# CHAPTER 1

## Theory of Helium Fine Structure for the Determination of $\alpha$

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Recent advances in the application of effective field theory to the helium atom have allowed the calculation of all contributions up to order $m\alpha^7$ to the fine structure of $2^3P_J$ states along with recoil corrections up to order $m\alpha^6\frac{m}{M}$. Combined with very precise experiments these calculations allow a determination of the fine structure constant $\alpha$. The derivation of $\alpha$ from helium fine structure, while not at present competitive in accuracy with the value of $\alpha$ available from electron $g$-2, has a very different dependence on theory. A discrepancy with another calculation and directions for future progress are discussed.

### 1. Introduction

The fine structure constant, $\alpha = \frac{e^2}{4\pi\epsilon_0\hbar c} \approx 1/137$, was introduced in 1916 by Sommerfeld [1], who made Bohr's derivation of hydrogen energy levels consistent with relativistic theory. He showed that the nonrelativistic degeneracy of energy levels for a given principal quantum number $n$ is partially removed by relativistic effects. Specifically, the first two terms in the Taylor expansion in $Z\alpha$ of his formula for energy levels, later rigorously derived from the Dirac equation, are

$$E(n,j) = -\frac{m(Z\alpha)^2}{2n^2} - \frac{m(Z\alpha)^4}{2n^3}\left[\frac{1}{j+1/2} - \frac{3}{4n}\right]. \tag{1}$$

We note they depend only on the total angular momentum $j$, but not on spin or orbital angular momentum. Here we introduce a convention of keeping the nuclear charge $Z$ general, which is useful for distinguishing loop corrections, which go as $\alpha^n$, from 'binding corrections', which scale as powers of $Z\alpha$. If this were the exact equation for the energy, and one had an accurate measurement of a splitting, one could use that measurement to deduce the value of $\alpha$ from atomic spectroscopy as the Rydberg constant

$$R_\infty = \frac{\alpha^2 m_e c}{2h} \tag{2}$$

is known with very high precision. An example we will concentrate on in the following is the frequency associated with the splitting $\Delta E$ between the $2p_{1/2}$ and $2p_{3/2}$ states in hydrogen, $\nu_0 \equiv \alpha^2 R_\infty c/16$. The most accurate direct experimental determination of this frequency is [2]

$$\nu(\mathrm{exp}) = \frac{\Delta E}{h} = 10\ 969.13(10)\,\mathrm{MHz}. \tag{3}$$

One can then solve for $\alpha_0$, the value of the fine structure constant in the infinite nuclear mass limit and with the neglect of relativistic and Quantum Electrodynamic (QED) corrections, through

$$\alpha_0^2 = \frac{16\nu(\mathrm{exp})}{R_\infty c}. \tag{4}$$

Using the CODATA value [3]

$$R_\infty c = 3.289\ 841\ 960\ 361(22)\ 10^9\ \mathrm{MHz} \tag{5}$$

then gives

$$\alpha_0^{-1}(\mathrm{H}) = 136.911\ 97(62). \tag{6}$$

In the first part of this chapter we describe an effective field theory approach, later generalized to the helium problem, that allows the systematic calculation of corrections associated with the finite mass of the nucleus, relativistic, and QED corrections up to order $\alpha^3\nu_0$, and show that their inclusion shifts this value of the fine structure constant to

$$\alpha^{-1}(\mathrm{H}) = 137.035\ 45(62). \tag{7}$$

In general there are both theory and experimental sources of errors, but in this case the uncertainty associated with uncalculated theoretical terms is negligible compared to the error coming from the experiment. This value of the fine structure constant is consistent with the most accurately known value of $\alpha$ at present,

$$\alpha^{-1}(g{-}2) = 137.035\ 999\ 084(51). \tag{8}$$

This value is determined from the measurement of the electron anomalous magnetic moment $a_e$ by Hanneke *et. al.* [4] ,

$$a_e = 0.001\ 159\ 652\ 180\ 73(28), \tag{9}$$

together with the recently revised four loop calculation by Kinoshita and collaborators [5]. The 4.5 ppm determination of $\alpha$ from hydrogen is much less precise than the 0.37 ppb value from $g$-2 because of the short lifetime of hydrogenic $2p$ states, of order $10^{-9}$ seconds. We note in passing that determinations of $\alpha$ that require much less QED calculations and are approaching the accuracy of the g-2 measurement are available from recoil measurements on rubidium [6] and cesium [7].

We now describe the corrections for hydrogen fine structure in some detail, as a similar approach will be used for the helium calculation, and in addition some contributions carry over to the latter case. We begin by describing how the corrections are categorized by size, and will then describe the actual calculation using an effective field theory. There are three expansion parameters in the bound state problem, the ratio of the electron mass to the nuclear mass, $\frac{m}{M}$, the fine structure constant $\alpha$, and $Z\alpha$. Any correction of order $\frac{m}{M}$ or higher will be called a recoil correction. As mentioned above, there are two sources of corrections of order $\alpha^n$, one without a factor of $Z$ that is associated with the number of photon-electron vertices, and one with that factor, associated with photon-nucleus vertices. A characteristic difficulty of applying QED to bound states is the fact that one sometimes encounters infinite sets of Feynman diagrams that all contribute to the same order in $Z\alpha$. Technically this comes from diagrams in which adding a photon exchange between the electron and nucleus, which nominally is down by a factor $(Z\alpha)^2$, stays the same order because the extra electron propagator is almost on mass shell and gives an inverse factor of $(Z\alpha)^2$. This is the case with the leading QED correction, which begins in order $m\alpha(Z\alpha)^4$. While the term 'Lamb shift' is sometimes used only for the $2s_{1/2} - 2p_{1/2}$ splitting in hydrogen, in the following we will refer to any QED contribution that starts in this order as a Lamb shift. While part of the Lamb shift is associated with one loop diagrams with free electron propagators, the so-called 'Bethe log' term involves an infinite set of diagrams which fortunately can be rewritten as a closed form expression with a bound electron propagator. Binding corrections to the one-loop Lamb shift of order $m\alpha(Z\alpha)^n$ have been carried out to $n = 6$ [8] and of the two-loop Lamb shift of order $m\alpha^2(Z\alpha)^n$ to $n = 5$ [9]. In addition the three-loop Lamb shift without binding corrections, which is of order $m\alpha^3(Z\alpha)^4$, has been evaluated [10]. At $Z = 1$ these orders are of course all $m\alpha^7$. Significant progress has been made on even higher orders from numerical evaluations of the one-loop Lamb shift [11] , effective field theory treatment of the two-loop Lamb shift [12], and numerical evaluation of the two-loop Lamb shift [13], but at this point we simply wish to stress that it has been a major effort to reach the $m\alpha^7$ level in hydrogen. It is only very recently that the same level has been reached for fine structure in helium using effective field theory [14], and the main purpose of this chapter is to describe this calculation. We note that a Bethe-Salpeter approach that claims the same accuracy has been used by Zhang [15], but our results differ from his significantly, as will be discussed in the conclusion.

As we will be using the tool of effective field theory to carry out the more challenging helium calculation, it is useful to introduce it in the simpler hydrogenic case. The basic idea of effective field theory is to represent various corrections to energies in terms of effective operators, the expectation values of which are evaluated with Schrödinger wave functions. There are various ways to obtain these operators. A particularly powerful method used for calculating the $m\alpha^7$ terms involves the Foldy-Wouthuysen transformation [16], but for the derivation of lower order terms we use a method based on considerations involving the scattering of free particles.

In this approach we carry out a matching procedure, where we first calculate scattering amplitudes of low velocity on-shell particles using QED. We then introduce an effective theory that has perturbations added to a nonrelativistic starting point that are determined by requiring that the two scattering amplitudes agree up to a given order in the velocities. We work in the center of mass system, so that if the incoming electron has momentum $\vec{p}_{\rm i}$ the incoming nucleus has momentum $-\vec{p}_{\rm i}$, and similarly if the outgoing electron is taken to have momentum $\vec{p}_{\rm f}$ the outgoing nucleus has momentum $-\vec{p}_{\rm f}$. The hydrogen fine structure problem is complicated by the presence of the proton spin, but at the level of accuracy of the experiment it is a valid approximation to ignore it, so in the following we will drop any terms depending on $\vec{\sigma}_p$ and write $\vec{\sigma}$ for the electron spin $\vec{\sigma}_e$.

The most appropriate gauge for this problem is Coulomb gauge, though Feynman gauge can be used for the QED part of the calculation providing a gauge invariant set of graphs is considered. If we start with an electron scattering on a nucleus, use of free Dirac spinors, normalized so that $u^\dagger u = 1$,

$$u(\vec{p}) = \sqrt{\frac{E+m}{2E}} \begin{pmatrix} 1 \\ \frac{\vec{\sigma}\cdot\vec{p}}{E+m} \end{pmatrix} \tag{10}$$

with $E = \sqrt{\vec{p}^{\,2} + m^2}$ gives for Coulomb photon exchange the following scattering amplitude,

$$\begin{aligned} \mathcal{M}_C(\vec{p}_{\rm f}, \vec{p}_{\rm i}) &= -\frac{4\pi Z\alpha}{\vec{q}^{\,2}} u^\dagger(p_{\rm f}) u(p_{\rm i}) \\ &= -\frac{4\pi Z\alpha}{\vec{q}^{\,2}} \left[ 1 - \frac{\vec{q}^{\,2}}{8m^2} + i\frac{\vec{\sigma}\cdot\vec{p}_{\rm f}\times\vec{p}_{\rm i}}{4m^2} + \frac{5}{128m^4}({p_{\rm f}}^2 - {p_{\rm i}}^2)^2 \right. \\ &\quad \left. + \frac{3}{64m^4}({p_{\rm f}}^2 + {p_{\rm i}}^2)(\vec{q}^{\,2} - 2i\vec{\sigma}\cdot\vec{p}_{\rm f}\times\vec{p}_{\rm i}) \right] + \ldots\ . \end{aligned} \tag{11}$$

Here $\vec{q} = \vec{p}_{\rm f} - \vec{p}_{\rm i}$ and we have made a Taylor expansion assuming $|\vec{p}_{\rm i}|/m << 1$ and $|\vec{p}_{\rm f}|/m << 1$. The nucleus has similar Dirac spinors, but their effect for Coulomb photon exchange enters in order $1/M^2$ and can be neglected. We can also account for the leading QED correction by making the replacement

$$\gamma_\mu \to \gamma_\mu F_1(q^2) + i\frac{\sigma_{\mu\nu}q^\nu}{2m} F_2(q^2), \tag{12}$$

with $q_0 \equiv E(\vec{p}_{\rm f}) - E(\vec{p}_{\rm i})$ and $\sigma_{\mu\nu} \equiv \frac{i}{2}[\gamma_\mu, \gamma_\nu]$. Note that $q_0$ is of order $\vec{p}^{\,2}/m$ so that $q^2 \approx -\vec{q}^{\,2}$. The one-loop form factor $F_2$ has the low $q^2$ expansion

$$F_2(q^2) = \frac{\alpha}{2\pi} + \frac{\alpha}{\pi}\frac{q^2}{12m^2} + \ldots\ . \tag{13}$$

The expansion of $F_1$ involves an infrared divergence that will be treated later, but its lowest order value is of course 1. If we make the approximation $F_2(q^2) = \frac{\alpha}{2\pi}$ and again consider only Coulomb photon exchange, a simple calculation shows that the $F_1$ term reproduces Eq. (11), and that the $F_2$ term gives

$$\begin{aligned} \mathcal{M}^{(0)}_{C(a_e)}(\vec{p}_{\rm f}, \vec{p}_{\rm i}) &= -\frac{4\pi Z\alpha}{\vec{q}^{\,2}} \bar{u}(p_{\rm f}) \frac{-i\sigma_{0j}q_j}{2m} u(p_{\rm i}) \frac{\alpha}{2\pi} \\ &= \frac{4\pi Z\alpha}{\vec{q}^{\,2}} \left[ \frac{\vec{q}^{\,2}}{4m^2} - i\frac{\vec{\sigma}\cdot\vec{p}_{\rm f}\times\vec{p}_{\rm i}}{2m^2} \right] \frac{\alpha}{2\pi}. \end{aligned} \tag{14}$$

Comparing this contribution with the lowest order one, we see that we can combine them by inserting a factor $1 + 2\frac{\alpha}{2\pi}$ in both the spin-independent part, which is the Darwin term, and in the spin dependent part, the spin-orbit term. In fact, we can automatically account for an infinite set of terms by making the replacement $\frac{\alpha}{2\pi} \to a_e$, since we know $F_2(0) = a_e$, and in the following we will always follow this convention. We observe that this practice eliminates a small $\alpha$ dependence of the theoretical fine structure that would arise if one used the theoretical expansion of $a_e$ in powers of $\alpha$ instead of the accurately known [4] experimental value $a_e$. We also note two higher order corrections from the $F_2$ vertex,

$$\begin{aligned}\mathcal{M}^{(2)}_{C(a_e)}(\vec{p}_{\rm f}, \vec{p}_{\rm i}) = \frac{4\pi Z\alpha}{\vec{q}^{\,2}} \frac{a_e}{32m^4}\Big[&-3p_{\rm i}^4 - 3p_{\rm f}^4 + 4(p_{\rm i}^2 + p_{\rm f}^2)\vec{p}_{\rm f}\cdot\vec{p}_{\rm i} \\ &- 2p_{\rm i}^2 p_{\rm f}^2 + 4i(p_{\rm i}^2 + p_{\rm f}^2)\vec{\sigma}\cdot\vec{p}_{\rm f}\times\vec{p}_{\rm i}\Big] - \frac{\alpha Z\alpha}{3m^2}\Big[\frac{\vec{q}^{\,2}}{4m^2} \\ &- \frac{i\vec{\sigma}\cdot\vec{p}_{\rm f}\times\vec{p}_{\rm i}}{2m^2}\Big],\end{aligned} \tag{15}$$

where the first correction comes from expanding the Dirac spinors further in velocities and the second from the second term in $F_2(q^2)$. In the bound state problem $p/m \propto Z\alpha$, so both these corrections will lead to $\alpha(Z\alpha)^2$ corrections to fine structure, that is, they will contribute in order $m\alpha(Z\alpha)^6$.

