u_1')_d\eta_{\frac{1}{2}}[\frac{1}{2}\chi_1\sin^2\theta\cos\theta+\frac{1}{2}\chi_{-1}\sin^2\theta\cos\theta e^{i2\phi} \\
&\quad +\sqrt{\frac{1}{2}}\chi_0\sin\theta\cos^2\theta e^{i\phi}-\sqrt{\frac{1}{18}}\chi_0\sin\theta e^{i\phi}+\chi_1\cos^3\theta-\frac{1}{3}\chi_1\cos\theta] \\
&= -H_1'\sqrt{\frac{1}{2}}(u_1')_d\eta_{\frac{1}{2}}[\frac{1}{2}\chi_1\cos^3\theta+\frac{1}{2}\chi_{-1}\sin^2\theta\cos\theta e^{i2\phi} \\
&\quad +\sqrt{\frac{1}{2}}\chi_0\sin\theta\cos^2\theta e^{i\phi}-\sqrt{\frac{1}{18}}\chi_0\sin\theta e^{i\phi}+\frac{1}{6}\chi_1\cos\theta].
\end{aligned}
\tag{3.45}
$$

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

$$
\begin{aligned}
(E_2^+)_d &= \int_0^\infty\int_0^\pi(\Psi_0^{+*})H_1(\Psi_1^+)_d r\mathrm{d}r\sin\theta\mathrm{d}\theta \\
&= \frac{1}{2}E_2'(2p\to d)\int_{-1}^{1}[\frac{1}{2}\cos^4\theta+\frac{1}{6}\cos^2\theta]\mathrm{d}\cos\theta \\
&= \frac{7}{45}E_2'(2p\to d).
\end{aligned}
\tag{3.46}
$$

Combining Eq. (3.37), Eq. (3.42) and Eq. (3.46) gives

$$
\begin{aligned}
E_2(2P_{\frac{1}{2}}, F=\frac{3}{2}) &= (E_2^-)+(E_2^+)_s+(E_2^+)_d \\
&= \frac{1}{9}E_2'(2p\to s)+\frac{5}{9}E_2'(2p\to d) \\
&= -\frac{1}{144}A^2.
\end{aligned}
\tag{3.47}
$$

3.5 $E_2(2P_{\frac{1}{2}},\ F=\frac{1}{2})$

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

$$
\Psi_0=\eta_{\frac{1}{2}}[\frac{1}{3}\Psi_{2p,0}\chi_0-\frac{2}{3}\Psi_{2p,-1}\chi_1]+\eta_{-\frac{1}{2}}[-\sqrt{\frac{2}{9}}\Psi_{2p,1}\chi_0+\sqrt{\frac{2}{9}}\Psi_{2p,0}\chi_1], \tag{3.48}
$$

which, upon substitution of Eq. (3.29) to Eq. (3.31), becomes

$$
\begin{aligned}
\Psi_0 &= \eta_{\frac{1}{2}}\frac{u_0'}{r}[\sqrt{\frac{1}{6}}\chi_0\cos\theta-\sqrt{\frac{1}{3}}\chi_1\sin\theta e^{-i\phi}] \\
&\quad +\eta_{-\frac{1}{2}}\frac{u_0'}{r}[\sqrt{\frac{1}{6}}\chi_0\sin\theta e^{i\phi}+\sqrt{\frac{1}{3}}\chi_1\cos\theta] \\
&\equiv \Psi_0^++\Psi_0^-.
\end{aligned}
\tag{3.49}
$$

