Note on the Electron EDM

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Abstract

This is a note on the setup of an electron EDM calculation and Schiff's Theorem.

1 Basic Relations

The well-known relativistic interaction of the electron's anomolous magnetic moment $\delta\mu$ with a magnetic field $\boldsymbol{B}$ is given by

$$H_I = -\delta\mu \; \beta \, \boldsymbol{\Sigma} \cdot \boldsymbol{B}.$$

If we now assume that the electron has an electric dipole moment (EDM) d, the corresponding relativistic interaction with an electric field $\boldsymbol{E}$ is given by

$$H_I = -d \; \beta \, \boldsymbol{\Sigma} \cdot \boldsymbol{E}.$$

This term is obviously rotationaly invariant and therefore conserves angular momentum; however, it violates both parity and time-reversal symmetry. Σ is even and E is odd under parity; whereas, Σ is odd and E is even under time reversal. In an external field $\boldsymbol{E}^{\rm ext}$, the many-body Hamiltonian for electrons (charge e and EDM d) is,

$$\begin{aligned} H &= \sum_i \left[h_0(i) + V_{\rm nuc}(i)\right] + \frac{1}{2}\sum_{ij}\frac{e^2}{r_{ij}} - d\sum_i \beta_i\, \boldsymbol{\Sigma}_i \cdot \boldsymbol{E}_i^{\rm int} \\ &- \sum_i \left[e\,\boldsymbol{r}_i + d\,\beta_i\,\boldsymbol{\Sigma}_i\right]\cdot \boldsymbol{E}^{\rm ext}\,. \end{aligned} \tag{1}$$

where

$$e\boldsymbol{E}_i^{\rm int} = -\boldsymbol{\nabla}_i V,$$

with

$$V = \sum_i V_{\rm nuc}(i) + \frac{1}{2}\sum_{ij}\frac{e^2}{r_{ij}}$$

is the electric field at the ith electron. The terms on the first line of Eq. (1) give the modified many-electron Hamiltonian in the absence of external fields, while those on the second line describe the interaction of the atomic electrons with an external electric field.

For an external electric field of strength E in the z direction, the atom-field interaction energy of an atom in a state v with projection $m_v$is

$$\Delta W = -\left\langle v m_v \left| \sum_i \left[e\, z_i + d\, \beta_i\, \Sigma_{3i} \right] \right| v m_v \right\rangle E = -\frac{m_v}{j_v} D E.$$

This equatiom serves to define the atomic dipole moment D. Thus

$$D = \left\langle v j_v \left| \sum_i \left[e\, z_i + d\, \beta_i\, \Sigma_{3i} \right] \right| v j_v \right\rangle . \tag{2}$$

The first term in this expression vanishes when evaluated with wave functions of the unperturbed Hamiltonian because of parity conservation. If we expand the wave function perturbatively, keeping terms of order d, we find that $D = D^{(0)} + D^{(1)}$ with

$$D^{(0)} = d\, \langle v j_v | \sum_i \beta_i\, \Sigma_{3i}\, | v j_v > \tag{3}$$

$$\begin{aligned} D^{(1)} &= d \sum_n \frac{\langle v j_v | \sum_i z_i\ |n\rangle\ \langle n| \sum_i \beta_i \boldsymbol{\Sigma}_i \cdot \boldsymbol{\nabla}_i V\ |v j_v\rangle}{E_v - E_n} \\ &+ d \sum_n \frac{\langle v j_v | \sum_i \beta_i \boldsymbol{\Sigma}_i \cdot \boldsymbol{\nabla}_i V\ |n\rangle\ \langle n| \sum_i z_i\ |v j_v\rangle}{E_v - E_n} . \end{aligned} \tag{4}$$

In the second term, we replace $\boldsymbol{\nabla}_i \rightarrow i\boldsymbol{p}_i$ to find

$$\begin{aligned} D^{(1)} &= id \sum_n \frac{\langle v j_v | \sum_i z_i\ |n\rangle\ \langle n| \left[\sum_i \beta_i \boldsymbol{\Sigma}_i \cdot \boldsymbol{p}_i, V \right]\ |v j_v\rangle}{E_v - E_n} \\ &+ id \sum_n \frac{\langle v j_v | \left[\sum_i \beta_i \boldsymbol{\Sigma}_i \cdot \boldsymbol{p}_i, V \right]\ |n\rangle\ \langle n| \sum_i z_i\ |v j_v\rangle}{E_v - E_n} . \end{aligned}$$

In this expression, we may replace $V = H - H_0$ where

$$H_0 = \sum_j \left[c\, \boldsymbol{\alpha}_j \cdot \boldsymbol{p}_j + \beta\, mc^2 \right].$$