Turning now to transverse photon exchange, we note that the Dirac spinors of the nucleus must now be treated, and the net result will be a recoil effect, as a single power of the nuclear mass $M$ is present in the denominator. The diagram leads to a scattering amplitude

$$\begin{aligned}\mathcal{M}_T(\vec{p}_{\rm f}, \vec{p}_{\rm i}) &= -\frac{2\pi Z\alpha}{Mq^2}(p_{\rm i} + p_{\rm f})_i\left(\delta_{ij} - \frac{q_i q_j}{\vec{q}^{\,2}}\right)\bar{u}(p_{\rm f})\gamma_j u(p_{\rm i}) \\ &\equiv -\frac{2\pi Z\alpha}{Mq^2}(p_{\rm i} + p_{\rm f})_i P_{ij}(q)\bar{u}(p_{\rm f})\gamma_j u(p_{\rm i}),\end{aligned} \tag{16}$$

where, as discussed above, terms involving the spin of the proton have been suppressed. Again expanding in powers of momentum divided by mass and keeping only the leading term gives

$$\mathcal{M}^{(0)}_T(\vec{p}_{\rm f}, \vec{p}_{\rm i}) = -\frac{4\pi Z\alpha}{Mm\vec{q}^{\,2}}\left(\frac{i}{2}\vec{\sigma}\cdot\vec{p}_{\rm f}\times\vec{p}_{\rm i} + \frac{\vec{q}^{\,2}\vec{p}_{\rm f}\cdot\vec{p}_{\rm i} - \vec{q}\cdot\vec{p}_{\rm f}\vec{q}\cdot\vec{p}_{\rm i}}{\vec{q}^{\,2}}\right). \tag{17}$$

After carrying out another calculation with the $F_2$ form factor, the spin-dependent part of the above gets multiplied by $1 + a_e$ rather than $1 + 2a_e$, while the spin independent term is unaffected. Our results up to second order can be summarized as

$$\begin{aligned}\mathcal{M}^{(2)}(\vec{p}_{\rm f}, \vec{p}_{\rm i}) = -\frac{4\pi Z\alpha}{\vec{q}^{\,2}}\Big[&1 - \frac{\vec{q}^{\,2}}{8m^2}(1 + 2a_e) + i\frac{\vec{\sigma}\cdot\vec{p}_{\rm f}\times\vec{p}_{\rm i}}{4m^2}(1 + 2a_e) + \\ &i\frac{\vec{\sigma}\cdot\vec{p}_{\rm f}\times\vec{p}_{\rm i}}{2mM}(1 + a_e) + \frac{\vec{q}^{\,2}\vec{p}_{\rm f}\cdot\vec{p}_{\rm i} - \vec{q}\cdot\vec{p}_{\rm f}\vec{q}\cdot\vec{p}_{\rm i}}{Mm\vec{q}^{\,2}}\Big].\end{aligned} \tag{18}$$

So far we have been doing a QED calculation of the scattering of low velocity particles in momentum space. In coordinate space we have corresponding operators defined by

$$O(\vec{r})\delta^3(\vec{r}-\vec{r}\,') = \frac{1}{(2\pi)^6}\int d^3p_\mathrm{f} d^3p_\mathrm{i} e^{i\vec{p}_\mathrm{f}\cdot\vec{r}}\mathcal{M}(\vec{p}_\mathrm{f},\vec{p}_\mathrm{i})e^{-i\vec{p}_\mathrm{i}\cdot\vec{r}\,'}. \tag{19}$$

If we consider only the first term in Eq. (18), the coordinate space form of the operator is $-Z\alpha/r$, as can be seen by changing variables from $\vec{p}_\mathrm{f}$ to $\vec{q}$. In general, whenever a scattering amplitude depends only on $\vec{q}$ an operator that is a function only of $\vec{r}$ results, but if additional factors of momentum are present in the numerator terms involving derivatives, which of course can be written as momentum operators, will be present.

The only spin dependent operators needed to make the nonrelativistic theory agree with QED are the spin orbit operator, the coordinate space version of the third term in Eq. (18),

$$H_{SO} = \frac{Z\alpha}{4m^2}\vec{\sigma}\cdot\frac{\vec{r}\times\vec{p}}{r^3}(1+2a_e), \tag{20}$$

along with the recoil term

$$H_R = \frac{Z\alpha}{2mM}\vec{\sigma}\cdot\frac{\vec{r}\times\vec{p}}{r^3}(1+a_e). \tag{21}$$

While not contributing to fine structure in lowest order, we note the presence of three spin-independent terms, the Darwin term,

$$H_D = \frac{\pi Z\alpha}{2m^2}\delta(\vec{r})(1+2a_e), \tag{22}$$

a second term frequently called the Breit term,

$$H_B = -\frac{Z\,\alpha}{2\,Mm\,r}\left(\delta_{ij}+\frac{r_ir_j}{r^2}\right)p_ip_j, \tag{23}$$

and finally the standard relativistic mass increase operator

$$H_{\mathrm{RM}} = -\frac{p^4}{8m^3}. \tag{24}$$

If we add these operators as perturbations to a nonrelativistic starting point, the theory will agree with QED to order $(v/c)^2$ for the scattering of slowly moving particles.

The Hamiltonian of the effective theory without relativistic corrections is the familiar one from elementary quantum mechanics with the electron mass replaced with the reduced mass, since the Hamiltonian in the system we have chosen is

$$\begin{aligned} H_{NR} &= \frac{\vec{p}^{\,2}}{2m} + \frac{\vec{p}^{\,2}}{2M} - \frac{Z\alpha}{r} \\ &\equiv \frac{\vec{p}^{\,2}}{2m_r} - \frac{Z\alpha}{r}. \end{aligned} \tag{25}$$

When used to solve the bound state problem this Hamiltonian gives the usual Schrödinger energies and wave functions in terms of the reduced mass. A crucial point in effective field theories is that the extra operators derived above from scattering considerations can also be treated as perturbations to this Hamiltonian for the bound state problem, so one can use standard Rayleigh-Schrödinger perturbation theory to evaluate their contributions, with the operator defined in Eq. (19) giving the energy shift

$$\Delta E = \int d^3 r \phi^*(\vec{r}) O(\vec{r}) \phi(\vec{r}). \tag{26}$$

Scaling arguments ($p \propto m_r\alpha$, $r \propto 1/m_r\alpha$) show that the reduced mass then enters as $(m_r/m)^3$ for both operators contributing to fine structure. Evaluating their expectation value gives a much more accurate replacement for our original formula $\nu_0 = \alpha^2 R_\infty c/16$, specifically

$$\begin{aligned} \bar{\nu}_0 &= \frac{\alpha^2 R_\infty c}{16}\left(\frac{m_r}{m}\right)^3 \left(1 + 2a_e + 2\frac{m}{M}(1+a_e)\right) \\ &\equiv A\,\alpha^2 \\ A &= 205\ 979\ 506.129(1)\ \text{MHz}. \end{aligned} \tag{27}$$

When we turn to helium, we will start with a form analogous to this. By including these dominant corrections we find

$$\bar{\alpha}_0^{-1} = 137.033\ 24(62), \tag{28}$$

now only 20 ppm smaller than the $g$-2 value of $\alpha^{-1}$.

We include higher order theoretical contributions by defining

$$\begin{aligned} \nu_{th} &\equiv \bar{\nu}_0 + \delta\nu_{\rm th} \\ &= \bar{\nu}_0 + \nu^{(4)} + \nu^{(4r)} + \nu^{(5)} + ..., \end{aligned} \tag{29}$$

where $\nu^{(4)}$ accounts for corrections of order $\alpha^4 R_\infty$, $\nu^{(4r)}$ for corrections of order $\frac{m}{M}\alpha^4 R_\infty$, and $\nu^{(5)}$ of order $\alpha^5 R_\infty$. These corrections are of course of order $\alpha^2\nu_0$, $\frac{m}{M}\alpha^2\nu_0$, and $\alpha^3\nu_0$. Once they are computed, the formula for determining $\alpha$ is

$$\alpha^2 = \frac{\nu_{exp} - \delta\nu_{\rm th}}{A}, \tag{30}$$

where we are assuming the validity of QED to identify $\nu_{th}$ with the measured value $\nu_{exp}$. In the following we will show that

$$\begin{aligned} \nu^{(4)} &= \frac{5m(Z\alpha)^6}{256} \\ \nu^{(4r)} &= -\frac{m^2(Z\alpha)^6}{64M} \\ \nu^{(5)} &= \frac{\alpha m(Z\alpha)^6}{8\pi}\left[\frac{1}{9}+\frac{1}{4}\ln(Z\alpha)^2+0.38442+\frac{1}{20}\right], \end{aligned} \tag{31}$$

which contribute 0.364 415 MHz, -0.000 159 MHz, and -0.008 495 MHz respectively (the factor 1/20 in $\nu^{(5)}$ is from the vacuum polarization). Since the experimental error is 0.10 MHz, only $\nu^{(4)}$ plays a significant role for hydrogen. Using it in Eq. (30) then allows one to derive the value of $\alpha$ given in Eq. (7). While much more complex, the helium calculation presented in the next section follows the same pattern, but in this case the experiment is far more precise, so that the accurate determination of all of the terms in $\delta\nu_{th}$ is essential.

We now present the theory for $\delta\nu_{th}$ in hydrogen, starting with $\nu^{(4)}$. Because we treat $\nu^{(4r)}$ separately, $\nu^{(4)}$ is to be evaluated in the nonrecoil limit, so the Dirac equation can be used. The next term in the expansion of Sommerfeld's formula,

$$\begin{aligned} E(n,j) &= mf(n,j) \\ &= m\left[1+\left(\frac{Z\alpha}{n-(j+\frac{1}{2})+\sqrt{(j+\frac{1}{2})^2-(Z\alpha)^2}}\right)^2\right]^{-1/2} \end{aligned} \tag{32}$$

contributes a relative factor $5/8\alpha^2$ to $n = 2$ hydrogen fine structure. However, since we are going to use an effective field theory approach for helium, there being no counterpart of the Dirac equation in that system [17], we show below how the $5/8\alpha^2$ correction is calculated using this approach. In Ref. [18] this procedure was carried out for the more difficult case of $s$-state energies, and we briefly describe it here to introduce techniques that will be used extensively in the helium calculation.

The use of effective field theory described above is, with the exception of the inclusion of the anomalous magnetic moment of the electron and carrying out some Taylor expansions to fourth rather than second order, very well known, with the derivation of the fine structure formula a standard exercise in quantum mechanics textbooks. However, in textbooks the discussion stops at first order perturbation theory. To obtain terms of order

$m(Z\alpha)^6$ one must go to second order perturbation theory with the operators already derived, and in addition new operators two orders of $\alpha$ smaller must be found by carrying out the matching procedure to higher orders in the velocities of the particles. At this point the fact that the operators are nearly singular becomes important. To show the problem, we first consider the effect of second order perturbation theory in the Darwin interaction. The general expression for second order perturbation theory is

$$\begin{aligned}\Delta E_2 &= \sum_{m\neq 0} \frac{\langle 0|V|m\rangle\langle m|V|0\rangle}{E_0 - E_m} \\ &= \sum_{m\neq 0} \int d^3r_1 d^3r_2 \frac{\phi_0^*(\vec{r}_1)V(\vec{r}_1)\phi_m(\vec{r}_1)\phi_m^*(\vec{r}_2)V(\vec{r}_2)\phi_0(\vec{r}_2)}{E_0 - E_m} \\ &\equiv \int d^3r_1 d^3r_2 \phi_0^*(\vec{r}_1)V(\vec{r}_1)G_R(\vec{r}_1,\vec{r}_2;E_0)V(\vec{r}_2)\phi_0(\vec{r}_2),\end{aligned} \tag{33}$$

where $G_R$ is a reduced Green's function that builds in the restriction $m \neq 0$. If this is transformed into momentum space we get

$$\Delta E_2 = \int \frac{d^3q_1 d^3q_2 d^3q_3 d^3q_4}{(2\pi)^{12}} \phi_0^*(\vec{q}_4)V(\vec{q}_4 - \vec{q}_3)G_R(\vec{q}_3,\vec{q}_2;E_0)V(\vec{q}_2 - \vec{q}_1)\phi(\vec{q}_1). \tag{34}$$

The part of the reduced propagator that gives rise to the strongest singularity is the free propagator,

$$G_0(\vec{q}_3,\vec{q}_2;E_0) = (2\pi)^3 \frac{\delta^3(\vec{q}_3 - \vec{q}_2)}{E_0 - \frac{\vec{q}_3^{\,2}}{2m}}. \tag{35}$$

Replacing $G_R$ with $G_0$ when both potentials are Darwin terms, which are simply constants in momentum space, leads to a linearly divergent integral of the form

$$\begin{aligned}\Delta E_2(G_0) &\propto \int d^3q_1 d^3q_2 d^3q_4 \phi_0^*(\vec{q}_4) \frac{1}{\vec{q}_2^{\,2} - 2mE_0} \phi_0(\vec{q}_1) \\ &\propto |\phi_0(0)|^2 \int d^3p \frac{1}{\vec{p}^{\,2} - 2mE_0}.\end{aligned} \tag{36}$$

We note that this term vanishes for $p$ states, but for $s$ states it must be dealt with. To do so one must first regularize the linear divergence, which can be done using either dimensional regularization [19] or by cutting off momentum integrals, either by multiplying by factors like $\Lambda^2/(\vec{p}^{\,2} + \Lambda^2)$ or simply restricting $|\vec{p}| < \Lambda$.

Another source of divergences is the Hamiltonian $H^{(6)}$ that comes from the part of Eq. (11) that is quartic in the momenta. This is to be treated in the first order of perturbation theory, and when $s$-states are treated linearly divergent terms arise. These can be shown to cancel the linear divergences discussed above that arise from second order perturbation theory, summing to the known Dirac equation result [18]. However, since we are treating fine structure, the only contributing part of $H^{(6)}$ comes from the last term in Eq. (11),

$$H^{(6)} = -\frac{3Z\alpha}{16m^4}\frac{1}{r^3}\vec{\sigma}\cdot(\vec{r}\times\vec{p})\vec{p}^{\,2}, \tag{37}$$

which has a finite expectation value for the $2p_{3/2} - 2p_{1/2}$ splitting, $-21/512\; m(Z\alpha)^6$. This disagrees with the value expected from the Dirac equation because the calculation is incomplete. To finish it, the second order perturbation theory expression must be evaluated, specifically

$$\sum_{m\neq 2p}\frac{\langle 2p|(H_{\rm RM}+H_{SO})|m\rangle\langle m|(H_{\rm RM}+H_{SO})|2p\rangle}{E_{2p}-E_m}, \tag{38}$$

where we have dropped the Darwin term, which vanishes for $p$ states. The contribution of this term to fine structure, which is also finite, can be evaluated with the method of Dalgarno and Lewis, and one finds $31/512\, m(Z\alpha)^6$, which gives the Dirac equation result, $5/256\; m(Z\alpha)^6$, when summed with the expectation value of $H^{(6)}$. We note that the factor of 31/512 is the sum of 49/4608 from two spin orbit interactions and 230/4608 from one spin orbit and one relativistic mass increase interaction, with two mass increase operators not contributing to fine structure.

We next turn to the evaluation of $\nu^{(4r)}$. We have already accounted for recoil corrections in the previous order, $\frac{m^2}{M}(Z\alpha)^4$, but note the interesting fact that in this order all corrections of order $m(\frac{m}{M})^n(Z\alpha)^4$ can be accounted for through the formula [20], [21]

$$\begin{aligned} E &= (M+m) + m_r(f(n,j)-1) - \frac{m_r^2}{2M}(f(n,j)-1)^2 \\ &\quad + (1-\delta_{l0})\frac{(Z\alpha)^4 m_r^3}{2n^3M^2}\Big[\frac{1}{j+\frac{1}{2}} - \frac{1}{l+\frac{1}{2}}\Big], \end{aligned} \tag{39}$$

where $f(n,j)$ is the Dirac energy function given above. We refer to this as the Barker-Glover contribution in the following. For the fine structure we are treating it has the $Z\alpha$ expansion

$$E_{{\rm f}s} = \frac{m_r(Z\alpha)^4}{32}\left(1-\frac{m_r^2}{M^2}\right) + \frac{5m_r(Z\alpha)^6}{256}\left(1+\frac{m_r}{5M}\right), \tag{40}$$

the first term of which reproduces the result shown in Eq. (27) when $a_e$ is dropped.