Taking first Ψ_0^+, we have

$$\begin{aligned} H_1\Psi_0^+ r &= H_1' u_0' \eta_{\frac{1}{2}} [\sqrt{\frac{1}{12}}\chi_1 \sin\theta\cos\theta e^{-i\phi} + \sqrt{\frac{1}{12}}\chi_{-1}\sin\theta\cos\theta e^{i\phi} \\ &\quad -\sqrt{\frac{1}{6}}\chi_0 \sin^2\theta - \sqrt{\frac{1}{3}}\chi_1 \cos\theta\sin\theta e^{-i\phi}] \\ &= H_1' u_0' \eta_{\frac{1}{2}} \Big[\{-\sqrt{\frac{1}{12}}\chi_1 \sin\theta\cos\theta e^{-i\phi} + \sqrt{\frac{1}{12}}\chi_{-1}\sin\theta\cos\theta e^{i\phi} \\ &\quad +\sqrt{\frac{1}{6}}\chi_0(\cos^2\theta - \frac{1}{3})\} - \sqrt{\frac{2}{27}}\chi_0 \Big] \end{aligned} \tag{3.50}$$

where the term $-\sqrt{\frac{2}{27}}\chi_0$ gives the $2p \rightarrow s$ perturbation, while the term between accolades leads to the $2p \rightarrow d$ perturbation.

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

$$(\Psi_1^+)_s r = -\sqrt{\frac{2}{27}}\chi_0 \eta_{\frac{1}{2}} (u_1')_s \tag{3.51}$$

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

$$\left(-\frac{\mathrm{d}^2}{\mathrm{d}r^2} - \frac{2Z}{r} + \frac{Z^2}{4}\right)(u_1')_s = -H_1' u_0'. \tag{3.52}$$

From Eq. (3.51) one obtains

$$H_1(\Psi_1^+)_s r = -\sqrt{\frac{1}{27}} H_1' \eta_{\frac{1}{2}} (u_1')_s [\chi_1 \sin\theta e^{-i\phi} + \chi_{-1}\sin\theta e^{i\phi}], \tag{3.53}$$

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

$$\begin{aligned} (E_2^+)_s &= \int_0^\infty \int_0^\pi (\Psi_0^+)^* r H_1 (\Psi_1^+)_s r \mathrm{d}r \sin\theta \mathrm{d}\theta \\ &= \frac{1}{9} E_2'(2p \rightarrow s) \int_{-1}^1 (1-\cos^2\theta)\mathrm{d}\cos\theta \\ &= \frac{4}{27} E_2'(2p \rightarrow s). \end{aligned} \tag{3.54}$$

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

$$\begin{aligned} (\Psi_1^+)_d r &= (u_1')_d \eta_{\frac{1}{2}} [-\sqrt{\frac{1}{12}}\chi_1 \sin\theta\cos\theta e^{-i\phi} \\ &\quad +\sqrt{\frac{1}{12}}\chi_{-1}\sin\theta\cos\theta e^{i\phi} + \sqrt{\frac{1}{6}}\chi_0(\cos^2\theta - \frac{1}{3})] \end{aligned} \tag{3.55}$$

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

$$\left(-\frac{\mathrm{d}^2}{\mathrm{d}r^2}+\frac{6}{r^2}-\frac{2Z}{r}+\frac{Z^2}{4}\right)(u_1')_d=-H_1'u_0'. \tag{3.56}$$

From Eq. (3.55) one obtains

$$H_1(\Psi_1^+)_d r \;=\; -\sqrt{\frac{1}{108}}H_1'(u_1')_d\eta_{\frac{1}{2}}\left[\chi_1\sin\theta e^{-i\phi}+\chi_{-1}\sin\theta e^{i\phi}\right] \tag{3.57}$$

so that the energy shift due to the $2p\rightarrow d$ perturbation of Ψ_0^+ is found to be

$$\begin{aligned}(E_2^+)_d &= \int_0^\infty\int_0^\pi(\Psi_0^+)^* rH_1(\Psi_1^+)_d r\mathrm{d}r\sin\theta\mathrm{d}\theta\\ &= \sqrt{\frac{1}{324}}E_2'(2p\rightarrow d)\int_0^\pi\sin^2\theta\sin\theta\mathrm{d}\theta\\ &= \frac{2}{27}E_2'(2p\rightarrow d).\end{aligned} \tag{3.58}$$

We shall now consider the $\eta_{-\frac{1}{2}}$ term Ψ_0^-:

$$\begin{aligned}H_1\Psi_0^- r \;=\; & H_1'u_0'\eta_{-\frac{1}{2}}\Big[\sqrt{\frac{4}{27}}\chi_1+\{\sqrt{\frac{1}{12}}\chi_{-1}\sin^2\theta e^{i2\phi}\\ &+\sqrt{\frac{1}{6}}\chi_0\sin\theta\cos\theta e^{i\phi}+\sqrt{\frac{1}{12}}\chi_1(\cos^2\theta-\frac{1}{3})\}\Big]\end{aligned} \tag{3.59}$$

where the term $\sqrt{\frac{4}{27}}\chi_1$ gives the $2p\rightarrow s$ perturbation, while the term between accolades leads to the $2p\rightarrow d$ perturbation.

