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Relativistic corrections to S_{-2} for atomic hydrogen

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Abstract. It is shown that, to order α^2,

$$S_{-2} = \sum_j \frac{|\langle 0|z|j\rangle|^2}{E_j - E_0} = 4{\cdot}499\,752\ldots$$

for the dipole sum over Dirac states of the hydrogen atom. This compares with the value $\frac{9}{2}$ for the sum over Schrödinger states.

1. Introduction

The interaction energy between two ground-state atoms separated by a large distance R is

$$U_7(\mathrm{a},\mathrm{b}) = -\frac{23}{4\pi\alpha}\frac{1}{R^7}S_{-2}(\mathrm{a})S_{-2}(\mathrm{b}). \tag{1}$$

α is the fine-structure constant and distances and energies are measured in atomic units. S_n is defined as the dipole sum

$$S_n = \sum_j (E_j - E_0)^n f_j \tag{2}$$

where

$$f_j = 2(E_j - E_0)|\langle 0|z|j\rangle|^2$$

is the oscillator strength. The potential U_7 in equation (1) is the retarded asymptotic energy calculated by Casimir and Polder (1948) from quantum electrodynamics and replaces at large R the London–van der Waals energy (London 1930)

$$U_6(\mathrm{a},\mathrm{b}) = -\frac{C_6(\mathrm{a},\mathrm{b})}{R^6} \tag{3}$$

which is calculated from Schrödinger wave mechanics.

The calculation of interatomic potentials for two ground-state hydrogen atoms has reached a stage of considerable sophistication and accuracy. Hirschfelder and Meath (1967) give the interaction energy in the region $8a_0$ to $200a_0$ in terms of an asymptotic series in R^{-1}. The energy, again in atomic units, is

$$\begin{aligned} E_{\mathrm{H-H}} = \ldots & -3986(1+0{\cdot}0054)R^{-11} \\ & -(1135+2150)(1+0{\cdot}0049)R^{-10} \\ & -124{\cdot}4(1+0{\cdot}0038)R^{-8} \\ & -6{\cdot}499\,027(1+0{\cdot}002\,723)R^{-6} \\ & +0{\cdot}4628\alpha^2R^{-4} \\ & +(W_3\alpha^2-0{\cdot}3714\alpha^3)R^{-3}+\ldots\,. \end{aligned} \tag{4}$$

The terms are: R^{-11} the third-order dispersion energy dipole–quadrupole–dipole, $-1135R^{-10}$ second-order quadrupole–quadrupole, $-2150R^{-10}$ octupole–dipole, R^{-8} quadrupole–dipole, R^{-6} the London dispersion (equation (3)), R^{-4} mixed dipole–Breit interaction, R^{-3} spin–spin ($W_3 = 0$ for gerade states, $+1$ for ungerade states) and part of the Casimir–Polder potential. The second terms in the brackets, of the order of 0·5%, are mass polarization corrections. One notes that the relativistic corrections are important for powers of R less singular than R^{-6}. The leading London term is now known to seven-figure accuracy (O'Carroll and Sucher 1968), so it is important to know if there are implicit relativistic corrections due to the Dirac nature of the electron clouds as well as those known and due to relativistic–retardation effects. The latter are the terms containing α in equation (4) for the range of R up to $200a_0$. This paper is aimed at improving the accuracy of the coefficients in the intermolecular potentials by finding relativistic corrections to S_{-2}. These are separate correction terms from those arising from the transverse photon exchange in the retardation region.

For atomic hydrogen, as calculated from Schrödinger's equation, S_{-2} is exactly 4·5, corresponding to a polarization $\frac{9}{2}a_0{}^3$. One of the easiest ways of obtaining this is by Dalgarno's method (Dalgarno and Lewis 1955). Here S_{-2} is calculated by the analogue of this method from the Dirac equation for the hydrogen atom. The result differs from 4·5 by terms of the order of $(e^2/\hbar c)^2$ as would be expected, since v^2/c^2 for an electron in a Bohr orbit is of the order of $(e^2/\hbar c)^2$. The calculation gives

$$S_{-2} = 4{\cdot}499\,752\ldots \tag{5}$$

for the case where $m = \frac{1}{2}$ relative to the z axis as defined in equation (3). The ground state of hydrogen $1S_{1/2}$ has quantum numbers $n = 1, l = 0, j = \frac{1}{2}$ with magnetic quantum number $m = \pm\frac{1}{2}$.