One method of studying the recoil corrections in order $(Z\alpha)^6$ is to carry out calculations to all orders in $Z\alpha$ using numerical methods, an approach originated by Shabaev [22] and applied to $2p_{1/2}$ states in Ref. [23] and $2p_{3/2}$ states in Ref. [24]. These results were recently confirmed by Adkins et. al. [25]. Carrying out a numerical fit to the exact calculation at low $Z$ reproduces the Barker-Glover result above, even though that formula is supposed to be valid only to order $m^2/M(Z\alpha)^4$. There are in fact terms of order $m^2/M(Z\alpha)^6$, but we now show that they cancel for fine structure, leading to

$$\nu^{(4r)} = -\frac{m^2(Z\alpha)^6}{64M}. \tag{41}$$

The Barker-Glover result follows from working with the Hamiltonian

$$H_{\text{eff}} = \vec{\alpha}\cdot\vec{p} + \beta m + \frac{\vec{p}^{\,2}}{2M} + V_{\text{eff}}, \tag{42}$$

where the Breit interaction is included in $V_{\text{eff}}$,

$$V_{\text{eff}} = -\frac{Z\alpha}{r}\left[1 + \frac{1}{2M}\left(\delta_{ij} + \frac{r_i r_j}{r^2}\right)\alpha^i p^j\right]. \tag{43}$$

This is corrected by three terms coming from loop diagrams with either 0, 1, or 2 transverse photons present. All three terms involve the Dirac-Coulomb propagator, though when considering fine structure to the order we are interested in it suffices to use a free electron propagator.

The first, all-Coulomb term does not contribute to fine structure. The 1 transverse photon term is

$$E_T = -\frac{Z\alpha}{M}\int \frac{d\omega}{2\pi i}\frac{1}{\omega - i\epsilon}\int \frac{d^3k}{(2\pi)^3}\frac{P_{ij}(k)}{\omega^2 - k^2}$$
$$\langle\phi|\gamma^i e^{ikr} S_F(E-\omega)\gamma^0[p^j, V]|\phi\rangle + c.c.. \tag{44}$$

A short analysis gives a fine structure contribution of

$$E_T(fs) = \frac{m^2}{2M}(Z\alpha)^6\langle\phi|\frac{\vec{L}\cdot\vec{S}}{r^4}|\phi\rangle. \tag{45}$$

Finally, the two-transverse photon term is

$$E_{TT} = -\frac{Z^2\alpha^2}{M}\int \frac{d\omega}{2\pi i}\int \frac{d^3k_1}{(2\pi)^3}\int \frac{d^3k_2}{(2\pi)^3}\frac{P_{ik}(k_1)}{\omega^2 - k_1^2}\frac{P_{jk}(k_2)}{\omega^2 - k_2^2}$$
$$\langle\phi|\gamma^i e^{-ik_1 r} S_F(E-\omega)\gamma^j e^{ik_2 r}|\phi\rangle. \tag{46}$$

Another short analysis that relies on the integral

$$\int \frac{d^3k}{(2\pi)^3}\frac{1}{k^2}P_{ij}(k)e^{-i\vec{k}\cdot\vec{r}} = \frac{\delta_{ij}r^2 + r_ir_j}{8\pi r^3} \tag{47}$$

gives

$$E_{TT}(fs) = -\frac{m^2}{2M}(Z\alpha)^6\langle\phi|\frac{\vec{L}\cdot\vec{S}}{r^4}|\phi\rangle, \tag{48}$$

which cancels $E_T(fs)$, so that there is in fact no contribution to fine structure in this order beyond the Barker-Glover formula.

We now turn to radiative corrections, which are the most difficult part of the calculation [28]. The leading order radiative correction has already been accounted for through our use of the $(1+a_e)$ and $(1+2a_e)$ factors in Eq. (27). There are other contributions of order $m\alpha(Z\alpha)^4$, but they cancel in the difference. An additional simplification is the fact that the first binding corrections to the Lamb shift, of order $m\alpha(Z\alpha)^5$, vanish for $p$ states. In terms of scattering diagrams, this is connected with the behavior of one-loop corrections to two-Coulomb exchange diagrams. These diagrams were studied by Baranger, Bethe, and Feynman [26] in the early days of QED, and found to behave as a delta function of position, which contributes only for $s$ states. We note that this order is the same when $Z=1$ as the $m(Z\alpha)^6$ correction discussed above. However, the next term in the binding expansion, of order $m\alpha(Z\alpha)^6$, not only does not vanish for $p$ states, but also has a nonvanishing contribution to the fine structure that contains a logarithm of $Z\alpha$. It in fact changes $\alpha$ by about 1 ppm, and its counterpart in the helium calculation will play an important role. We now turn to a discussion of the evaluation of this logarithmic term along with the associated constant term using effective field theory.

Before evaluating the logarithmic term, we calculate the two terms associated with using the $F_2$ form factor beyond first order given in Eq. (15). The part of the first equation that contributes to fine structure can be seen to be proportional to $H^{(6)}$, with the constant of proportionality being $\frac{4}{3}a_e$. Thus no new calculation is needed, and in fact the calculation could be subsumed into the $H^{(6)}$ calculation as was done for the basic formula Eq. (27). When we turn to the helium calculation, where there are a set of operators $H_i^{(6)}$ first derived by Douglas and Kroll [27], we will see that the effect of $F_2$ is to multiply each operator by $1+A_ia_e$, where $A_i$ is always a simple integer or rational fraction. The other contribution comes from the known $q^2$ behavior of the form factor, and gives a spin dependent effective operator

$$\frac{\alpha(Z\alpha)}{6m^4}\vec{\sigma}\cdot(\vec{\nabla}\delta^3(\vec{r}))\times\vec{p}, \tag{49}$$

that contributes $-\frac{m\alpha(Z\alpha)^6}{64\pi}$ to fine structure. We now discuss the other form factor.

We introduced the form factor $F_1$ above, but put off defining it. This is because it has an infrared divergence. This can be regularized either by introducing a photon mass, using dimensional regularization, or making a cutoff. Making the last choice, we introduce a parameter $\epsilon$ that divides the calculation into a low energy part, with photon energies $\omega < \epsilon$, and a high energy part, with $\omega > \epsilon$. In the high energy part we can account for QED effects by evaluating $F_1$ with this cutoff, and find

$$F_1(q^2) = 1 + \frac{\alpha}{3\pi}\frac{q^2}{m^2}\left[\ln\left(\frac{m}{2\epsilon}\right) + \frac{11}{24}\right]. \tag{50}$$

With this regularized form of $F_1$ we can continue the matching procedure discussed above to derive the effective operator arising from the $q^2$ term in $F_1$,

$$\frac{\alpha(Z\alpha)}{3m^4}\left[\ln\frac{m}{2\epsilon} + \frac{11}{24}\right]\vec{\sigma}\cdot(\vec{\nabla}\delta^3(\vec{r}))\times\vec{p}, \tag{51}$$

which leads to the energy shift

$$E_H{}^1 = -\frac{m\alpha(Z\alpha)^6}{32\pi}\left[\ln\frac{m}{2\epsilon} + \frac{11}{24}\right]. \tag{52}$$

To show how the regularized divergence cancels, we have to now consider the effective theory in second order perturbation theory. Now, the matching procedure we have carried out so far has not yet included diagrams in which a radiated photon is present, but nonrelativistically we of course know that such photons couple to the current $\vec{p}/m$ in the dipole approximation. Using this interaction in second order gives a nonrelativistic form of the Lamb shift,

$$\Delta E = \alpha\int_0^\epsilon \frac{d^3k}{(2\pi)^3 2k}P_{ij}(k)\langle\phi|\frac{p^i}{m}\frac{1}{E - H_{NR} - k}\frac{p^j}{m}|\phi\rangle, \tag{53}$$

which is linearly divergent because diagrams with an electron-positron pair, the so-called '$Z$' graphs, which cancel that divergence are not present in the nonrelativistic theory. The cutoff is required because we have chosen to regularize the effective theory by not allowing photons to have energy greater than $\epsilon$. The linear divergence of this integral is reduced to a logarithmic divergence after mass renormalization, which process replaces

$$\frac{1}{E-H-k} \to \frac{E-H}{k(E-H-k)}. \tag{54}$$

In full QED one starts with a logarithmic divergence that is made finite by renormalization, but here a logarithmic divergence remains that is cancelled by the $F_1$ term discussed above.

As mentioned above, most of the Lamb shift, which the above integral is representing the nonrelativistic part of, does not contribute to the fine structure splitting. To get a splitting we must include the effect of the spin orbit operator. This can occur in three ways; through the shift of the energy, the shift of the propagator, and the shift of the wave function. This requires the evaluation of

$$\begin{aligned} E_{L1} = \frac{2\alpha}{3\pi}\int_0^\epsilon kdk[2\langle\delta\phi|\frac{p^i}{m}\frac{1}{E-H-k}\frac{p^i}{m}|\phi\rangle \\ + \langle\phi|\frac{p^i}{m}\frac{1}{E-H-k}(H_{SO}-\langle\phi|H_{SO}|\phi\rangle)\frac{1}{E-H-k}\frac{p^i}{m}|\phi\rangle. \end{aligned} \tag{55}$$

In addition to this calculation, we must also consider corrections to the current the photon couples to. In QED this is of course $\bar{u}(\vec{p}_{\rm f})\gamma_i u(\vec{p}_{\rm i})$ instead of $(\vec{p}_{\rm f}+\vec{p}_{\rm i})/m$. The difference has already been discussed in connection with transverse photon exchange. Including corrections to the dipole approximation, the current changes to

$$\begin{aligned} \frac{\vec{p}}{m} &\to \frac{\vec{p}}{m} - \frac{Z\alpha}{2m^2r^3}\vec{r}\times\vec{\sigma} + \frac{1}{2m}(\vec{k}\cdot\vec{r})\vec{k}\times\vec{\sigma} \\ &\equiv \frac{\vec{p}}{m} + \delta\vec{j}. \end{aligned} \tag{56}$$

The first part of $\delta\vec{j}$ can be thought of as arising from a $Z$ graph, and the second comes from the first term in the expansion of $e^{i\vec{k}\cdot\vec{r}}$ together with a magnetic interaction. $\delta\vec{j}$ gives rise to the additional shift

$$E_{L2} = 2\alpha\int_0^\infty \frac{d^3k}{(2\pi)^3 2k}P_{ij}(k)\langle\phi|\delta j^i\frac{1}{E-H-k}\frac{p^j}{m}|\phi\rangle. \tag{57}$$

The calculation of $E_{L1}$ and $E_{L2}$ must be done numerically, and the result is

$$E_L = m\frac{\alpha}{\pi}\frac{(Z\alpha)^6}{8}\left[-\frac{1}{4}\ln\frac{2\epsilon}{m(Z\alpha)^2} + 0.384\ 42(1)\right]. \tag{58}$$

Finally putting everything together the complete correction is cutoff independent and equal to

$$E_{FS} = \frac{m\alpha(Z\alpha)^6}{8\pi}\left[\frac{1}{9} + \frac{1}{4}\ln(Z\alpha)^2 + 0.38442\right]. \tag{59}$$

The derivation of this $m(Z\alpha)^6$ correction is seen to be quite complicated even in hydrogen. While it is a sort of 'proof of principle' that effective field theory methods can be applied to the bound state problem, and means that the helium calculation is possible, it also indicates that the calculation will be very complex, and in fact the approach here was completed only recently [14]. We now turn to this more challenging problem.

## 2. Helium Fine Structure

Our interest here is in determining $\alpha$ from the simplest many-electron atom, helium. This program was initiated in 1964 by Schwartz [29]. The problems faced in carrying out calculations of the same accuracy as has been only recently achieved for hydrogen are considerable, but the much higher experimental precision achieved in helium means these calculations can lead to an accurate determination of $\alpha$ that depends on the low energy scales characteristic of atomic physics. There are certain simplifying features of the calculation that stem from the form of the helium wave functions, which we now describe.

Helium fine structure is associated with states that can be thought of as having one electron in the ground state and the other in a $2p$ state. However, while in hydrogen the fine structure would be associated with the energy difference between the $2p_{1/2}$ and $2p_{3/2}$ states, in this two-electron system LS coupling instead of jj coupling is obeyed, so one first sums the electron spins to form either a singlet (S=0) or triplet (S=1), and then adds this spin to the orbital angular momentum, which in this case is L=1. The fine structure studied here is associated with triplets, so the allowed values of total angular momentum are $J$=0,1, and 2. The spectroscopic notation for the three states is $2^3P_J$, with a onefold, threefold, and fivefold degeneracy for $J$=0,1, and 2 respectively. Nonrelativistically they are degenerate, but relativistic effects lead to a frequency splitting of order $\alpha^2 R_\infty c$. We will be concerned in particular with two intervals, the 'large interval'

$$\nu_{01} = \frac{E(2^3P_0) - E(2^3P_1)}{h} \tag{60}$$

and the 'small interval'

$$\nu_{12} = \frac{E(2^3P_1) - E(2^3P_2)}{h}. \tag{61}$$

The former will be used for determining $\alpha$ and the latter as a test of theory. The energy diagram is shown in Fig. 1. The linewidths of these states are approximately 100 times narrower than hydrogen, which is why Schwartz [29] proposed their study for an accurate fine structure constant determination. The experiments are still extremely challenging, but have reached accuracies such that, were there no theoretical uncertainties, a value of $\alpha$ accurate to 10 ppb could be determined. We further note that while we will use $M$ to refer to the mass of the nucleus of an arbitrary isotope of helium, in practice we are interested in the nucleus being an alpha particle, with [3]

$$Mc^2 = 3727.379\ 109(93)\text{MeV}. \tag{62}$$

Since the nucleus has spin 0 the degeneracy mentioned above remains in the absence of external fields.

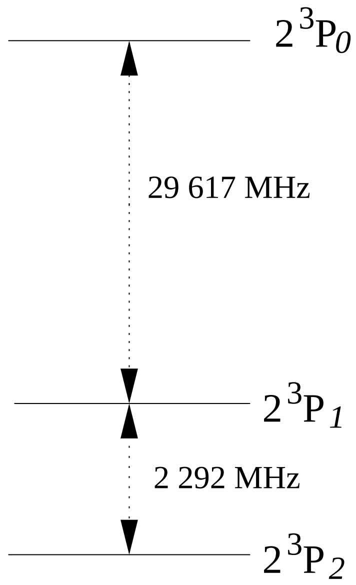


Fig. 1. Energy levels of the 2P triplet states in helium.

The theoretical simplicity of these states comes from the fact that the helium wave function can be written as a product of spatial and spin wave functions. Since the spin part of the wave function for triplets is symmetric, the spatial part is antisymmetric, so any operator that behaves as $\delta^3(\vec{r}_1 - \vec{r}_2)$ can be dropped. It was for this reason that Douglas and Kroll [27] were able to derive operators contributing at the level $m\alpha^6$ to helium fine structure more than 2 decades before it became possible to carry out calculations of equivalent accuracy for energies of singlet states [30].