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

$$(\Psi_1^-)_s r=\sqrt{\frac{4}{27}}\chi_1\eta_{-\frac{1}{2}}(u_1')_s \tag{3.60}$$

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

$$\left(-\frac{\mathrm{d}^2}{\mathrm{d}r^2}-\frac{2Z}{r}+\frac{Z^2}{4}\right)(u_1')_s=-H_1'u_0'. \tag{3.61}$$

From Eq. (3.60) one obtains

$$H_1(\Psi_1^-)_s r=\sqrt{\frac{4}{27}}\eta_{-\frac{1}{2}}H_1'(u_1')_s[\sqrt{\frac{1}{2}}\chi_0\sin\theta e^{i\phi}+\chi_1\cos\theta]. \tag{3.62}$$

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

$$\begin{aligned}(E_2^-)_s &= \int_0^\infty\int_0^\pi(\Psi_0^-)^* rH_1(\Psi_1^-)_s r\mathrm{d}r\sin\theta\mathrm{d}\theta\\ &= \sqrt{\frac{4}{27}}E_2'(2p\rightarrow s)\int_0^\pi[\sqrt{\frac{1}{12}}\sin^2\theta+\sqrt{\frac{1}{3}}\cos^2\theta]\mathrm{d}r\sin\theta\mathrm{d}\theta\\ &= \frac{8}{27}E_2'(2p\rightarrow s).\end{aligned} \tag{3.63}$$

The $2p \to d$ perturbation $(\Psi_1^-)_d$ is given by

$$
\begin{aligned}
(\Psi_1^-)_d r &= \eta_{-\frac{1}{2}} (u_1')_d [\sqrt{\frac{1}{12}} \chi_{-1} \sin^2\theta e^{i2\phi} \\
&\quad + \sqrt{\frac{1}{6}} \chi_0 \sin\theta \cos\theta e^{i\phi} + \sqrt{\frac{1}{12}} \chi_1 (\cos^2\theta - \frac{1}{3})] \quad (3.64)
\end{aligned}
$$

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

$$
\left(-\frac{\mathrm{d}^2}{\mathrm{d}r^2} + \frac{6}{r^2} - \frac{2Z}{r} + \frac{Z^2}{4} \right) (u_1')_d = -H_1' u_0'. \quad (3.65)
$$

From Eq. (3.64) one obtains

$$
H_1 (\Psi_1^-)_d r = \eta_{-\frac{1}{2}} H_1' (u_1')_d [\sqrt{\frac{1}{54}} \chi_0 \sin\theta e^{i\phi} + \sqrt{\frac{1}{27}} \chi_1]. \quad (3.66)
$$

The resulting energy shift due to the $2p \to d$ perturbation of (Ψ_0^-) is given by

$$
\begin{aligned}
(E_2^-)_d &= \int_0^\infty \int_0^\pi (\Psi_0^-)^* r H_1 (\Psi_1^-)_d r \mathrm{d}r \sin\theta \mathrm{d}\theta \\
&= \int_0^\infty \int_0^\pi |\eta_{-\frac{1}{2}}|^2 u_0'^* H_1' (u_1')_d [\sqrt{\frac{1}{324}} |\chi_0|^2 \sin^2\theta + \frac{1}{9} |\chi_1|^2 \cos\theta] \mathrm{d}r \sin\theta \mathrm{d}\theta \\
&= \frac{2}{27} E_2'(2p \to d). \quad (3.67)
\end{aligned}
$$