The part of $D^{(1)}$ from H may be evaluated using completeness:

$$\begin{aligned}
D^{(1)}_a &= id \sum_n \Big[\langle vj_v| \sum_j z_j \; |n\rangle \; \langle n| \sum_i \beta_i \boldsymbol{\Sigma}_i \cdot \boldsymbol{p}_i \; |vj_v\rangle \\
&\qquad - \langle vj_v| \sum_i \beta_i \boldsymbol{\Sigma}_i \cdot \boldsymbol{p}_i \; |n\rangle \; \langle n| \sum_j z_j \; |vj_v\rangle \Big] \\
&= id \; \langle vj_v| \; \Big[\sum_j z_j \,, \; \sum_i \beta_i \boldsymbol{\Sigma}_i \cdot \boldsymbol{p}_i \Big] |vj_v\rangle \\
&= -d \; \langle vj_v| \sum_i \beta_i \Sigma_{3i} \, |vj_v\rangle \\
&= -D^{(0)}.
\end{aligned}$$

From this, it follows that the sum $D^{(0)} + D^{(1)}_a = 0$. Therefore, the atomic dipole moment reduces to

$$\begin{aligned}
D &\rightarrow -id \sum_n \frac{\langle vj_v| \sum_j z_j \; |n\rangle \; \langle n| \Big[\sum_i \beta_i \boldsymbol{\Sigma}_i \cdot \boldsymbol{p}_i, H_0 \Big] \; |vj_v\rangle}{E_v - E_n} \\
&+ \; id \sum_n \frac{\langle vj_v| \Big[\sum_i \beta_i \boldsymbol{\Sigma}_i \cdot \boldsymbol{p}_i, H_0 \Big] \; |n\rangle \; \langle n| \sum_j z_j \; |vj_v\rangle}{E_v - E_n}. \qquad (5)
\end{aligned}$$

One can simplify this expression using

$$\begin{aligned}
&\Big[\beta \boldsymbol{\Sigma} \cdot \boldsymbol{p} \,, \, H_0 \Big] \equiv \Big[\beta \boldsymbol{\Sigma} \cdot \boldsymbol{p} \,, \big(c \boldsymbol{\alpha} \cdot \boldsymbol{p} + mc^2 \beta \big) \Big] = \\
&\quad c \left[\begin{pmatrix} \boldsymbol{\sigma} \cdot \boldsymbol{p} & 0 \\ 0 & -\boldsymbol{\sigma} \cdot \boldsymbol{p} \end{pmatrix} \begin{pmatrix} 0 & \boldsymbol{\sigma} \cdot \boldsymbol{p} \\ \boldsymbol{\sigma} \cdot \boldsymbol{p} & 0 \end{pmatrix} - \begin{pmatrix} 0 & \boldsymbol{\sigma} \cdot \boldsymbol{p} \\ \boldsymbol{\sigma} \cdot \boldsymbol{p} & 0 \end{pmatrix} \begin{pmatrix} \boldsymbol{\sigma} \cdot \boldsymbol{p} & 0 \\ 0 & -\boldsymbol{\sigma} \cdot \boldsymbol{p} \end{pmatrix} \right] \\
&\quad + mc^2 \left[\begin{pmatrix} \boldsymbol{\sigma} \cdot \boldsymbol{p} & 0 \\ 0 & -\boldsymbol{\sigma} \cdot \boldsymbol{p} \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} - \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} \boldsymbol{\sigma} \cdot \boldsymbol{p} & 0 \\ 0 & -\boldsymbol{\sigma} \cdot \boldsymbol{p} \end{pmatrix} \right] \\
&\quad = 2cp^2 \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} = 2cp^2 \beta \gamma_5. \qquad (6)
\end{aligned}$$

Here,

$$\gamma_5 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}.$$

We are thereby led to introduce the effective (one-particle) edm Hamiltonian

$$H_{\mathrm{edm}} = -2id \, c \sum_j p_j^2 \, \beta_j \, (\gamma_5)_j = H^\dagger_{\mathrm{edm}} \, .$$

The expression for the atomic dipole moment then takes the form

$$D = \sum_n \frac{\langle vj_v|Z|n\rangle \; \langle n|H_{\mathrm{edm}} \; |vj_v\rangle}{E_v - E_n} + \sum_n \frac{\langle vj_v|H_{\mathrm{edm}} \; |n\rangle \; \langle n|Z \; |vj_v\rangle}{E_v - E_n}, \qquad (7)$$

where

$$Z = \sum_i z_i$$

Since $H_{\rm edm}$ is Hermetian, we may write

$$D = 2 \sum_n \frac{\langle v j_v | Z | n \rangle \; \langle n | H_{\rm edm} \; | v j_v \rangle}{E_v - E_n} .$$

It is worth mentioning that if we replace $\beta \boldsymbol{\Sigma}$ by $\boldsymbol{\Sigma}$ in Eq. (6), which is permissable in nonrelativistic cases, we obtain $\left[\boldsymbol{\Sigma} \cdot \boldsymbol{p} \, , \, H_0 \right] = 0$. Thus, in the nonrelativistic limit, $D = 0$. This is a well-known result referred to as Schiff's theorem.