To illustrate how one determines $\alpha$ from helium fine structure, we use a recent measurement of $\nu_{01}$ [31],

$$\nu_{01}(\text{exp}) = 29\ 616.951\ 66(70)\text{MHz}, \tag{63}$$

which we note has an accuracy of 24 ppb. As with hydrogen, the leading recoil corrections together with the leading radiative corrections can be built into the lowest order formula, where we replace the constant $A$ defined in Eq. (27) for hydrogen with $B$, defined in Eq. (71). In terms of this constant,

$$\begin{aligned} \bar{\nu}_{01} &= B\alpha^2, \\ B &= 556\ 200\ 289.46\ \text{MHz}. \end{aligned} \tag{64}$$

The coefficient above has to be obtained numerically instead of analytically, as was the case for hydrogen. We note that highly accurate wave functions are required, which was a major issue at the beginning of Schwartz program [29], but since then this problem has been solved [32], [33], and all digits shown are correct. Were this all there was to the theoretical calculation, one would solve for $\alpha_0^2$ by setting the approximated theory equal to the experiment, giving

$$\alpha_0^2 = \frac{\nu_{01}(\text{exp})}{B}, \tag{65}$$

which leads to

$$\alpha_0^{-1} = 137.039\ 9791(2). \tag{66}$$

As with hydrogen, inclusion of the leading recoil and radiative corrections gives a starting value of $\alpha$ within 30 ppm of the $g$-2 value, and we will see that the bulk of the difference comes from the order $\alpha^2$ corrections that have not yet been included. It is the accurate and complete determination of these and higher order corrections using effective field theory together with accurate helium wave functions that will be described in the rest of this chapter.

## 3. Organization of helium fine structure calculation

The analog of the factor 1/16 in $\nu_0$ for hydrogen involves evaluating the expectation value of three operators with accurate nonrelativistic helium wavefunctions. One of the operators is the same spin-orbit coupling between the electron and nucleus that gives rise to the 1/16 in hydrogen, the second is a spin-orbit coupling where the electron spin interacts with the magnetic field associated with the motion of the other electron, and the third involves the magnetic interaction of the electrons' spins with each other. The explicit form of these operators will be given in the following section. There are three corresponding expectation values denoted $\tilde{E}_1$, $\tilde{E}_2$, and $\tilde{E}_3$, where the tilde indicates that the mass of the nucleus is taken to infinity, and they shift the energy of the three states to

$$\begin{aligned}
\nu(2^3P_0) &= \alpha^2 R_\infty c\left[\frac{\tilde{E}_1}{2} + \frac{\tilde{E}_2}{2} + \frac{\tilde{E}_3}{2}\right], \\
\nu(2^3P_1) &= \alpha^2 R_\infty c\left[-\frac{\tilde{E}_1}{4} + \frac{\tilde{E}_2}{4} + \frac{\tilde{E}_3}{4}\right], \\
\nu(2^3P_2) &= \alpha^2 R_\infty c\left[\frac{\tilde{E}_1}{20} - \frac{\tilde{E}_2}{4} - \frac{\tilde{E}_3}{4}\right].
\end{aligned} \tag{67}$$

We note that $\tilde{E}_1$, the expectation value of the spin-spin operator, contributes to $J = 0, 1, 2$ as $(1/2, -1/4, 1/20)$, while $\tilde{E}_2$ and $\tilde{E}_3$, the spin-orbit operators, contribute as $(1/2, 1/4, -1/4)$, which follows from an angular momentum analysis of the three states. The leading QED correction to these formulas can be obtained by including the electron anomalous magnetic moment operator in effective field theory in a manner analogous to the hydrogen calculation. Again as with hydrogen there is another operator that is pure recoil we will also describe in the next section, with expectation value $\tilde{E}_4$. However, to fully account for recoil, in addition to introducing scaling factors of $m_r/m$ account must be taken of an additional term known as the mass polarization operator, given in Eq. (81), in the nonrelativistic Hamiltonian. This can be accounted for by simply generating wave functions with Hamiltonians including mass polarization, and we denote such constants as $E_i$. The net result is the somewhat more complicated looking, but much more accurate set of formulas,

$$
\begin{aligned}
\nu(2^3P_0) &= (\frac{m_r}{m})^3\alpha^2 R_\infty c\Big[\frac{E_1}{2}(1+a_e)^2 + \frac{E_2}{2}(1+2a_e) \\
&\quad + \frac{E_3}{2}(1+\frac{4}{3}a_e) + \frac{m}{M}\frac{E_4}{2}(1+a_e)\Big], \\
\nu(2^3P_1) &= (\frac{m_r}{m})^3\alpha^2 R_\infty c\Big[-\frac{E_1}{4}(1+a_e)^2 + \frac{E_2}{4}(1+2a_e) \\
&\quad + \frac{E_3}{4}(1+\frac{4}{3}a_e) + \frac{m}{M}\frac{E_4}{4}(1+a_e)\Big], \\
\nu(2^3P_2) &= (\frac{m_r}{m})^3\alpha^2 R_\infty c\Big[\frac{E_1}{20}(1+a_e)^2 - \frac{E_2}{4}(1+2a_e) \\
&\quad - \frac{E_3}{4}(1+\frac{4}{3}a_e) - \frac{m}{M}\frac{E_4}{4}(1+a_e)\Big].
\end{aligned} \tag{68}
$$

While the dominant QED and recoil corrections are included in the above, QED corrections of relative order $\alpha^2$, $\alpha^3$, and $\alpha^4$ are not completely included, and in addition recoil corrections of relative order $\alpha^2\frac{m}{M}$ need to be calculated. It is important to emphasize the fact that many higher order QED and recoil corrections *are* included in these formulas through the inclusion of $a_e$, which can be written as a power series in $\alpha$ with the first 4 terms known, along with recoil effects that could be treated separately, for example by using $\tilde{E}_i$ and including mass polarization perturbatively. Therefore any future calculations designed to check the two discrepant results that presently exist need to avoid double counting if they adopt the approach of this chapter.

We then write the four corrections to the large interval, following the treatment of hydrogen in the previous section, as

$$\delta\nu_{01} \equiv \nu_{01}^{(4)} + \nu_{01}^{(4r)} + \nu_{01}^{(5)}. \tag{69}$$

The complete equation that determines $\alpha$ from a measurement of $\nu_{01}$ is

$$\alpha^2 = \frac{\nu_{01}(\exp) - \delta\nu_{01}}{B}, \tag{70}$$

where $B$, the numerical value of which has been given above in Eq. (64), is the helium analog of Eq. (27),

$$B = (\frac{m_r}{m})^3 R_\infty c\Big[\frac{3E_1}{4}(1+a_e)^2 + \frac{E_2}{4}(1+2a_e) + \frac{E_3}{4}(1+\frac{4}{3}a_e) + \frac{m}{M}\frac{E_4}{4}(1+a_e)\Big]. \tag{71}$$

The numerical values of the $E_i$ are given in Eq. (94). The values of the first three contributions to $\delta\nu_{01}$ are

$$\begin{aligned} {\nu_{01}}^{(4)} &= -1.547\ 06(10)\,\text{MHz} \\ {\nu_{01}}^{(4r)} &= -0.010\ 38 \qquad \text{MHz} \\ {\nu_{01}}^{(5)} &= \ \ 0.081\ 72(16)\,\text{MHz}. \end{aligned} \tag{72}$$

Putting these in the above formula gives our final answer for $\alpha$ as determined by helium fine structure,

$$\alpha^{-1}(\text{He fs}) = 137.035\ 979(2). \tag{73}$$

This is in poor agreement with other fine structure constant determinations, and also in significant disagreement with another theoretical calculation: this unsatisfactory situation will be described in the concluding section. We now derive the operators whose expectation values give the constants $E_i$.

## 4. Lowest order contributions

As with hydrogen, we begin by studying the scattering of free particles, in this case two electrons and an alpha particle nucleus. The $\alpha$ particle has spin 0, so our previous neglect of spin as an approximation for the hydrogen problem is not an issue. The two electrons have incoming momenta $\vec{p}_1, \vec{p}_2$, and outgoing momenta $\vec{p}_3, \vec{p}_4$. The nucleus then has in the center of mass system incoming momentum $-\vec{p}_1 - \vec{p}_2$ and outgoing momentum $-\vec{p}_3 - \vec{p}_4$. The general formula that connects an operator to an energy shift is

$$E_i = \frac{1}{(2\pi)^{12}} \int d^3p_1 d^3p_2 d^3p_3 d^3p_4 \phi^*(\vec{p}_3, \vec{p}_4) O_i(\vec{p}_3, \vec{p}_4; \vec{p}_1, \vec{p}_2) \phi(\vec{p}_1, \vec{p}_2). \tag{74}$$

When the electrons interact only with each other momentum conservation allow us to write

$$O_i^{ee}(\vec{p}_3, \vec{p}_4; \vec{p}_1, \vec{p}_2) = (2\pi)^3 \delta^3(\vec{p}_3 + \vec{p}_4 - \vec{p}_1 - \vec{p}_2) \mathcal{M}_i^{e-e}(\vec{p}_3; \vec{p}_1, \vec{p}_2). \tag{75}$$

If the interaction is through the exchange of a Coulomb photon one has

$$\mathcal{M}_i^{ee-C} = \frac{4\pi\alpha}{|\vec{p}_3 - \vec{p}_1|^2}, \tag{76}$$

which corresponds in coordinate space to the interaction

$$\begin{aligned} H_{eeC} &= \frac{\alpha}{|\vec{r}_1 - \vec{r}_2|} \\ &\equiv \frac{\alpha}{r}. \end{aligned} \tag{77}$$

When one of the electrons interacts only with the nucleus and the other electron is a spectator we have

$$O_i^{eN}(\vec{p}_3, \vec{p}_4; \vec{p}_1, \vec{p}_2) = (2\pi)^3 \delta^3(\vec{p}_4 - \vec{p}_2) \mathcal{M}_i^{e-N}(\vec{p}_3; \vec{p}_1). \tag{78}$$

In this case a Coulomb photon exchange is

$$\mathcal{M}_i^{eN_1} = -\frac{4\pi Z\alpha}{|\vec{p}_3 - \vec{p}_1|^2} \tag{79}$$

for one electron, with a similar expression involving $\vec{p}_2$ and $\vec{p}_4$ for the other, which corresponds in coordinate space to

$$\begin{aligned} H_{eN} &= -\frac{Z\alpha}{|\vec{r}_1|} - \frac{Z\alpha}{|\vec{r}_2|} \\ &\equiv -\frac{Z\alpha}{r_1} - \frac{Z\alpha}{r_2}. \end{aligned} \tag{80}$$

In addition the kinetic energy is

$$\begin{aligned} &\frac{\vec{p}_1^{\,2}}{2m} + \frac{\vec{p}_2^{\,2}}{2m} + \frac{(-\vec{p}_1 - \vec{p}_2)^2}{2M} \\ &= \frac{\vec{p}_1^{\,2}}{2m_r} + \frac{\vec{p}_2^{\,2}}{2m_r} + \frac{\vec{p}_1 \cdot \vec{p}_2}{M}. \end{aligned} \tag{81}$$

While the electron mass is replaced by the reduced mass, as in the hydrogen case, helium is complicated by the presence of the last term, which is the mass polarization correction mentioned above. However, in practice this term is simple to deal with when we solve the Schrödinger equation for helium, and in the following it is always assumed to be built into the nonrelativistic wavefunctions. It is still the case that momenta scale proportionally to $m_r$ and distances to $m_r{}^{-1}$, so that lowest order fine structure comes with a multiplicative factor $(m_r/m)^3$.

To get the lowest order operators contributing to fine structure for helium, we generalize the above discussion to relativistic corrections to $\mathcal{M}^{eN}$ and $\mathcal{M}^{ee}$. The non-recoil part of the former is essentially identical to the hydrogen case, and consists of the sum of the spin-orbit interactions of the two electrons,

$$H_{SL}(eN) = \frac{Z\alpha}{4m^2}\left[\frac{1}{r_1^3}\vec{\sigma}_1 \cdot (\vec{r}_1 \times \vec{p}_1) + \frac{1}{r_2^3}\vec{\sigma}_2 \cdot (\vec{r}_2 \times \vec{p}_2)\right]. \tag{82}$$

The expectation value of this operator is $E_2$ times the appropriate $J$-dependent factor.

Continuing with $\mathcal{M}^{eN}$, we next consider exchange of a transverse photon. While in hydrogen the spin dependent part of this effect is simply proportional to the spin-orbit interaction, here the presence of the second electron, even though it does not have a direct interaction, leads to an additional term because of its momentum. Specifically, since the initial nuclear momentum is $-\vec{p}_1 - \vec{p}_2$ and the final $-\vec{p}_3 - \vec{p}_2$, the convection current has an additional term $-2\vec{p}_2$. Thus, while $E_4$ has one contribution from $2\frac{m}{M}H_{SL}(eN)$, it has another that can be written

$$H_{SL}(eN)(\text{recoil}) = \frac{Z\alpha}{2mM}\left[\frac{1}{r_1^3}\vec{\sigma}_1 \cdot (\vec{r}_1 \times \vec{p}_2) + \frac{1}{r_2^3}\vec{\sigma}_2 \cdot (\vec{r}_2 \times \vec{p}_1)\right]. \tag{83}$$

The expectation value of the sum of these two gives $E_4$.

The remaining terms contributing to lowest order fine structure are specific to helium, as they involve exchange of a photon between the electrons. The exchange of a Coulomb photon has the scattering amplitude

$$\begin{aligned}\mathcal{M}^{ee}(C) &= \frac{4\pi\alpha}{|\vec{q}|^2}u^\dagger(\vec{p}_3)u(\vec{p}_1)u^\dagger(\vec{p}_4)u(\vec{p}_2)\\ &\to \frac{\pi\alpha}{m^2|\vec{q}|^2}[i\vec{\sigma}_1 \cdot (\vec{p}_3 \times \vec{p}_1) + i\vec{\sigma}_2 \cdot (\vec{p}_4 \times \vec{p}_2)],\end{aligned} \tag{84}$$

where we have kept only the lowest order spin-dependent terms. In the same approximation transverse photon exchange leads to the scattering amplitude ($\vec{q} = \vec{p}_3 - \vec{p}_1 = \vec{p}_2 - \vec{p}_4$)

$$\begin{aligned}\mathcal{M}^{ee}(T) &= -\frac{4\pi\alpha}{|\vec{q}|^2}u^\dagger(\vec{p}_3)\alpha_i u(\vec{p}_1)u^\dagger(\vec{p}_4)\alpha_j u(\vec{p}_2)P_{ij}(q)\\ &= -\frac{\pi\alpha}{m^2|\vec{q}|^2}[2i\vec{\sigma}_1 \cdot (\vec{p}_2 \times \vec{p}_4) + 2i\vec{\sigma}_2 \cdot (\vec{p}_1 \times \vec{p}_3)\\ &\quad + \vec{\sigma}_1 \cdot (\hat{i} \times \vec{q})\vec{\sigma}_2 \cdot (\hat{i} \times \vec{q})].\end{aligned} \tag{85}$$

The constant $E_3$ is associated with the terms in the above two expressions with a single Pauli matrix, being the expectation value of the coordinate space form

$$H_{SL} = \frac{\alpha}{4\,m^2\,r^3}\left[(\vec{\sigma}_2 + 2\,\vec{\sigma}_1) \cdot \vec{r} \times \vec{p}_2 - (\vec{\sigma}_1 + 2\,\vec{\sigma}_2) \cdot \vec{r} \times \vec{p}_1\right]. \tag{86}$$

Finally, the constant $E_1$ comes from the spin-spin interaction in the transverse photon term,

$$H_{SS} = \frac{\alpha}{4\,m^2}\left(\frac{\vec{\sigma}_1 \cdot \vec{\sigma}_2}{r^3} - 3\,\frac{\vec{\sigma}_1 \cdot \vec{r}\,\vec{\sigma}_2 \cdot \vec{r}}{r^5}\right). \tag{87}$$

In addition to these spin dependent effective Hamiltonians we will later need a spin-independent effective Hamiltonian, denoted $H_{SI}$, for higher order calculations. Its explicit form is

$$H_{SI} = -\frac{1}{8\,m^3}\,(p_1^4 + p_2^4) + \frac{Z\,\alpha\,\pi}{2\,m^2}\left(\delta^3(r_1) + \delta^3(r_2)\right) \\ -\frac{\alpha}{2\,m^2}\,p_1^i\left(\frac{\delta^{ij}}{r} + \frac{r^i\,r^j}{r^3}\right)p_2^j - \frac{\pi\,\alpha}{m^2}\,\delta^3(r) - \frac{2\pi\alpha}{3m^2}\vec{\sigma}_1\cdot\vec{\sigma}_2\delta^3(r). \quad (88)$$

As with the hydrogenic case, relativistic mass increase operators are included in the above along with two kinds of Darwin operator, one familiar from the hydrogenic case and the other a new one involving the electron-electron interaction.