Finally, combining equations (3.54), (3.58), (3.63) and (3.67) gives

$$
\begin{aligned}
E_2(2P_{\frac{1}{2}}, F = \frac{1}{2}) &= (E_2^+)_s + (E_2^+)_d + (E_2^-)_s + (E_2^-)_d \\
&= \frac{4}{9} E_2'(2p \to s) + \frac{4}{27} E_2'(2p \to d) = \frac{10}{648} A^2. \quad (3.68)
\end{aligned}
$$

3.6 Summary of the Energy Level Shifts

For reasons of surveyability all the second-order corrections to the deuterium energy levels due to the supposed deuteron edm, as calculated above, are listed:

$$
\begin{aligned}
1S_{\frac{1}{2}} : &\quad E_2(F = \frac{1}{2}) = E_2(F = \frac{3}{2}) = -\frac{2}{3} A^2 \quad (3.69) \\
2S_{\frac{1}{2}} : &\quad E_2(F = \frac{1}{2}) = E_2(F = \frac{3}{2}) = -\frac{1}{12} A^2 \quad (3.70) \\
2P_{\frac{1}{2}} : &\quad E_2(F = \frac{1}{2}) = \frac{10}{648} A^2 \quad (3.71) \\
&\quad E_2(F = \frac{3}{2}) = -\frac{1}{144} A^2. \quad (3.72)
\end{aligned}
$$

These energy corrections are in agreement with the results found by Sternheimer [1], except for E_2 $(2P\frac{1}{2},\ F = \frac{1}{2})$, which was calculated as $\frac{1}{72}A^2$. Although calculating this energy correction by utilising the $M_F = -\frac{1}{2}$ state might lead to the decisive answer, both results have the same order of magnitude, which is all that is relevant for our purposes.

4 Upper Limit for the Deuteron and Proton EDM

In order to obtain an upper limit for the deuteron edm, the calculated correction to the $1S_{\frac{1}{2}} - 2S_{\frac{1}{2}}$ transition energy due to the supposed edm (i.e. $-\frac{7}{12}A^2\,Ry$) is equated to the maximum allowed by the appropriate agreement between the experimental and theoretical values of the transition energy. The theoretical and experimental values of the difference between the deuterium and hydrogen $1S_{\frac{1}{2}} - 2S_{\frac{1}{2}}$ transition frequencies are reported by Jentschura [18] [19] to be identical:

$$\left[\nu_D(1S_{\frac{1}{2}} - 2S_{\frac{1}{2}}) - \nu_H(1S_{\frac{1}{2}} - 2S_{\frac{1}{2}})\right]_{exp/th} = 670994334.64(15)\ kHz. \quad (4.1)$$

Neglecting the uncertainty in the transition frequency of hydrogen [18] gives the following difference between the theoretical and experimental transition frequencies of deuterium:

$$\nu_D(1S_{\frac{1}{2}} - 2S_{\frac{1}{2}})_{exp} - \nu_D(1S_{\frac{1}{2}} - 2S_{\frac{1}{2}})_{th} = 0 \pm 2.1\ kHz. \quad (4.2)$$

Here it is assumed that the experimental and theoretical uncertainties are uncorrelated. Whether this is justified is irrelevant, since we want a conservative estimate. The energy corresponding to 2.1 kHz is given by [15]

$$\Delta E_D(1S_{\frac{1}{2}} - 2S_{\frac{1}{2}}) = 8,69 \cdot 10^{-13}\ eV. \quad (4.3)$$

If the deuteron edm exists, this is the maximum correction to the $1S_{\frac{1}{2}} - 2S_{\frac{1}{2}}$ transition energy it could produce[2]. Therefore, since the Rydberg constant for deuterium is given by [15]

$$R_D = R_\infty \frac{M_D}{m_e + M_D} = 13.6020\ eV, \quad (4.4)$$

it follows that

$$\frac{7}{12}A^2 < 8,69 \cdot 10^{-13}/13.6020 = 6.38576 \cdot 10^{-14} \quad (4.5)$$

[2]To be precise, an edm could maximally produce an energy correction of this order of magnitude. Detailed statistical calculations of the limits found in this section would change them slightly, but would not be of any real consequence.

so that

$$A < 3.31 \cdot 10^{-7} \tag{4.6}$$

and

$$|d_{deuteron}| < \frac{1}{2} e \cdot (3.31 \cdot 10^{-7}) \cdot a_H = 8.8 \cdot 10^{-16}\ e \cdot cm, \tag{4.7}$$

where the Bohr radius is given by $a_H = 0.529 \cdot 10^{-8} cm$.