2. Method

The method called after Dalgarno is to solve an inhomogeneous differential equation for the perturbed part of the wave function. If χ is square integrable and satisfies

$$(H-E_0)\chi = z\psi_0 \tag{6}$$

where H is the appropriate Hamiltonian, E_0 the ground-state energy and ψ_0 the unperturbed ground-state wave function, then

$$\begin{aligned} S_{-2} &= 2\sum_j \frac{\langle 0|z|j\rangle\langle j|z|0\rangle}{E_j-E_0} \\ &= 2\int \chi^* z\psi_0 \,\mathrm{d}V. \end{aligned} \tag{7}$$

One notes that the square integrable solution of the homogeneous equation $(H-E_0)\chi = 0$ is ψ_0 and this gives no contribution to equation (7). Thus a particular integral of equation (6) is all that is required.

For the Schrödinger equation in atomic units one has

$$\psi_0 = \frac{1}{\sqrt{\pi}}\mathrm{e}^{-r} \tag{8}$$

and

$$\chi = (\tfrac{1}{2}r^2+r)\cos\theta\,\psi_0. \tag{9}$$

So

$$\begin{aligned} S_{-2} &= \frac{2}{\pi}\int\left(\frac{r^2}{2}+r\right)\cos^2\theta\,\mathrm{e}^{-2r}r^3\,\mathrm{d}r\,\mathrm{d}\Omega \\ &= \frac{8}{3}\int\left(\frac{r^5}{2}+r^4\right)\mathrm{e}^{-2r}\,\mathrm{d}r \qquad (10) \\ &= 4{\cdot}5. \qquad (11) \end{aligned}$$

If the substitution

$$\chi = r\cos\theta h(r)\psi_0 \tag{12}$$

is made for χ in equation (6) the ordinary differential equation for $h(r)$ is

$$rh''+(4-2r)h'-2h = -2r. \tag{13}$$

Equation (13) has the general solution

$$h(r) = \frac{r}{2}+1+A\frac{e^{2r}}{r^3}+B\left(\frac{2}{r}+\frac{2}{r^2}+\frac{1}{r^3}\right). \tag{14}$$

If the A term is used in χ the integral equation (7) diverges. Although the B term if used in χ gives a finite value for this integral, the corresponding χ is not square integrable. One knows in fact that there are no square integrable solutions of the homogeneous equation corresponding to equation (13) or else there would be a p state of hydrogen with energy E_0. Hence the only well-behaved solution of equation (13) is $\frac{1}{2}r+1$, which corresponds to the result for χ used in equation (9).

For the Dirac equation, with $m = +\frac{1}{2}$,

$$\psi_0 = \begin{bmatrix} Y_0{}^0(\theta,\phi)g(r) \\ 0 \\ -\mathrm{i}\sqrt{\tfrac{1}{3}}\; Y_1{}^0(\theta,\phi)f(r) \\ -\mathrm{i}\sqrt{\tfrac{2}{3}}\; Y_1{}^1(\theta,\phi)f(r) \end{bmatrix} \tag{15}$$

where

$$g(r) = 2^\gamma\left\{\frac{1+\gamma}{\Gamma(2\gamma+1)}\right\}^{1/2} e^{-r}r^{\gamma-1} \tag{16}$$

$$f(r) = -\frac{\alpha}{1+\gamma}g(r) \tag{17}$$

and

$$\gamma = (1-\alpha^2)^{1/2} \tag{18}$$

and again, exactly as before,

$$S_{-2} = 2\int \tilde{\chi}^* Q\,\mathrm{d}V \tag{19}$$

where

$$Q = z\psi_0, \text{ and } \tilde{\chi} \text{ is the transpose of } \chi. \tag{20}$$

The analogue of equation (6) is now the set of coupled differential equations

$$(\boldsymbol{\alpha}\,.\,\boldsymbol{p}c+\beta mc^2+V-E_0)\chi = Q \tag{21}$$

where $\boldsymbol{\alpha}$, β are the Dirac matrices. It is not difficult to separate out the angular behaviour of the spinor χ (see Brown *et al.* 1955). There are two four-spinors, both behaving as $zY_0{}^0$ in their first elements:

$$\chi^{(1)} = \begin{bmatrix} \sqrt{\tfrac{2}{3}}\,Y_1{}^0\,\mathscr{G}^{(1)}(r) \\ -\sqrt{\tfrac{1}{3}}\,Y_1{}^1\,\mathscr{G}^{(1)}(r) \\ -\mathrm{i}\sqrt{\tfrac{2}{5}}\,Y_2{}^0\mathscr{F}^{(1)}(r) \\ -\mathrm{i}\sqrt{\tfrac{3}{5}}\,Y_2{}^1\mathscr{F}^{(1)}(r) \end{bmatrix} \tag{22}$$

and

$$\chi^{(2)} = \begin{bmatrix} -\sqrt{\tfrac{1}{3}}\,Y_1{}^0\,\mathscr{G}^{(2)}(r) \\ \sqrt{\tfrac{2}{3}}\,Y_1{}^1\,\mathscr{G}^{(2)}(r) \\ -\mathrm{i}\,Y_0{}^0\mathscr{F}^{(2)}(r) \\ 0 \end{bmatrix}. \tag{23}$$

The solution χ can be written

$$\chi = \chi^{(1)}+\chi^{(2)} = \mathscr{G}^{(1)}q_+{}^{(1)}+\mathscr{G}^{(2)}q_+{}^{(2)}+\mathscr{F}^{(1)}q_-{}^{(1)}+\mathscr{F}^{(2)}q_-{}^{(2)}$$

where $q_\pm^{(1)}$, $q_\pm^{(2)}$ are spherical spinors, and $q_\pm^{(1)}$ has angular momentum $j = \frac{1}{2}$ and $q_\pm^{(2)}$ has $j = \frac{3}{2}$. The coupled equations for the radial functions $\mathscr{F}$ and $\mathscr{G}$ are

$$\left(\frac{d}{dr}+\frac{3}{r}\right)\mathscr{F}^{(1)}+(E_0-V-mc^2)\,\mathscr{G}^{(1)} = -\left(\frac{3}{2}\right)^{1/2}\int (Y_1{}^0)^*Q_1\,d\Omega = -rg(r)\frac{\sqrt{2}}{3} \tag{24}$$

$$\left(\frac{d}{dr}-\frac{1}{r}\right)\mathscr{G}^{(1)}+(E_0-V+mc^2)\mathscr{F}^{(1)} = i\left(\frac{5}{2}\right)^{1/2}\int (Y_2{}^0)^*Q_3\,d\Omega = rf(r)\frac{\sqrt{2}}{3} \tag{25}$$

together with

$$\frac{d}{dr}\mathscr{F}^{(2)}+(E_0-V-mc^2)\,\mathscr{G}^{(2)} = -\tfrac{1}{3}rg(r) \tag{26}$$

$$\left(\frac{d}{dr}+\frac{2}{r}\right)\mathscr{G}^{(2)}-(E_0+V+mc^2)\mathscr{F}^{(2)} = \tfrac{1}{3}rf(r). \tag{27}$$

In terms of the functions $\mathscr{F}^{(1)}$, $\mathscr{G}^{(1)}$, $\mathscr{F}^{(2)}$ and $\mathscr{G}^{(2)}$ the required sum is

$$S_{-2} = \tfrac{2}{3}\int \{\mathscr{G}^{(1)*}rg(r)\sqrt{2}+\mathscr{F}^{(1)*}rf(r)\sqrt{2}+\mathscr{G}^{(2)*}rg(r)+\mathscr{F}^{(2)*}rf(r)\}r^2\,dr \tag{28}$$

after the angular integrations are carried out. Equation (28) is the analogue to equation (10) in the non-relativistic theory.

3. The radial equations

The radial equations (24)–(27) are simplified by the substitutions

$$\mathscr{F} = 2\left\{\frac{1+\gamma}{\Gamma(2\gamma+1)}\right\}^{1/2}\lambda(r), \qquad \mathscr{G} = 2\left\{\frac{1+\gamma}{\Gamma(2\gamma+1)}\right\}^{1/2}\mu(r) \tag{29}$$

when the explicit forms for f and g (equations (16) and (17)) are substituted on the right-hand sides of equations (24)–(27). Changing the variable to x and inserting the values of m, E_0 and V, namely

$$mc^2 = \frac{1}{\alpha}\hbar c a_0{}^{-1}$$
$$E_0 = \frac{\gamma}{\alpha}\hbar c a_0{}^{-1} \tag{30}$$
$$V = -\frac{\alpha}{x}\hbar c a_0{}^{-1}$$