### 4.1. *Leading QED corrections*

As with hydrogen, making the replacement

$$\gamma_\mu \to i\frac{\sigma_{\mu\nu}q^\nu}{2m}a_e, \quad (89)$$

allows the leading QED corrections to helium fine structure to be included with the lowest order corrections. The manipulations are identical for $E_2$ and $E_4$, which get multiplied by factors of $1+2a_e$ and $1+a_e$ respectively, as in Eq. (18). Further discussion is needed for $E_1$ and $E_3$. The factor $(1+a_e)^2$ in the former comes from 4 diagrams, the lowest order, two with one uncorrected vertex and one corrected vertex, and finally one with both vertices corrected. The factor of $(1+4/3\;a_e)$ in $E_3$ arises because this term has contributions both from Coulomb and transverse photon exchange, and the first has a factor $1+2a_e$ and the second $1+a_e$. Because for triplet states one can replace a single occurrence of $\vec{\sigma}_2$ with $\vec{\sigma}_1$, expressing the operator giving rise to $E_3$ in terms only of $\vec{\sigma}_1$ and putting in the appropriate anomalous magnetic moment corrections leads to the overall correction factor of $1+4/3\;a_e$. There are also $a_e$ corrections to $H_{SI}$, with the electron-nucleus Darwin term multiplied by $1+2a_e$, the electron-electron Darwin term by $1+a_e$, and the spin-spin term by $(1+a_e)^2$. The net result is that the spin dependent Hamiltonian including leading radiative corrections, which we denote $H_{SD}$, is the following combination of Eqns. (87), (82), and (86):

$$H_{SD} = \frac{\alpha}{4\,m^2}\left(\frac{\vec{\sigma}_1\cdot\vec{\sigma}_2}{r^3} - 3\,\frac{\vec{\sigma}_1\cdot\vec{r}\,\vec{\sigma}_2\cdot\vec{r}}{r^5}\right)(1+a_e)^2 \\ + \frac{Z\alpha}{4m^2}[\frac{1}{r_1^3}\vec{\sigma}_1\cdot(\vec{r}_1\times\vec{p}_1) + \frac{1}{r_2^3}\vec{\sigma}_2\cdot(\vec{r}_2\times\vec{p}_2)](1+2a_e) \quad (90) \\ + \frac{\alpha}{4\,m^2\,r^3}\left[(\vec{\sigma}_2 + 2\,\vec{\sigma}_1)\cdot\vec{r}\times\vec{p}_2 - (\vec{\sigma}_1 + 2\,\vec{\sigma}_2)\cdot\vec{r}\times\vec{p}_1\right](1+\frac{4}{3}a_e).$$

To accurately evaluate the expectation value of the spin dependent operators, and thus determine $E_1$, $E_2$, $E_3$, and $E_4$, a high quality numerical representation of the wave function is needed, and we now turn to the description of a particularly simple and accurate method of determining it.

## 5. Helium wavefunctions

The helium wave function used here has been described in Ref. [33]. We represent the spatial part of the triplet $P$ states we are concerned with here as

$$\vec{\phi}(\vec{r}_1, \vec{r}_2) = \sum_i C_i(\vec{r}_1 e^{-\alpha_i r_1 - \beta_i r_2 - \gamma_i r} - \vec{r}_2 e^{-\alpha_i r_2 - \beta_i r_1 - \gamma_i r}). \tag{91}$$

By choosing the constants $\alpha_i, \beta_i$, and $\gamma_i$ to lie randomly in certain ranges, and then minimizing the energy with respect to these ranges and the linear coefficients $C_i$, energies accurate to 18 digits or more are obtained with as few as 1200 basis functions. While this may seem 'overkill', energies accurate to order $\delta^2$ are associated with wave functions accurate only to order $\delta$, so this accuracy is required to calculate matrix elements accurate to 9 digits. The nonrelativistic triplet $P$ state energy for infinite nuclear mass, obtained in this way is

$$E(2^3P)_{\mathrm{N}R} = 2.133\;164\;190\;779\;283\;205\;147(1), \tag{92}$$

which is in agreement with the less accurate result of Drake [32], who uses a modified Hylleraas basis set. Manipulations with this basis set are particularly straightforward, since all integrals encountered in the calculation can be related to the basic integral

$$\int d^3r_1 \int d^3r_2 \frac{e^{-\alpha r_1 - \beta r_2 - \gamma r}}{r_1 r_2 r} = \frac{16\pi^2}{(\alpha+\beta)(\alpha+\gamma)(\beta+\gamma)}. \tag{93}$$

Clearly any integral with a factor $r_1^m r_2^n r^t$ with $m, n, t$ greater than or equal to $-1$ can be obtained by differentiating this formula. When a power is less than $-1$ one can integrate the formula, getting terms involving logarithms and dilogarithms. With the use of this wave function we determine for the constants $E_i$, $i = 1..4$, the values

$$\begin{aligned} E_1 &= \phantom{-}0.180\;220\;618\;633(1) \\ E_2 &= -0.277\;401\;358\;713(1) \\ E_3 &= \phantom{-}0.411\;999\;963\;626(1) \\ E_4 &= \phantom{-}0.241\;945\;125\;694(9). \end{aligned} \tag{94}$$

These determinations are so accurate that they are essentially exact, in the sense that the experimental uncertainty is 100 times greater. If experimental precision were to increase, there is no difficulty in determining the constants to even greater accuracy. We have already used these values along with reduced mass and the anomalous magnetic moment of the electron in the above to determine $\alpha$ to be within 30 ppm of the CODATA value. As with the hydrogenic case, the next step is to determine the $\alpha^2$ corrections, to which we now turn.

## 6. Determination of $\nu^{(4)}$

For hydrogen we noted that this contribution could be directly obtained from the Dirac eigenvalue, but instead derived it with effective field theory, noting that a Dirac equation for helium does not exist [17]. The calculation involved two parts, given in Eqns. (37) and (38), each of which generalizes to helium. The first part of the calculation involves deriving the spin-dependent parts of $H^{(6)}$ for helium. This was first carried out in a Bethe-Salpeter framework by Douglas and Kroll [27]. A much more compact derivation using effective field theory was given in Ref. [34], and will be summarized below. The second part involves evaluating second order perturbation theory with the full Breit Hamiltonian, and was first carried out by Lewis and Serafino [35]. The total result can be written as

$$\nu^{(4)} = \nu_A^{(4)} + \nu_B^{(4)}, \tag{95}$$

with

$$\nu_A^{(4)} = \langle H^{(4)} \frac{1}{(E-H)'} H^{(4)} \rangle \tag{96}$$

and

$$\nu_B^{(4)} = \sum_{i=1}^{15} \langle H_i^{(6)} \rangle, \tag{97}$$

where the single $H^{(6)}$ for hydrogen given in Eq. (37) becomes 15 terms. We now give a brief description of how these terms can be derived using old-fashioned perturbation theory [34], followed by a briefer discussion of $\nu_A^{(4)}$.

For the calculation of the effective Hamiltonian we use time–ordered perturbation theory to derive the Douglas-Kroll operators, with the relevant diagrams being given in Fig. 2. We will classify the operators in terms of six terms, $V_1 - V_6$, each associated with one of the diagrams, but note

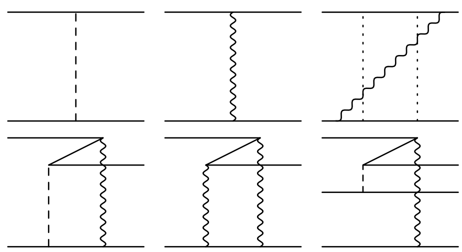

Fig. 2. Time ordered diagrams contributing to fine structure splitting in order $m\alpha^6$. The middle horizontal line corresponds to helium, two outer horizontal lines correspond to two electrons. The wavy line is a transverse photon, the dashed line is a Coulomb photon, and the dotted line denotes retardation.

that all 15 operators found by Douglas and Kroll are contained in them. The rules for deriving an expression from the corresponding diagram are as follows. We continue to use Coulomb gauge, with a dashed line representing a Coulomb photon and a wavy line a transverse photon: the dotted line is a Coulomb photon together with a kinetic energy term as discussed below. Three-momentum is conserved at each vertex, and there are projection operators between the vertices on electron lines onto positive or negative energy states, depending on the time arrow. Any diagram with more than one vertex on an electron line has energy denominators associated with it, where each denominator is $E - \Sigma_i E_i$, where the sum goes over all intermediate states. There is also a factor -1 for any electron positron pair creation. When a transverse photon is involved, the leading term in the denominator is the photon energy, and for most cases one can neglect other terms in the denominator. The transverse photon in this approximation is denoted by a vertical wavy line. In some cases the denominator is expanded to account for the electron kinetic energy, and this effect is grouped together with Coulomb photon exchange and described graphically with the dotted line mentioned above. Since either electron could first emit a photon with the other electron absorbing it, an overall factor of $-2/q$ is present. The whole expression is enclosed by $u^\dagger(p')$ and $u(p)$, the free fermion bispinors, which correspond to the external lines. The simplifying features coming from working with $2^3P_J$ states mentioned above, specifically the fact that all expectation values with $(\vec{\sigma}_1 - \vec{\sigma}_2)$ vanish and that the wave function vanishes when $\vec{r}_1 = \vec{r}_2$, play an important role in the following.

The electron–nucleus part $V_0$ can be obtained from the first diagram in Fig. 2, with the lower line indicating in this case the nucleus, in a manner basically identical to that given for Coulomb photon exchange in hydrogen, the only difference being that a second electron is present. We have

$$V_0 = -\frac{Z\,\alpha}{q^2}\,\bar{u}(p_1')\gamma^0 u(p_1)\,, \tag{98}$$

where $\vec{q}$ is given by $\vec{q} = \vec{p_1}\,' - \vec{p_1}$ and $u(p)$ is the positive energy solution of the free Dirac equation previously given in Eq. (10). Using the expansion given in Eq. (11) leads to

$$V_0 = \frac{Z\,\alpha}{q^2}\,\frac{3\,i}{32\,m^4}(p_1^2 + p_1'^2)\,\vec{\sigma}_1\cdot\vec{p_1}\,'\times\vec{p_1}\,. \tag{99}$$

Fourier transforming to coordinate space gives

$$V_0 = -\frac{3}{32\,m^4}\left(p_1^2\,\frac{Z\,\alpha}{r_1^3}\,\vec{\sigma}_1\cdot\vec{r}_1\times\vec{p}_1 + \frac{Z\,\alpha}{r_1^3}\,p_1^2\,\vec{\sigma}_1\cdot\vec{r}_1\times\vec{p}_1\right)\,. \tag{100}$$

We can account for the second electron by simply doubling the result, and the final result is

$$V_0 = -\frac{3\,Z\,\alpha}{8\,m^4}\,p_1^2\,\frac{1}{r_1^3}\,\vec{\sigma}_1\cdot\vec{r}_1\times\vec{p}_1\,. \tag{101}$$

Now interpreting the lower line of diagram 1 as an electron, we have the simplest electron–electron term. The initial expression is

$$V_1 = \frac{\alpha}{q^2}\,u^\dagger(p_1')u(p_1)\;u^\dagger(p_2')u(p_2)\,, \tag{102}$$

where

$$\vec{q}\; = \vec{p_1}\,' - \vec{p_1} = \vec{p}_2 - \vec{p}\,'_2\,. \tag{103}$$

As usual, $V_1$ is expanded in momenta up to $p^4$, and we keep only the spin dependent terms that give an $m\alpha^6$ correction to fine structure. After this procedure we find

$$\begin{aligned} V_1 = -&\frac{1}{16\,m^4}\,\frac{\alpha}{q^2} \\ &\Big\{\frac{i}{2}\,q^2\,\left(\vec{\sigma}_1\cdot\vec{p}\,'_1\times\vec{p}_1 + \vec{\sigma}_2\cdot\vec{p}\,'_2\times\vec{p}_2\right) + \vec{\sigma}_1\cdot\vec{p}\,'_1\times\vec{p}_1\,\vec{\sigma}_2\cdot\vec{p}\,'_2\times\vec{p}_2 \\ &+\frac{3}{2}\,\left(p_1^2 + p_1'^2\right)\,i\,\vec{\sigma}_1\cdot\vec{p}\,'_1\times\vec{p}_1 + \frac{3}{2}\,\left(p_2^2 + p_2'^2\right)\,i\,\vec{\sigma}_2\cdot\vec{p}\,'_2\times\vec{p}_2\Big\}\,. \end{aligned} \tag{104}$$

It is convenient at this point to introduce what we call a D-K simplification, in which we compress an expression by changing the index 2 to 1, so long as it gives the same matrix element. In coordinate space we then have

$$\begin{aligned} V_1 = & \frac{3\,\alpha}{8\,m^4}\,\vec{\sigma}_1 \cdot \frac{\vec{r}}{r^5}\,(\vec{r}\cdot\vec{p_2})\times\vec{p}_1 + \frac{3\,\alpha}{8\,m^4}\,\vec{p}_1{}^2\,\vec{\sigma}_1\cdot\frac{\vec{r}}{r^3}\times\vec{p}_1 \\ & -\frac{3\,\alpha}{16\,m^4\,r^5}\,\vec{r}(\vec{r}\times\vec{p}_1\cdot\vec{\sigma}_1)\times\vec{p}_2\cdot\vec{\sigma}_2 - \frac{\alpha}{16\,m^4\,r^3}\,(\vec{\sigma}_1\cdot\vec{p}_2)\,(\vec{\sigma}_2\cdot\vec{p}_1 \quad (105) \end{aligned}$$

If a transverse photon is exchanged, we first set the energy transfer in its propagator to zero, which is called the no retardation limit, with the correction to this procedure accounted for in diagram 3. In this limit diagram 2 in Fig. 2 gives

$$V_2 = -\frac{\alpha}{q^2}\,[u^\dagger(p_1')\,\alpha^i\,u(p_1)]\,[u^\dagger(p_2')\,\alpha^j\,u(p_2)]\,P_{ij}(q). \tag{106}$$