Another upper limit for the deuteron edm can be determined in a similar vein using the $1S$ Lamb shift. However, the experimental and theoretical values agree only within approximately 0.1 MHz [16]. The resulting upper limit, $\sim 2 \cdot 10^{-14}\ e \cdot cm$, is therefore less stringent than the limit found previously. The $2S$ Lamb shift, i.e. the $2S_{\frac{1}{2}} - 2P_{\frac{1}{2}}$ transition, is of no use since no theoretical value is known in the literature.

As mentioned before, the calculations in this thesis are analogous to Sternheimer's calculations for hydrogen [1]. The improvement in hydrogen spectroscopy and energy level calculation over the past five decades allows for an update of Sternheimer's upper limit for the proton edm. The theoretical and experimental values of the $1S$ Lamb shift by Weitz *et al.* [16] and Bourzeix *et al.* [20] differ approximately 0.3 and 0.15 MHz respectively. Ascribing these differences to the proton edm leads in both cases to an upper limit for the proton edm of approximately $2 \cdot 10^{-14}\ e \cdot cm$. The theoretical and experimental values of the $2S$ Lamb shift by Lundeen and Pipkin [21] differ approximately 0.03 MHz. Ascribing this difference to the proton edm also gives an upper limit of $2 \cdot 10^{-14}\ e \cdot cm$. However, using instead the theoretical value calculated by Jentschura [18] lowers this limit to $1 \cdot 10^{-14} e \cdot cm$. The $1S_{\frac{1}{2}} - 2S_{\frac{1}{2}}$ transition cannot be used, since the theoretical value is by definition equal to the experimental value [18]. Thus, these updated transition frequencies lower Sternheimer's upper limit for the proton edm, $1.30 \cdot 10^{-13} e \cdot cm$, by one order of magnitude. Off course other methods have by now obtained a much lower upper limit. The current limit is $|d_{proton}| < 5 \cdot 10^{-24}\ e \cdot cm$ [6].

5 Discussion

Although the calculated upper limit for the deuteron edm is several orders of magnitude higher than, for instance, the neutron and proton edm, which suggests that the actual deuteron edm is much smaller than the found limit, the current result is a useful first step. Further improvement might be made by searching for an effect that varies linearly with the edm. Muonic deuterium could also be used, since the high mass of the muon increases the Rydberg energy by a factor of 196. This would reduce the upper limit of the edm by a factor 14 ceteris paribus. Unfortunately there are no experimental values of the 2S lamb shift available yet to be compared with the theoretical values calculated by Borie [22]. However, the most promising option to find a deuteron edm is the recently proposed method using a magnetic storage ring and a radial electric field [10] [11].

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Appendices

A First-Order Corrections to the Energy Levels

In this appendix the Wigner-Eckart theorem is used to explain the vanishing of the first-order correction to the energy as mentioned in section 2. The first order correction to the energy is given by [12]

$$E_1 = \int \Psi_0^* H_1 \Psi_0 \mathrm{d}V. \tag{A.1}$$

Since H_1 is a superposition of spherical harmonics with $l = 1$ (cf. Eq. (3.5)), every term in Eq. (A.1) is of the form

$$\int_0^{\pi}\int_0^{2\pi} (Y_l^m)^* Y_1^{m'} Y_l^{m''} \sin\theta \mathrm{d}\theta \mathrm{d}\phi, \tag{A.2}$$

where Y_l^m denotes a spherical harmonic with azimuthal quantum number l and magnetic quantum number m. According to a special case of the Wigner-Eckart theorem, this integral is proportional to either the following Wigner $3j$ symbol [23] [24]:

$$\begin{pmatrix} l & 1 & l \\ 0 & 0 & 0 \end{pmatrix} \tag{A.3}$$

or equivalently to the following Clebsch-Gordan coëfficient: $C(l1l;000)$. Since both are equal to zero, the first order correction to the energy level vanishes.