2 Lowest Approximation

In the lowest order many-body perturbation theory, one may show that for an atom with one electron beyond closed shells,

$$D = 2 \sum_{n > f} \frac{\langle v j_v | z | n \rangle \; \langle n | h_{\rm edm} | v j_v \rangle}{\epsilon_v - \epsilon_n} + 2 \sum_{\substack{a, \, n > f \\ n \neq v}} \frac{\langle a | z | n \rangle \; \langle n | h_{\rm edm} | a \rangle}{\epsilon_a - \epsilon_n} ,$$

where $h_{\rm edm} = -2 i d \, c \, \beta \, \gamma_5 \, p^2$. Sums over closed subshells n in the second term vanish. Therefore, only those terms with n in the partially occupied valence subshell contribute. Summing n over the entire valence subshell and subtracting the term with $n = v$ leads to

$$D = 2 \sum_{n > f} \frac{\langle v j_v | z | n \rangle \; \langle n | h_{\rm edm} | v j_v \rangle}{\epsilon_v - \epsilon_n} - 2 \sum_a \frac{\langle a | z | v j_v \rangle \; \langle v j_v | h_{\rm edm} | a \rangle}{\epsilon_a - \epsilon_n} .$$

Since z and $h_{\rm edm}$ are Hermetian operators, we may re-express the above equation in the form:

$$D = 2 \sum_i \frac{\langle v j_v | z | i \rangle \; \langle i | h_{\rm edm} | v j_v \rangle}{\epsilon_v - \epsilon_i} \; , \qquad (8)$$

where i ranges over all possible one-electron states, both core states a and virtual ststes n.

2.1 Angular Decomposition

We may write

$$\begin{aligned} h_{\rm edm} \; \phi_v(\boldsymbol{r}) \quad &= \quad -2 i \, c \, d \, p^2 \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} \frac{1}{r} \begin{pmatrix} i G_v(r) \; \Omega_{\kappa_v m_v} \\ F_v(r) \; \Omega_{-\kappa_v m_v} \end{pmatrix} \\ &= \quad 2 c \, d \, \frac{1}{r} \left[\begin{array}{c} i \left(\frac{d^2}{dr^2} - \frac{\kappa_v (\kappa_v - 1)}{r^2} \right) F_v(r) \; \Omega_{-\kappa_v m_v} \\ \left(\frac{d^2}{dr^2} - \frac{\kappa_v (\kappa_v + 1)}{r^2} \right) G_v(r) \; \Omega_{\kappa_v m_v} \end{array} \right] \end{aligned}$$

Table 1: Dirac-Hartree-Fock and RPA calculations of shielding factors D/d for alkali-metal atoms and Au.

Atom	State	Z	$D^{\rm DHF}/d$	$D_W^{\rm RPA}/d$	$D_{W+Z}^{\rm RPA}/d$
Li	$2s_{1/2}$	3	0.00297	0.00412	0.00409
Na	$3s_{1/2}$	11	0.241	0.327	0.324
K	$4s_{1/2}$	19	2.00	2.82	2.71
Rb	$5s_{1/2}$	37	19.6	26.6	25.3
Cs	$6s_{1/2}$	55	94.0	126.6	117.9
Au	$6s_{1/2}$	79	326.7	339.6	256.0

The matrix element of $h_{\rm edm}$ is therefore

$$\langle n m_n | h_{\rm edm} | v j_v \rangle = 2c\, d\, \delta_{\kappa_n\, -\kappa_v} \delta_{m_n j_v}\ \langle n \| h_{\rm eff} \| v \rangle, \tag{9}$$

with

$$\langle n \| h_{\rm eff} \| v \rangle = 2\, c\, d \times \int_0^\infty dr \left[G_n \frac{d^2 F_v}{dr^2} - \frac{\kappa_v(\kappa_v - 1)}{r^2} G_n F_v + F_n \frac{d^2 G_v}{dr^2} - \frac{\kappa_v(\kappa_v + 1)}{r^2} F_n G_v \right]. \tag{10}$$

Similarly,

$$\langle v j_v | z | n j_v \rangle = \sqrt{\frac{j_v}{(2j_v+1)(j_v+1)}}\ \langle v \| z \| n \rangle \tag{11}$$

with

$$\langle v \| z \| n \rangle = \langle \kappa_v \| C_1 \| - \kappa_v \rangle \int_0^\infty r dr \left[G_v G_n + F_v F_n \right]. \tag{12}$$

The expression for the atomic dipole moment is therefore

$$D = 2 \sqrt{\frac{j_v}{(2j_v+1)(j_v+1)}}\ \sum_i \frac{\langle v \| z \| i \rangle\ \langle i \| h_{\rm eff} \| v \rangle}{\epsilon_v - \epsilon_i}. \tag{13}$$

In Table 1, we present DHF values of the dipole enhancement factor for alkali-metal atoms. The forth column contains values $D_W^{\rm RPA}/d$ with RPA corrections to matrix elements of $h_{\rm edm}$ and the fifth column contains values $D_{W+Z}^{\rm RPA}/d$ that include RPA corrections to matrix elements of both $h_{\rm edm}$ and z.