The matrix element of $\alpha^i$ is expanded as

$$\begin{aligned} u^\dagger(p')\,\alpha^i\,u(p) = & \frac{1}{2\,m}\,(p^i + p'^i) + \frac{i}{2\,m}(\vec{\sigma}\times\vec{q})^i \\ & -\frac{1}{16\,m^3}\left[p^i\,(p'^2 + 3\,p^2) + p'^i\,(p^2 + 3\,p'^2)\right] \\ & +\frac{i}{16\,m^3}\left[(\vec{p}'\times\vec{\sigma})^i\,(p^2+3\,p'^2) - (\vec{p}\times\vec{\sigma})^i\,(p'^2+3\,p^2)\right], \end{aligned} \tag{107}$$

which leads to (using the $D-K$ simplification)

$$\begin{aligned} V_2 = & -\frac{\alpha}{8\,m^4\,q^2}\Big\{4\,i\,p_1'^2\,\vec{\sigma}_1\times\vec{q}\cdot\vec{p}_1 + p_1'^2\,\vec{\sigma}_1\cdot\vec{q}\,\vec{\sigma}_2\cdot(\vec{p}_1{}' + \vec{p}_1) \\ & +2\,p_1'^2\,(\vec{\sigma}_1\cdot\vec{q})\,(\vec{\sigma}_2\cdot\vec{q}) \\ & +2\,i\,p_1'^2\,P_{ij}(q)p_2^j\,[2\,\vec{p}_1\times\vec{\sigma}_1 + 3\,\vec{q}\times\vec{\sigma}_1]^i\;. \end{aligned} \tag{108}$$

In configuration space $V_2$ takes the form

$$\begin{aligned} V_2 = & \frac{\alpha}{2\,m^4}\,p_1^2\,\vec{\sigma}_1\cdot\frac{\vec{r}}{r^3}\times\vec{p}_1 + \frac{9\,\alpha}{8\,m^4}\,p_1^2\,\frac{1}{r^5}\,(\vec{\sigma}_1\cdot\vec{r})\,(\vec{\sigma}_2\cdot\vec{r}) \\ & -\frac{i\,\alpha}{4\,m^4}\,p_1^2\,\frac{1}{r^3}\,(\vec{\sigma}_1\cdot\vec{r})\,(\vec{\sigma}_2\cdot\vec{p}_1) + \frac{i\,\alpha}{4\,m^2}\,p_1^2\,\frac{1}{r}\,\vec{\sigma}_1\cdot\vec{p}_1\times\vec{p}_2 \\ & -\frac{i\,\alpha}{4\,m^2}\,p_1^2\,\frac{\vec{r}}{r^3}\,\big(\vec{\sigma}_1\cdot\vec{r}\times\vec{p}_1\big)\vec{p}_2 - \frac{3\,\alpha}{4\,m^2}p_1^2\vec{\sigma}_1\cdot\frac{\vec{r}}{r^3}\times\vec{p}_2\,. \end{aligned} \tag{109}$$

Diagram 3, representing the retardation part of single transverse photon exchange, requires the most care. It is given by

$$V_3 = \alpha \int \frac{d^3k}{(2\,\pi)^3\,2\,k}\,P_{ij}(k)\left(\frac{p_1^i}{m} + \frac{i\,(\vec\sigma_1\times\vec k)^i}{2\,m}\right)$$
$$\left\{e^{i\,\vec k\cdot\vec r_1}\,\left(\frac{1}{E_0-k-H_0}+\frac{1}{k}\right)e^{-i\,\vec k\cdot\vec r_2}\right\}\left(\frac{p_2^j}{m} - \frac{i\,(\vec\sigma_2\times\vec k)^j}{2\,m}\right) + (1\leftrightarrow 2)\,. \tag{110}$$

Only the second term in the retardation expansion contributes in order $m\,\alpha^6$ (notice two dotted lines in the corresponding diagram):

$$\frac{1}{E_0-k-H_0}+\frac{1}{k} = \frac{(H_0-E_0)}{k^2} - \frac{(H_0-E_0)^2}{k^3} + \ldots\,, \tag{111}$$

and the retardation part $V_3$ becomes

$$\begin{aligned} V_3 &= -\alpha \int \frac{d^3k}{(2\,\pi)^3\,2\,k}\,P_{ij}(k)\left(\frac{p_1^i}{m} + \frac{i\,(\vec\sigma_1\times\vec k)^i}{2\,m}\right) \\ &\quad \left\{e^{i\,\vec k\cdot\vec r_1}\,\frac{(H_0-E_0)^2}{k^3}e^{-i\,\vec k\cdot\vec r_2}\right\}\left(\frac{p_2^j}{m} - \frac{i\,(\vec\sigma_2\times\vec k)^j}{2\,m}\right) + (1\leftrightarrow 2) \\ &= V_3^A + V_3^B\,, \end{aligned} \tag{112}$$

where we have split the spin-dependent part of the calculation into two parts. Considering first the spin–spin term $V_3^A$ we have

$$V_3^A = \frac{\alpha}{8\,m^2}\int\frac{d^3k}{(2\,\pi)^3}\,\frac{\vec\sigma_1\cdot\vec k\,\vec\sigma_2\cdot\vec k}{k^4}e^{i\,\vec k\cdot\vec r_1}\,(H_0-E_0)^2e^{-i\,\vec k\cdot\vec r_2} + (1\leftrightarrow 2)\,. \tag{113}$$

Because $(H_0-E_0)$ gives zero if next to a wave function, we can carry out the manipulation

$$\begin{aligned} &e^{i\,\vec k\,\vec r_1}\,(H_0-E_0)^2e^{-i\,\vec k\cdot\vec r_2} + (1\leftrightarrow 2) \\ &\to \left[e^{i\,\vec k\cdot\vec r_1}\,,\,\left[(H_0-E_0)^2\,,\,e^{-i\,\vec k\cdot\vec r_2}\right]\right] \\ &= -\frac{1}{2\,m^2}\,\left[p_1^2\,,\,\left[p_2^2\,,\,e^{i\,\vec k\cdot\vec r}\right]\right] \end{aligned} \tag{114}$$

to show

$$V_3^A = -\frac{\alpha}{16\,m^4}\,\sigma_1^i\,\sigma_2^j\left[p_1^2\,,\,\left[p_2^2\,,\,\int\frac{d^3k}{(2\,\pi)^3}\,\frac{k^i\,k^j}{k^4}\,e^{i\,\vec k\cdot\vec r}\right]\right]\,. \tag{115}$$

Performing the $k$–integral with

$$\int\frac{d^3k}{(2\,\pi)^3}\,\frac{1}{k^2}\left(\frac{\delta^{ij}}{3}-\frac{k^i\,k^j}{k^2}\right)e^{i\,\vec k\cdot\vec r} = \frac{1}{8\,\pi\,r}\,\left(\frac{r^i\,r^j}{r^2}-\frac{\delta^{ij}}{3}\right) \tag{116}$$

then leads to, after some further manipulations, to

$$V_3^A = \frac{\alpha}{16\,m^4}\,p_1^2\left[p_2^2, \frac{r^i\,r^j}{r^3}\right]\,{\sigma_1}^i\,{\sigma_2}^j \tag{117}$$

$$= \frac{3\,\alpha}{8\,m^4}\,p_1^2\,\frac{\vec{\sigma}_1\cdot\vec{r}\,\vec{\sigma}_2\cdot\vec{r}}{r^5}$$
$$+\,\frac{\alpha}{8\,m^4}\,p_1^2\,\frac{i}{r^2}\,[(\hat{r}\cdot\vec{\sigma}_2)\,\vec{\sigma}_1 + (\hat{r}\cdot\vec{\sigma}_1)\,\vec{\sigma}_2 - 3\,(\hat{r}\cdot\vec{\sigma}_1)\,(\hat{r}\cdot\vec{\sigma}_2)\,\hat{r}]\cdot\vec{p}_2 \tag{118}$$

The second part, the spin–orbit term $V_3^B$, is obtained from Eq. (112)

$$V_3^B = -\frac{i\,\alpha}{4\,m^2}\int\frac{d^3k}{(2\,\pi)^3}\,\frac{1}{k^4}\Big[e^{i\,\vec{k}\cdot\vec{r}_1}\,(H_0-E_0)^2 e^{-i\,\vec{k}\cdot\vec{r}_2}\,\vec{\sigma}_1\times\vec{k}\cdot\vec{p}_2$$
$$-\vec{\sigma}_2\times\vec{k}\cdot\vec{p}_1\,e^{i\,\vec{k}\cdot\vec{r}_1}\,(H_0-E_0)^2 e^{-i\,\vec{k}\cdot\vec{r}_2}\Big] + (1\leftrightarrow 2)\,. \tag{119}$$

Using

$$e^{i\,\vec{k}\,\vec{r}_1}\,(H_0-E_0)^2 e^{-i\,\vec{k}\cdot\vec{r}_2}$$
$$= (H_0-E_0)\,e^{i\,\vec{k}\cdot\vec{r}}\,(H_0-E_0) + (H_0-E_0)\,\left[\frac{p_2^2}{2\,m}\,,\,e^{i\,\vec{k}\cdot\vec{r}}\right]$$
$$+\left[e^{i\,\vec{k}\cdot\vec{r}}\,,\,\frac{p_1^2}{2\,m}\right]\,(H_0-E_0) + \left[\frac{p_2^2}{2\,m}\,,\,\left[e^{i\,\vec{k}\cdot\vec{r}}\,,\,\frac{p_1^2}{2\,m}\right]\right] \tag{120}$$

allows it to be rewritten as

$$V_3^B = -\frac{i\,\alpha}{m^2}\int\frac{d^3k}{(2\,\pi)^3}\,\frac{1}{k^4}\,\Big\{\left[e^{i\,\vec{k}\cdot\vec{r}}\,,\,\frac{p_1^2}{2\,m}\right]\,\left[H_0\,,\,\vec{\sigma}_1\times\vec{k}\cdot\vec{p}_2\right]$$
$$+\left[\frac{p_2^2}{2\,m}\,,\,\left[e^{i\,\vec{k}\cdot\vec{r}}\,,\,\frac{p_1^2}{2\,m}\right]\right]\,\vec{\sigma}_1\times\vec{k}\cdot\vec{p}_2\Big\}\,. \tag{121}$$

Carrying out the $k$–integral using

$$\int\frac{d^3k}{(2\,\pi)^3}\,\frac{4\,\pi}{k^4}\,\left(e^{i\,\vec{k}\cdot\vec{r}}-1\right) = -\frac{r}{2} \tag{122}$$

and evaluating the commutators gives

$$V_3^B = \frac{\alpha^2}{2\,m^3}\,\vec{\sigma}_1\cdot\frac{\vec{r}}{r^4}\times\vec{p}_1 + \frac{Z\,\alpha^2}{2\,m^3\,r}\,\vec{\sigma}_1\cdot\frac{\vec{r}_1}{r_1^3}\times\vec{p}_2 + \frac{Z\,\alpha^2}{2\,m^3}\,\vec{\sigma}_1\cdot\frac{\vec{r}\times\vec{r}_1}{r^3 r_1^3}\,\vec{r}\cdot\vec{p}_2$$
$$-\frac{\alpha}{2\,m^4}\,p_1^2\,\vec{\sigma}_1\cdot\frac{\vec{r}}{r^3}\times\vec{p}_2 + \frac{\alpha}{2\,m^2}\,p_1^2\,\vec{\sigma}_1\cdot\frac{i\,\vec{r}}{r^3}\,(\vec{r}\cdot\vec{p}_2)\times\vec{p}_2\,. \tag{123}$$

Diagrams 4 and 5 of Fig. 2 are the time-ordered perturbation theory forms of the 'box' and 'crossed box' diagrams with one transverse and one Coulomb, or two transverse photons respectively. Beginning with diagram

4, we first analyze the upper electron line. We use $q_1$ and $q_2$ to denote the momenta transfered by the transverse and Coulomb photons respectively,

$$u^\dagger(p_1')\,\alpha^j\,\Lambda_-(p_1+q_2)\,u(p_1)+u^\dagger(p_1')\,\Lambda_-(p_1'-q_2)\;\alpha^j\,u(p_1)$$
$$=-\frac{i}{m}\,(\vec{q}_2\times\vec{\sigma}_1)^j\,. \tag{124}$$

The lower electron line is

$$u^\dagger(p_2')\,\alpha^i\,\Lambda_+(p_2'+q_1)\,u(p_2)+u^\dagger(p_2')\,\Lambda_+(p_2-q_1)\;\alpha^i\,u(p_2)$$
$$=\frac{1}{m}(p_2^i+p_2'^i)+\frac{i}{m}\,(\vec{q}_1\times\vec{\sigma}_2)^i\,. \tag{125}$$

Combining these expressions we find the effective interaction $V_4$ to be

$$\begin{aligned}V_4=2\int\frac{d^3q_1}{(2\,\pi)^3}\int\frac{d^3q_2}{(2\,\pi)^3}\,(2\,\pi)^3\,\delta^3(\vec{q}_1+\vec{q}_2-\vec{q})\,\frac{\alpha}{q_2^2}\,\frac{\alpha}{2\,q_1^2}\,P_{ij}(q_1)\\ \frac{1}{2\,m}\,\frac{i}{m}\,(\vec{q}_2\times\vec{\sigma}_1)^j\,\left[\frac{1}{m}(p_2^i+p_2'^i)+\frac{i}{m}\,(\vec{q}_1\times\vec{\sigma}_2)^i\right] \qquad (126)\\ =\frac{1}{2\,m^3}\int\frac{d^3q_1}{(2\,\pi)^3}\int\frac{d^3q_2}{(2\,\pi)^3}\,(2\,\pi)^3\,\delta^3(\vec{q}_1+\vec{q}_2-\vec{q})\,\frac{\alpha}{q_1^2}\,\frac{\alpha}{q_2^2}\\ \left[(\vec{\sigma}_1\cdot\vec{q}_1)\,(\vec{\sigma}_2\cdot\vec{q}_2)-i\,P_{ij}(q)\,(\vec{\sigma}_1\times\vec{q}_2)^i\,(\vec{p}_2+\vec{p}_2')^j\right]\,. \qquad (127)\end{aligned}$$

The factor 2 in front of the first integral comes from the fact that $Z$ is on upper or on the lower electron line. In configuration space $V_4$ is

$$V_4=\frac{\alpha^2}{2\,m^3\,r^4}\;(\vec{\sigma}_1\cdot\vec{r}\times\vec{p}_2-\vec{\sigma}_1\cdot\hat{r}\,\vec{\sigma}_2\cdot\hat{r})\;. \tag{128}$$

The next contribution is the exchange of two transverse photons with a single $Z$, diagram 5 in Fig. 2. This contribution consists of twelve diagrams. They reduce to two diagrams in the non retardation limit,

$$\begin{aligned}V_5=\int\frac{d^3q_1}{(2\,\pi)^3}\int\frac{d^3q_2}{(2\,\pi)^3}\,(2\,\pi)^3\,\delta^3(\vec{q}_1+\vec{q}_2-\vec{q})\\ \frac{\alpha}{q_1^2}\,P_{ik}(q_1)\,\frac{\alpha}{q_2^2}\,P_{jk}(q_2)\,\frac{1}{2\,m}\\ \left[\frac{(2\,\vec{p}_2+i\,\vec{q}_1\times\vec{\sigma}_2)^i}{2\,m}\,\frac{(2\,\vec{p}'_2+i\,\vec{q}_2\times\vec{\sigma}_2)^j}{2\,m}\right.\\ \left.+\frac{(2\,\vec{p}_1-i\,\vec{q}_1\times\vec{\sigma}_1)^i}{2\,m}\,\frac{(2\,\vec{p}'_1-i\,\vec{q}_2\times\vec{\sigma}_1)^j}{2\,m}\right]. \qquad (129)\end{aligned}$$