the radial equations (24) and (25) become

$$\left(\frac{d}{dx}+\frac{3}{x}\right)\lambda^{(1)}(x)+\left(\frac{\gamma-1}{\alpha}+\frac{\alpha}{x}\right)\mu^{(1)}(x) = -\frac{\sqrt{2}}{3}x\,e^{-x}(2x)^{\gamma-1} \tag{31}$$

$$\left(\frac{d}{dx}-\frac{1}{x}\right)\mu^{(1)}(x)-\left(\frac{\gamma+1}{\alpha}+\frac{\alpha}{x}\right)\lambda^{(1)}(x) = -\frac{\alpha}{1+\gamma}\frac{\sqrt{2}}{3}x\,e^{-x}(2x)^{\gamma-1} \tag{32}$$

and the radial equations (26) and (27) become

$$\frac{d}{dx}\lambda^{(2)}(x)+\left(\frac{\gamma-1}{\alpha}+\frac{\alpha}{x}\right)\mu^{(2)}(x) = -\frac{x}{3}e^{-x}(2x)^{\gamma-1} \tag{33}$$

$$\left(\frac{d}{dx}+\frac{2}{x}\right)\mu^{(2)}(x)-\left(\frac{\gamma+1}{\alpha}+\frac{\alpha}{x}\right)\lambda^{(2)}(x) = -\frac{\alpha}{1+\gamma}\frac{x}{3}e^{-x}(2x)^{\gamma-1}. \tag{34}$$

Further simplification follows from the substitutions

$$\lambda = x^{-1}\,\mathrm{e}^{-x}\,\frac{F+G}{2} \tag{35}$$

$$\mu = -\frac{1+\gamma}{\alpha}\,x^{-1}\,\mathrm{e}^{-x}\,\frac{F-G}{2}. \tag{36}$$

The four equations for the new F's and G's are

$$\frac{\mathrm{d}F^{(1)}}{\mathrm{d}x}+3\frac{G^{(1)}}{x}-\gamma\frac{F^{(1)}}{x} = -\frac{2^{\gamma+\frac{1}{2}}\gamma}{3(1+\gamma)}\,x^{\gamma+1} \tag{37}$$

$$\frac{\mathrm{d}G^{(1)}}{\mathrm{d}x}+\frac{F^{(1)}}{x}+\gamma\frac{G^{(1)}}{x}-2G^{(1)} = -\frac{2^{\gamma+\frac{1}{2}}}{3(1+\gamma)}\,x^{\gamma+1} \tag{38}$$

$$\frac{\mathrm{d}F^{(2)}}{\mathrm{d}x}-\gamma\frac{F^{(2)}}{x} = -2^{\gamma}\frac{\gamma}{3(1+\gamma)}\,x^{\gamma+1} \tag{39}$$

and

$$\frac{\mathrm{d}G^{(2)}}{\mathrm{d}x}-2\frac{F^{(2)}}{x}+\gamma\frac{G^{(2)}}{x}-2G^{(2)} = -\frac{2^{\gamma}}{3(1+\gamma)}\,x^{\gamma+1}. \tag{40}$$

In terms of these functions the required sum S_{-2} becomes

$$S_{-2} = S_{-2}^{(1)}+S_{-2}^{(2)} \tag{41}$$

where

$$S_{-2}^{(1)} = -\frac{2^{\gamma+\frac{5}{2}}}{3}\,\frac{1+\gamma}{\Gamma(2\gamma+1)}\int_0^{\infty}\left(F^{(1)}-\gamma G^{(1)}\right)\mathrm{e}^{-2x}\,x^{\gamma+1}\,\mathrm{d}x \tag{42}$$

and

$$S_{-2}^{(2)} = -\frac{2^{\gamma+2}}{3}\,\frac{1+\gamma}{\Gamma(2\gamma+1)}\int_0^{\infty}\left(F^{(2)}-\gamma G^{(2)}\right)\mathrm{e}^{-2x}\,x^{\gamma+1}\,\mathrm{d}x. \tag{43}$$

4. Solutions for $F^{(2)}$, $G^{(2)}$ and evaluation of $S_{-2}^{(2)}$

The equations for the $\chi^{(2)}$ part of the perturbed wave function have much simpler solutions than the equations for the $\chi^{(1)}$ part. This is because the substitutions (35) and (36) have decoupled $F^{(2)}$ from $G^{(2)}$, as can be seen in the form of equation (39). The particular solutions required are

$$F^{(2)} = -\frac{2^{\gamma-1}}{3}\,\frac{\gamma}{1+\gamma}\,x^{\gamma+2}+\frac{2^{\gamma-2}}{3}\,\gamma(2\gamma+1)x^{\gamma} \tag{44}$$

and

$$G^{(2)} = \frac{2^{\gamma-1}}{3}\,x^{\gamma+1}+\frac{2^{\gamma-2}}{3}(2\gamma+1)x^{\gamma}. \tag{45}$$