B Proof of Feinberg's Theorem

In section 3 of his article [1], Sternheimer calculates the values of E_2' for $ns \rightarrow p$, $np \rightarrow s$ and $np \rightarrow d$ (cf. Eq. (2.7) to Eq. (2.11) in this thesis) after solving analytically the corresponding radial perturbations u_1' from Eq. (2.6). Hereby the following property is used, which was noticed by Feinberg [13] and will be proven below:

$$\int_0^{\infty} u_0'(n, l_1) \frac{1}{r^2} u_0'(n, l_2) \mathrm{d}r = 0, \tag{B.1}$$

where $u_0'(n, l_1)$ and $u_0'(n, l_2)$ are any two non-relativistic hydrogenic radial wave functions (multiplied by r), e.g. deuterium wave functions, pertaining to degenerate energy levels with the same n but different l; e.g. $2s$ and $2p$.

Eq. (B.1) follows directly from inserting $E_1 = E_2$ (i.e. $n_1 = n_2$) into the following theorem by Feinberg, which holds for the radial wave functions of the nonrelativistic Schrödinger equation for any central potential $V(r)$ [13]:

$$\int R_1(r)R_2(r)\mathrm{d}r(E_1 - E_2) + [l_2(l_2+1) - l_1(l_1+1)] \times \int R_1(r)R_2(r)\mathrm{d}r = 0, \tag{B.2}$$

where $R_1 = \frac{u_0'(n_1,l_1)}{r}$ and $R_2 = \frac{u_0'(n_2,l_2)}{r}$ are the radial wave functions for two states with energy E_1, E_2 and orbital angular momentum l_1, l_2, respectively. The proof of Eq. (B.2) utilises the following two radial wave equations:

$$\frac{1}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}\Big(r^2\frac{\mathrm{d}R_1}{\mathrm{d}r}\Big) + 2m(E_1 - V)R_1 - \frac{l_1(l_1+1)}{r^2}R_1 = 0, \tag{B.3}$$

$$\frac{1}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}\Big(r^2\frac{\mathrm{d}R_2}{\mathrm{d}r}\Big) + 2m(E_2 - V)R_2 - \frac{l_2(l_2+1)}{r^2}R_2 = 0. \tag{B.4}$$

Subtracting R_1 times Eq. (B.4) from R_2 times Eq. (B.3) gives, after multiplication by r^2,

$$R_2\frac{\mathrm{d}}{\mathrm{d}r}\Big(r^2\frac{\mathrm{d}R_1}{\mathrm{d}r}\Big) - R_1\frac{\mathrm{d}}{\mathrm{d}r}\Big(r^2\frac{\mathrm{d}R_2}{\mathrm{d}r}\Big) + 2m(E_1 - E_2)R_1R_2r^2 + [l_2(l_2+1) - l_1(l_1+1)]R_1R_2 = 0. \tag{B.5}$$

(Partial) integration over r gives

$$r^2\Big(R_2\frac{\mathrm{d}R_1}{\mathrm{d}r} - R_1\frac{\mathrm{d}R_2}{\mathrm{d}r}\Big)\Big|_0^\infty + 2m(E_1 - E_2)\int_0^\infty R_1R_2r^2\mathrm{d}r + [l_2(l_2+1) - l_1(l_1+1)]\int_0^\infty R_1R_2\mathrm{d}r = 0. \tag{B.6}$$

Since $R_i \propto r^{l_i}$ as $r \to 0$ and $R_i \propto \frac{e^{-cr}}{r}$ as $r \to \infty$ where c is a positive constant [12], the first term in Eq. (B.6) vanishes, thereby yielding Feinberg's Theorem, Eq. (B.2). The $2m$ term has accidentally been omitted by Feinberg. This multiplicative term is however irrelevant for our purposes.

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