In coordinate space

$$V_5=-\frac{\alpha^2}{2\,m^2}\,\vec{\sigma}_1\cdot\frac{\vec{r}}{r^4}\times\vec{p}_1\,. \tag{130}$$

The last diagram, Fig. 6 is a three–body effect, with the horizontal line in the middle being the nucleus. We note its similarity to diagram 4, and a similar analysis leads to

$$V_6 = \frac{1}{4\,m^3}\int\frac{d^3q_1}{(2\,\pi)^3}\int\frac{d^3q_2}{(2\,\pi)^3}\,(2\,\pi)^3\,\delta^3(\vec{q}_1+\vec{q}_2-\vec{q})\,\frac{\alpha}{q_1^2}\,\frac{Z\,\alpha}{q_2^2}$$
$$\left[-\vec{\sigma}_1\cdot\vec{q}_1\,\vec{\sigma}_2\cdot\vec{q}_2+i\,P_{ij}(q_1)\,(\vec{\sigma}_1\times\vec{q}_2)^i\,(\vec{p}_2+\vec{p}_2\,')^j\right]$$
$$+(1\leftrightarrow 2)\,. \tag{131}$$

Its coordinate space representation is

$$V_6 = \frac{Z\,\alpha^2}{2\,m^3}\left[\frac{\vec{\sigma}_1\cdot\vec{r}}{r^3}\,\frac{\vec{\sigma}_2\cdot\vec{r}_1}{r_1^3}-\frac{1}{r\,r_1^3}\,\vec{\sigma}_1\cdot\vec{r}_1\times\vec{p}_2-\frac{1}{r^3\,r_1^3}\,\vec{\sigma}_1\cdot\vec{r}_1\times\vec{r}\,(\vec{r}\cdot\vec{p}_2)\right] \tag{132}$$

We note that the second term of $V_6$ cancels the second term of $V_{3B}$: we will see later when including the effect of $F_2(q^2)$ that this cancellation is no longer present.

The effective Hamiltonian $H^{(6)}$ is the sum of the $V_i$'s derived above,

$$H^{(6)} = \Sigma_{i=0}^{6} V_i\,. \tag{133}$$

This complete result agrees with the Bethe-Salpeter equation based derivation of Douglas and Kroll [27], though those authors included other operators that lead to the $a_e^2 H_{SS}$ part of $(1+a_e)^2 H_{SS}$ that we have already included in our organization of the calculation.

We now discuss the contribution $\nu_A^{(4)}$, which comes from second order perturbation theory. As mentioned above, in this case the entire Breit Hamiltonian must be included, as one can get fine structure from terms with one Hamiltonian being $H_{SI}$ and the other $H_{SD}$ as well as when both are $H_{SD}$. While straightforward in principle, these calculations, first carried out by Lewis and Serafino [35], are algebraically complicated and numerically challenging. The operators one is dealing with are nearly singular, so without very high quality numerical techniques significant wave function related errors can arise. While it is evaluated in the non-recoil limit, it is trivial to incorporate radiative corrections proportional to $a_e$, as they enter as simple algebraic factors. Results with and without the radiative corrections are given in Table 2, but we note that Eq. (72) includes the $a_e$ terms.

## 7. Determination of $\nu^{(4r)}$

Recoil corrections of order $\frac{m^2}{M}(Z\alpha)^6$ have been treated by Drake in Ref. [32] and by us in Refs. [36], [37]. A first set of contributions of this order is obtained by evaluating the Douglas-Kroll operators with a nonrelativistic

Table 1. Douglas-Kroll terms in the infinite nuclear mass limit $\nu_B^{(4)}$, reduced mass and mass polarization corrections $\nu_B^{(4r)}$, in units of $\alpha^4$ Ry = 9.329027 MHz.

| contribution | $\nu_{01B}^{(4)}$ | $\nu_{12B}^{(4)}$ | $\nu_{01B}^{(4r)}$ | $\nu_{12B}^{(4r)}$ |
|---|---|---|---|---|
| $\frac{3\,Z}{8}\,\nabla_1^2\,\frac{1}{r_1^3}\,\vec\sigma_1\cdot(\vec r_1\times\vec p_1)$ | 0.224 210 | 0.448 420 | 0.000 081 | 0.000 162 |
| $-\frac{Z}{r^3\,r_1^3}\,\vec\sigma_1\cdot(\vec r_1\times\vec r)\,(\vec r\cdot\vec p_2)$ | 0.016 418 | 0.032 836 | -0.000 013 | -0.000 026 |
| $\frac{Z}{2}\,\frac{1}{r^3\,r_1^3}\,(\vec\sigma_1\cdot\vec r)\,(\vec\sigma_2\cdot\vec r_1)$ | 0.010 203 | -0.004 081 | -0.000 045 | 0.000 018 |
| $\frac{1}{2}\,\frac{1}{r^4}\,\vec\sigma_1\cdot(\vec r\times\vec p_2)$ | 0.034 557 | 0.069 115 | -0.000 002 | -0.000 003 |
| $-\frac{1}{2}\,\frac{1}{r^6}\,(\vec\sigma_1\cdot\vec r)\,(\vec\sigma_2\cdot\vec r)$ | 0.081 157 | -0.032 463 | -0.000 009 | 0.000 003 |
| $-\frac{5}{8}\,\nabla_1^2\,\frac{1}{r^3}\,\vec\sigma_1\cdot(\vec r\times\vec p_1)$ | -0.093 084 | -0.186 167 | -0.000 009 | -0.000 018 |
| $\frac{3}{4}\,\nabla_1^2\,\frac{1}{r^3}\,\vec\sigma_1\cdot(\vec r\times\vec p_2)$ | -0.171 228 | -0.342 456 | 0.000 054 | 0.000 108 |
| $\frac{i}{4}\,\nabla_1^2\,\frac{1}{r}\,\vec\sigma_1\cdot(\vec p_1\times\vec p_2)$ | 0.000 221 | 0.000 442 | 0.000 007 | 0.000 015 |
| $\frac{3\,i}{4}\,\nabla_1^2\,\frac{1}{r^3}\,(\vec r\cdot\vec p_2)\,\vec\sigma_1\cdot(\vec r\times\vec p_1)$ | 0.006 456 | 0.012 912 | -0.000 022 | -0.000 044 |
| $\frac{3\,i}{8}\,\frac{1}{r^5}\,\vec\sigma_1\cdot(\vec r\times(\vec r\cdot\vec p_2)\,\vec p_1)$ | -0.008 671 | -0.017 343 | 0.000 001 | 0.000 002 |
| $-\frac{3}{16}\,\frac{1}{r^5}\,\vec\sigma_2\cdot(\vec r\times(\vec\sigma_1\cdot(\vec r\times\vec p_1))\,\vec p_2)$ | -0.004 457 | 0.001 783 | 0.000 004 | -0.000 001 |
| $-\frac{1}{16}\,\frac{1}{r^3}\,(\vec\sigma_1\cdot\vec p_2)\,(\vec\sigma_2\cdot\vec p_1)$ | -0.010 325 | 0.004 130 | 0.000 000 | 0.000 000 |
| $-\frac{3}{2}\,\nabla_1^2\,\frac{1}{r^5}\,(\vec\sigma_1\cdot\vec r)\,(\vec\sigma_2\cdot\vec r)$ | -0.786 253 | 0.314 501 | 0.000 235 | -0.000 094 |
| $\frac{i}{4}\,\nabla_1^2\,\frac{1}{r^3}\,(\vec\sigma_1\cdot\vec r)\,(\vec\sigma_2\cdot\vec p_1)$ | 0.135 711 | -0.054 284 | -0.000 032 | 0.000 013 |
| $-\frac{i}{8}\,\nabla_1^2\,\frac{1}{r^3}\,(\vec\sigma_1\cdot\vec r)\,(\vec\sigma_2\cdot\vec p_2)$ | 0.213 103 | -0.085 241 | -0.000 061 | 0.000 024 |
| Total | -0.351 982 | 0.162 103 | 0.000 190 | 0.000 158 |

Table 2. Contributions to $\nu_A^{(4)}$ broken down contributing intermediate states: for each $J$, first row with and second row without $a_e$ factors included in Breit Hamiltonian. Units $\alpha^4$ Ry.

| State | $^3P$ | $^1P$ | $^3D$ | $^1D$ | $^3F$ |
|---|---|---|---|---|---|
| $J=0$ | -0.653470(9) | 0.0 | 0.0 | 0.0 | 0.0 |
| | -0.651602(9) | 0.0 | 0.0 | 0.0 | 0.0 |
| $J=1$ | -0.127293(5) | -0.709495(9) | -0.002831 | 0.0 | 0.0 |
| | -0.126969(5) | -0.707000(9) | -0.002823 | 0.0 | 0.0 |
| $J=2$ | 0.041297(5) | 0.0 | -0.008262 | -0.002385 | -0.005626(1) |
| | 0.041278(5) | 0.0 | -0.008236 | -0.002379 | -0.005600(1) |

Hamiltonian that includes mass polarization, which is analogous to using $E_i$ rather than $\tilde{E}_i$ in the lowest order calculation, in addition including scaling factors of $m_r/m$. Since the original evaluation of the expectation value of the Douglas-Kroll operators [38] was carried out in the infinite nuclear mass limit, we tabulate the difference in Table 1 (see Ref. [36] for more details), finding excellent agreement with Ref. [32]. Secondly, a set of operators analogous to those giving rise to $E_4$ must be derived for this order. These operators were derived in Ref. [37] using effective field theory, and also by Zhang in his Bethe-Salpeter approach [39], [40]. We note that we found four terms of the same form but with opposite sign in comparing with his results. As with the Douglas-Kroll operators there are a number of contributions, and we only illustrate them by showing how a transverse photon exchange with the nucleus leads to a recoil operator of order $\frac{m^2}{M}(Z\alpha)^6$. We recall that this exchange in lowest order led to a recoil operator characterized by the constant $E_4$: the scattering amplitude associated with this term was

$$\mathcal{M}^{eN}(1T) = \frac{Z\alpha}{2M\vec{q}^{\,2}}\bar{u}(\vec{p}_3)\gamma_i u(\vec{p}_1)P_{ij}(q)(-p_1 - 2p_2 - p_3)_j. \tag{134}$$

The order $\alpha^2$ corrections to this come from

$$\begin{aligned}\mathcal{M}_6^{eN}(1T) = \frac{Z\alpha}{32Mm^3\vec{q}^{\,2}} & P_{ij}(q)(p_1 + p_3 + 2p_2)_j \\ & [\sigma_{1i}\vec{\sigma}_1\cdot\vec{p}_1(3\vec{p}_1^{\;2} + \vec{p}_3^{\;2}) + \vec{\sigma}_1\cdot\vec{p}_3\sigma_{1i}(3\vec{p}_3^{\;2} + \vec{p}_1^{\;2})],\end{aligned} \tag{135}$$

which has a spin dependent part

$$\begin{aligned}\mathcal{M}_6^{eN}(1T)(fs) = \frac{i(Z\alpha)}{32Mm^3\vec{q}^{\,2}}\Big[ & 4\vec{\sigma}_1\cdot(\vec{p}_3\times\vec{p}_1)(\vec{p}_1^{\;2} + \vec{p}_3^{\;2}) \\ & + 2\vec{\sigma}_1\cdot(\vec{p}_3\times\vec{p}_2)(\vec{p}_1^{\;2} + 3\vec{p}_3^{\;2}) - 2\vec{\sigma}_1\cdot(\vec{p}_1\times\vec{p}_2)(3\vec{p}_1^{\;2} + \vec{p}_3^{\;2}) \\ & - 2\frac{\vec{q}\cdot(\vec{p}_1 + \vec{p}_3 + 2\vec{p}_2)}{\vec{q}^{\,2}}\vec{\sigma}_1\cdot(\vec{p}_3\times\vec{p}_1)(\vec{p}_3^{\;2} - \vec{p}_1^{\;2})\Big].\end{aligned} \tag{136}$$

Fourier transforming to coordinate space leads to the effective operator

$$\begin{aligned}V_1(R) = {} & \frac{i(Z\alpha)}{4Mm^3}\vec{p}_1^{\;2}\frac{1}{r_1}\vec{\sigma}_1\cdot(\vec{p}_1\times\vec{p}_2) - \frac{i(Z\alpha)}{4Mm^3}\vec{p}_1^{\;2}\frac{\vec{r}_1}{r_1^3}(\vec{\sigma}_1\cdot(\vec{r}_1\times\vec{p}_1))\cdot(\vec{p}_1 + \vec{p}_2) \\ & - \frac{3Z\alpha}{4Mm^3}\vec{p}_1^{\;2}\vec{\sigma}_1\cdot\frac{\vec{r}_1}{r_1^3}\times(\vec{p}_1 + \vec{p}_2).\end{aligned} \tag{137}$$

While 6 other contributions have to be considered, it is remarkable that their sum can be given in the compact form, where now the operators are understood to be in dimensionless units,

$$\begin{aligned}V_{\rm rec}^{DK} = {} & 2\alpha^4\frac{m}{M}\mathrm{Ry}_\infty c \\ & \Big[\frac{Z}{4}p_1^2\Big(\frac{i}{r_1}\vec{\sigma}_1\cdot\vec{p}_1\times\vec{p}_2 - i\frac{\vec{r}_1}{r_1^3}(\vec{\sigma}_1\cdot\vec{r}_1\times\vec{p}_1)\cdot(\vec{p}_1 + \vec{p}_2) - \frac{3}{r_1^3}\vec{\sigma}_1\cdot\vec{r}_1\times(\vec{p}_1 + \vec{p}_2)\Big) \\ & + Z^2\Big(\frac{\vec{\sigma}_1\cdot\vec{r}_1\times\vec{r}_2}{r_1^3 r_2^3}\vec{r}_1\cdot\vec{p}_1 - \frac{1}{2}\vec{\sigma}_1\cdot\frac{\vec{r}_1}{r_1^4}\times(\vec{p}_1 + \vec{p}_2) - \frac{1}{4}\vec{\sigma}_1\cdot\frac{\vec{r}_2}{r_2^3}\vec{\sigma}_2\cdot\frac{\vec{r}_1}{r_1^2}\Big) \\ & + Z\Big(\frac{\vec{\sigma}_1\cdot\vec{r}\times(\vec{p}_1 + \vec{p}_2)}{r_1 r^3} - \frac{\vec{\sigma}_1\cdot(\vec{r}_1\times\vec{r})}{r_1^3 r^3}\vec{r}_1\cdot(\vec{p}_1 + \vec{p}_2)\Big)\Big].\end{aligned} \tag{138}$$

Table 3. Results in kHz for the recoil correction operators, listed with prefactor $2\,\alpha^4 \frac{m}{m_\alpha}\mathrm{Ry}_\infty c$ understood, for the large and small helium fine structure intervals.