The non-relativistic limit is obtained by letting $\gamma\to 1$ $(\alpha\to 0)$. In equation (43) one sees that the combination $F-G$ survives in this limit; in fact

$$F^{(2)}-\gamma G^{(2)}\to F_0^{(2)}-G_0^{(2)} = -\frac{1}{3}\left(\frac{x^3}{2}+x^2\right). \tag{46}$$

Thus

$$S_{-2}^{(2)}\to\frac{1}{3}\times\frac{8}{3}\int\left(\frac{x^5}{2}+x^4\right)\mathrm{e}^{-2x}\,\mathrm{d}x \tag{47}$$

$$=\frac{1}{3}\times(\text{non-relativistic } S_{-2}\text{, equation (10)}). \tag{48}$$

We shall see in § 5 that the contribution of the (1) part of the perturbed wave function is $\frac{2}{3}$ of the non-relativistic S_{-2} as given in equation (10).

It is not difficult to compute the exact value of $S_{-2}{}^{(2)}$. Inserting equations (44) and (45) into equation (43) and integrating gives

$$S_{-2}{}^{(2)} = \frac{\gamma(\gamma+1)(2\gamma+1)(4\gamma+5)}{36} \tag{49}$$

$$\simeq \frac{3}{2} - \frac{47}{24}\alpha^2. \tag{50}$$

5. Solutions for $S_{-2}{}^{(1)}$ and S_{-2} to order α^2

Equations (37) and (38) are two inhomogeneous coupled equations for $F^{(1)}$ and $G^{(1)}$ and they cannot be solved so simply as the equations for $F^{(2)}$ and $G^{(2)}$. By elimination it is possible to find second-order inhomogeneous equations for $F^{(1)}$ and $G^{(1)}$ separately. They are

$$x^2\frac{d^2F^{(1)}}{dx^2} - x(2x-1)\frac{dF^{(1)}}{dx} - \{(4-\alpha^2)-2\gamma x\}F^{(1)}$$

$$= 2^{\gamma+\frac{1}{2}}\frac{3-2\gamma-2\gamma^2}{3(1+\gamma)}x^{\gamma+2} + \frac{2^{\gamma+\frac{3}{2}}\gamma}{3(1+\gamma)}x^{\gamma+3} \tag{51}$$

and

$$x^2\frac{d^2G^{(1)}}{dx^2} - x(2x-1)\frac{dG^{(1)}}{dx} - \{4-\alpha^2+2(1-\gamma)x\}G^{(1)} = -2^{\gamma+\frac{1}{2}}\frac{2-\gamma}{3(1+\gamma)}x^{\gamma+2}. \tag{52}$$

These equations have been investigated by one of us (Bartlett 1969). The particular integrals which are obtained by a series method are combinations of generalized hypergeometric functions ${}_2F_2(\alpha_1, \alpha_2; \beta_1, \beta_2; 2x)$ which are exponentially increasing at infinity. So, in this case, a contribution is required from the complementary functions which are confluent hypergeometric functions. However, the non-relativistic equations, obtained by letting $\gamma \to 1$, namely

$$x^2\frac{d^2F_0{}^{(1)}}{dx^2} - x(2x-1)\frac{dF_0{}^{(1)}}{dx} - (4+2x)F_0{}^{(1)} = -\frac{\surd 2}{3}x^3 + 2\frac{\surd 2}{3}x^4 \tag{53}$$

and

$$x^2\frac{d^2G_0{}^{(1)}}{dx^2} - x(2x-1)\frac{dG_0{}^{(1)}}{dx} - 4G_0{}^{(1)} = -\frac{\surd 2}{3}x^3 \tag{54}$$

have the simple particular solutions

$$F_0{}^{(1)} = -\frac{\surd 2}{6}x^3 - \frac{\surd 2}{4}x^2 \tag{55}$$

$$G_0{}^{(1)} = \frac{\surd 2}{12}x^2. \tag{56}$$

From these the non-relativistic contribution to $S_{-2}{}^{(1)}$, equation (42), can be found, namely

$$S_{-2}{}^{(1)} \to \frac{2}{3}\times\frac{8}{3}\int\left(\frac{x^5}{2} - x^4\right)e^{-2x}\,dx \tag{57}$$

$$= \frac{2}{3}\times(\text{non-relativistic } S_{-2}, \text{ equation (10)}). \tag{58}$$

It follows from equations (42) and (43) that the only combination of F's and G's required is $F-\gamma G$. In fact if

$$H = F^{(1)} - \gamma G^{(1)} \tag{59}$$

then

$$S_{-2}^{(1)} = -\frac{(1+\gamma)2^{\gamma+\frac{5}{2}}}{3\Gamma(2\gamma+1)}\int_0^\infty H(x)\,\mathrm{e}^{-2x}x^{\gamma+1}\,\mathrm{d}x. \tag{60}$$

If we eliminate $F^{(1)}$ in favour of H the differential equations (37) and (38) become

$$\frac{\mathrm{d}G}{\mathrm{d}x}+\frac{H}{x}+2\gamma\frac{G}{x}-2G = dx^{\gamma+1} \tag{61}$$

and

$$\frac{\mathrm{d}H}{\mathrm{d}x}-2\gamma\frac{H}{x}+\frac{3(1-\gamma^2)G}{x}+2\gamma G = 0 \tag{62}$$

where

$$d = -\frac{2^{\gamma+\frac{1}{2}}}{3}\frac{1}{1+\gamma}. \tag{63}$$

We note that equation (62) is homogeneous. Finally, the substitution

$$H(x) = dx^{\gamma+1}h(x) \tag{64}$$

gives for the differential equation for $h(x)$

$$xh''+\left\{3+2\gamma-2x-\frac{2^\gamma x}{3(1-\gamma^2)+2\gamma x}\right\}h' + \left\{-2-\frac{2(1-\gamma)}{x}-\frac{2\gamma(1-\gamma)}{3(1-\gamma^2)+2\gamma x}\right\}h = -3(1-\gamma^2)-2\gamma x. \tag{65}$$

Since it is sufficient, because α^2 is so small, to find the corrections to S_{-2} of order α^2 a perturbation approach was made in order to find the appropriate solution to this equation. When $\gamma \to 1$ the differential equation becomes

$$xh_0''+h_0'(4-2x)-2h_0 = -2x \tag{66}$$

in complete analogy to equation (13) in the non-relativistic theory. The non-relativistic solution with the correct boundary conditions is

$$h_0 = \frac{x}{2}+1 \tag{67}$$

and equation (65) was solved to find the next term in α^2 by making the substitution

$$h = h_0+\alpha^2\phi(x) \tag{68}$$

and keeping terms in α^2. The solution which does not get exponentially large at infinity and is square integrable with the appropriate weight as in equation (60) is

$$\phi(x) = -\frac{9}{32}\frac{1}{x^3}+\frac{3}{16}\frac{1}{x^2}+\frac{3}{8}-\frac{x}{4}-\frac{3}{16}\left(\frac{1}{x^3}+\frac{2}{x^2}+\frac{2}{x}\right)\left(\ln 2x+C-\frac{3}{2}\right)-\frac{3}{16}\frac{\mathrm{e}^{2x}}{x^3}E_1(2x). \tag{69}$$

$E_1(2x)$ is the exponential integral

$$E_1(2x) = -C-\ln 2x-\sum_{n=1}^{\infty}(-1)^n\frac{(2x)^n}{n\times n!} \tag{70}$$

and C is Euler's constant. Thus, to order α^2,

$$S_{-2}^{(1)} \simeq \frac{2^{5-\alpha^2}}{9\Gamma(3-\alpha^2)} \int_0^\infty \left\{\frac{x}{2} + 1 + \alpha^2\phi(x)\right\} e^{-2x} x^{4-\alpha^2}\, dx \tag{71}$$

$$\simeq 3 - \frac{65}{24}\alpha^2. \tag{72}$$

Finally, collecting the two contributions $S_{-2}^{(1)}$, equation (72), and $S_{-2}^{(2)}$, equation (50), the required value of S_{-2} is

$$S_{-2} = 4{\cdot}5\left(1 - \frac{28}{27}\alpha^2\right)$$

$$= 4{\cdot}499\,752\ldots\,. \tag{73}$$

S_{-3} is also calculable by this method and again the result differs by terms of the order of α^2 for the Dirac equation from the value 10·75 for the Schrödinger equation.

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