| Contribution | $\nu_{01}$ | $\nu_{12}$ |
|---|---|---|
| $\frac{iZ}{4}p_1^2\frac{1}{r_1}\vec{\sigma}_1\cdot(\vec{p}_1\times\vec{p}_2)$ | 0.480 | 0.959 |
| $-\frac{iZ}{4}\,p_1^2\,\frac{\vec{r}_1}{r_1^3}\,(\vec{\sigma}_1\cdot\vec{r}_1\times\vec{p}_1)\cdot(\vec{p}_1+\vec{p}_2)$ | 0.165 | 0.330 |
| $-\frac{3Z}{4}\,p_1^2\,\vec{\sigma}_1\cdot\frac{\vec{r}_1}{r_1^3}\times(\vec{p}_1+\vec{p}_2)$ | -1.103 | -2.206 |
| $Z\,\vec{\sigma}_1\cdot\frac{\vec{r}}{r_1\,r^3}\times(\vec{p}_1+\vec{p}_2)$ | 0.129 | 0.258 |
| $Z\,\vec{\sigma}_1\cdot\frac{\vec{r}}{r^3}\times\frac{\vec{r}_1}{r_1^3}\,(\vec{r}_1\cdot(\vec{p}_1+\vec{p}_2))$ | 0.042 | 0.085 |
| $Z^2\,\vec{\sigma}_1\cdot\frac{\vec{r}_1}{r_1^3}\times\frac{\vec{r}_2}{r_2^3}\,(\vec{r}_1\cdot\vec{p}_1)$ | -0.236 | -0.472 |
| $-\frac{Z^2}{2}\,\vec{\sigma}_1\cdot\frac{\vec{r}_1}{r_1^4}\times(\vec{p}_1+\vec{p}_2)$ | -0.471 | -0.941 |
| $-\frac{Z^2}{4}\vec{\sigma}_1\cdot\frac{\vec{r}_2}{r_2^3}\,\vec{\sigma}_2\cdot\frac{\vec{r}_1}{r_1^3}$ | -0.354 | 0.141 |
| sum | -1.348 | -1.847 |

Finally, recoil corrections to the Lewis-Serafino calculation of the second order contribution must be treated. This is a far less trivial task than including leading QED corrections, and has at present only been carried out by Drake [32], who quotes 0.010 19 MHz for the contribution to $\nu_{12}^{(4r)}$ and $-0.010$ 81 MHz for $\nu_{01}^{(4r)}$. The result given for $\nu^{(4r)}$ in Eq. (72) is the sum of the three corrections discussed above.

## 8. Determination of $\nu^{(5)}$

By far the most difficult part of this calculation is the accurate determination of corrections of order $m\alpha^7$. As can be seen from the discussion of the hydrogenic case, even for a one-electron system these calculations are extremely complex. Several recent advances in bound state QED have made the calculation of higher order corrections to helium fine structure possible. Firstly, Yelkhovsky in Ref. [41] has shown how to use dimensional regularization in the calculation of helium energy levels, and together with Korobov has obtained in [42] numerical values for the $\alpha^4$ Ry contributions to the ground state. Although their results contain several mistakes [30], the approach in general is a very powerful one. Secondly, in Ref. [16], a Foldy-Wouthuysen (F.W) transformed QED Langrangian was used to derive all effective $\alpha^4$ Ry operators for arbitrary states of few electron atoms. It will be demonstrated below that instead of the full QED Lagrangian, one can use an approximate F.W. form when, as is the case here, all electron momenta involved are much smaller than the electron mass. This includes corrections involving the anomalous magnetic moment $a_e$. More recently, K.P. together with Jentschura and Czarnecki, has obtained in Ref. [43] general formulae for $\alpha^5$ Ry corrections to hydrogenic energy levels. The calculational approach of these works [42,43,44] and the present chapter is based on dimensionally regularized QED. The parameter $\epsilon$, related to the space dimension $d = 3 - 2\,\epsilon$, plays the role of both an infrared and ultraviolet regulator, as some $\alpha^5$ Ry terms are divergent in $d = 3$ space. This artificial parameter $\epsilon$ is used to regulate various terms, and we will explicitly demonstrate its cancellation in their sum.

The fine structure in order $m\,\alpha^7$ ($\alpha^5\,$Ry) can be written as [45]

$$E^{(7)} = \langle H^{(7)} \rangle + 2 \left\langle H^{(4)} \, \frac{1}{(E_0 - H_0)'} \, H^{(5)} \right\rangle + E_L, \tag{139}$$

where $E_L$ is the Bethe logarithmic correction defined below in Eq. (161), and $H^{(i)}$ is an effective Hamiltonian of order $m\,\alpha^i$. We now present complete derivations of $H^{(7)}$, the second order term (which will be referred to in the following as $E_S$), and $E_L$. These contributions have been derived and calculated in a series of works [45,14]. Important terms of order $m\,\alpha^7\,\ln\alpha$, previously calculated in Ref. [46], have been confirmed in [45].

$H^{(7)}$ consists of exchange terms, where photons are exchanged between the electrons, and radiative corrections, where a photon is emitted and absorbed by the same electron. We consider first the exchange terms. Their derivation in general is quite complicated. We find that only two-photon exchange diagrams contribute and there are no three-body terms, the result of an internal cancellation. A feature of the calculation that leads to considerable simplification is the fact that the order being calculated is nonanalytic in $\alpha^2$. For example, $H^{(5)}$ (see Eq. (157)) consists of Dirac delta $\delta^3(r)$ and $1/r^3$ terms only, and they can be derived from the two-photon exchange scattering amplitude. Similar results hold for the spin dependent $m\,\alpha^7$ terms. If $H^{(7)}$ represents an effective Hamiltonian, it has to give the same scattering amplitude as in full QED. Therefore, we obtain the exchange contribution $\delta H$ from the spin dependent part of the two-photon scattering amplitude, which is

$$
\begin{aligned}
\delta_1 H = \frac{i\,e^4}{(2\,\pi)^D} \int d^D k \, \frac{1}{(k+q/2)^2} \, \frac{1}{(k-q/2)^2} \\
\Big[ \bar{u}(p_1')\,\gamma^\mu \, \frac{1}{\not k + (\not p_1 + \not p_1')/2 - 1} \, \gamma^\nu \, u(p_1) \\
+ \bar{u}(p_1')\,\gamma^\nu \, \frac{1}{-\not k + (\not p_1 + \not p_1')/2 - 1} \, \gamma^\mu \, u(p_1) \Big] \\
\times \bar{u}(p_2')\,\gamma^\nu \, \frac{1}{\not k + (\not p_2 + \not p_2')/2 - 1} \, \gamma^\mu \, u(p_2)
\end{aligned}
\tag{140}
$$

where $q$ has been defined in Eq. (103). There are three scales of the $k$ integral: $m$, $m\,\alpha$, and $m\,\alpha^2$. Only the first two are included here, with the low energy part $k \sim \alpha^2$ treated separately as a contribution to $E_L$. From the above scattering amplitude one extracts the spin dependent terms using

$$
\bar{u}(p')\,Q\,u(p) = \mathrm{Tr}\,Q\,u(p) \otimes \bar{u}(p') \to \begin{cases} \mathrm{Tr}\,Q\,\left(\frac{\not p + m}{2\,m}\right)\left(\frac{\gamma^0 + I}{4}\right)\left(\frac{\not p' + m}{2\,m}\right) \\ \sigma^{ij}\,\mathrm{Tr}\,Q\,\left(\frac{\not p + m}{2\,m}\right)\left(\frac{\gamma^0 + I}{2}\right)\frac{\sigma^{ij}}{4}\left(\frac{\not p' + m}{2\,m}\right) \end{cases}
\tag{141}
$$

If one expands this amplitude in small external momenta and assumes $k \sim m$, one obtains

$$
\begin{aligned}
\delta_{1H} H = \alpha^2 \Big\{ \sigma_1(j,q)\,\sigma_2(j,q)\, \left[-\frac{23}{36} + \frac{7}{12\,\epsilon}\right] \\
+ i\,[\sigma_1(p_1',p_1) + \sigma_2(p_2',p_2)]\, \left[-\frac{1}{6} - \frac{1}{4\,\epsilon}\right] \\
+ i\,[\sigma_1(p_2',p_2) + \sigma_2(p_1',p_1)] \left[\frac{1}{4}\right] \\
+ \frac{1}{8}\,\sigma_1(j, p_1 + p_1')\,\sigma_2(j, p_2 + p_2') \\
- \frac{1}{8}\,\sigma_1(j, p_2 + p_2')\,\sigma_2(j, p_1 + p_1') \\
+ \frac{17}{72}\,\sigma_1(j, p_1 - p_2 + p_1' - p_2')\,\sigma_2(j, p_1 - p_2 + p_1' - p_2') \Big\}
\end{aligned}
\tag{142}
$$

A similar expansion, but now assuming that $k \sim m\,\alpha$ leads to

$$
\begin{aligned}
\delta_{1M} H = \alpha^2 \Big\{ \sigma_1(j,q)\,\sigma_2(j,q)\, \left[-\frac{5}{12} - \frac{1}{4\,\epsilon} + \frac{1}{2}\,\ln(q)\right] \\
+ i\,[\sigma_1(p_1',p_1) + \sigma_2(p_2',p_2)]\, \left[\frac{7}{12} - \frac{1}{12\,\epsilon} + \frac{1}{6}\,\ln(q)\right] \\
+ i\,[\sigma_1(p_2',p_2) + \sigma_2(p_1',p_1)] \left[\frac{2}{3} - \frac{2}{3\,\epsilon} + \frac{4}{3}\,\ln(q)\right] \Big\}.
\end{aligned}
\tag{143}
$$

The sum of $\delta_{1H} H$ and $\delta_{1M} H$ is

$$\begin{aligned}\delta_1 H = \alpha^2 \Big\{ &\sigma_1(j,q)\,\sigma_2(j,q)\,\left[-\frac{19}{18} + \frac{1}{3\,\epsilon} + \frac{1}{2}\,\ln(q)\right] \\ &+ i\,[\sigma_1(p_1',p_1) + \sigma_2(p_2',p_2)]\,\left[\frac{5}{12} - \frac{1}{3\,\epsilon} + \frac{1}{6}\,\ln(q)\right] \\ &+ i\,[\sigma_1(p_2',p_2) + \sigma_2(p_1',p_1)]\left[\frac{11}{12} - \frac{2}{3\,\epsilon} + \frac{4}{3}\,\ln(q)\right] \\ &+ \frac{1}{8}\,\sigma_1(j,p_1+p_1')\,\sigma_2(j,p_2+p_2') \\ &- \frac{1}{8}\,\sigma_1(j,p_2+p_2')\,\sigma_2(j,p_1+p_1') \\ &+ \frac{17}{72}\,\sigma_1(j,p_1-p_2+p_1'-p_2')\,\sigma_2(j,p_1-p_2+p_1'-p_2')\Big\}, \end{aligned} \tag{144}$$

where $\sigma^{ij} = -i/2\,[\sigma^i,\sigma^j]$, $\sigma(j,q) = \sigma^{ji}\,q^i$, and $q = \sqrt{\vec{q}^2}$. The $1/\epsilon$ divergences cancel out with the low energy part where photon momenta are of the order of the binding energy. This low energy contribution is also evaluated in D-dimensions. Specifically, the integral over photon energy is split into two parts $\int_0^\infty d\omega = \int_0^\Lambda d\omega + \int_\Lambda^\infty d\omega$, then an expansion around $D=3$ is made, followed finally by an expansion in $\alpha$ and taking the limit of large $\Lambda$. The first part is finite at $D=3$, and will be evaluated later together with the self-energy contribution in Eq. (161), while the second part is given by

$$\begin{aligned}\delta E_L = \alpha \int_\Lambda^\infty &\frac{d^d k}{(2\,\pi)^d\,2\,k}\,P_{ij}(k) \\ &\times \delta\left\langle \phi \left| p_1^i\,\frac{1}{E-H-k}\,p_2^j \right| \phi \right\rangle + (1 \leftrightarrow 2). \end{aligned} \tag{145}$$

Here $\delta$ indicates both including the first order correction to $\phi$ along with the change in $H$ and $E$ due to the spin dependent part of the Breit-Pauli Hamiltonian $H^{(4)}$, which in $D-$dimensions is

$$\delta H = \frac{\alpha}{4\,m^2\,q^2}\left[i\,{p_1'}^i\,{p_1}^j(\sigma_1^{ij} + 2\,\sigma_2^{ij}) + i\,{p_2'}^i\,{p_2}^j(\sigma_2^{ij} + 2\,\sigma_1^{ij}) - \sigma_1^{ik}\,\sigma_2^{jk}\,q^i\,q^j\right]. \tag{146}$$

The resulting correction is a sum of two terms. The first one contributes to $E_S$ in Eq. (139), and the second term is the effective Hamiltonian

$$\begin{aligned}\delta_2 H = \alpha^2 &\left[\frac{5}{9} + \frac{1}{3\,\epsilon} + \frac{2}{3}\,\ln[(Z\,\alpha)^{-2}]\right]\,[i\,\sigma_1(p_1',p_1) \\ &+ i\,\sigma_2(p_2',p_2) + 2\,i\,\sigma_1(p_2',p_2) + 2\,i\,\sigma_2(p_1',p_1) \\ &- \sigma_1(j,q)\,\sigma_2(j,q)], \end{aligned} \tag{147}$$

where we have omitted $\ln 2\Lambda$. (A cancelling $\ln 2\Lambda$ appears in the $\int_0^\Lambda d\omega$ integral, and therefore can be consistently dropped in both parts of the calculation). Together with Eq. (144) this gives the complete contribution due to exchange terms. When calculating expectation values between ${}^3P_J$ states further simplifications can be performed. One of them is using the fact that the expectation value of a Dirac delta function with both momenta on the right or on the left hand side vanishes. Secondly, as noted earlier, the expectation value of $\sigma_1$ is equal to that of $\sigma_2$ for triplet states. As a result the total exchange contribution $H_E = \delta_1 H + \delta_2 H$ is

$$
\begin{aligned}
H_E = \alpha^2 & \left[ 6 + 4 \ln[(Z\,\alpha)^{-2}] + 3\,\ln q \right] i\,\sigma_1(p_1', p_1) \\
& + \alpha^2 \left[ -\frac{23}{9} - \frac{2}{3}\,\ln[(Z\,\alpha)^{-2}] + \frac{1}{2}\,\ln q \right] \\
& \times \sigma_1(j,q)\,\sigma_2(j,q).
\end{aligned} \tag{148}
$$

The treatment of radiative corrections is different. We argue that these corrections can be incorporated by the use of the same electromagnetic form factors introduced in the hydrogen section along with a Uehling correction to the Coulomb potential

$$
\begin{aligned}
F_1(-\vec{q}^{\,2}) &= 1 + \frac{\alpha}{\pi} \left( \frac{1}{8} + \frac{1}{6\,\epsilon} \right) \vec{q}^{\,2} \\
F_2(-\vec{q}^{\,2}) &= \frac{\alpha}{\pi} \left( \frac{1}{2} - \frac{1}{12}\,\vec{q}^{\,2} \right) \\
F_V(-\vec{q}^{\,2}) &= \frac{\alpha}{\pi}\,\frac{1}{15}\,\vec{q}^{\,2}.
\end{aligned} \tag{149}
$$

In principle there are additional corrections quadratic in the electromagnetic field. However, terms formed out of $\vec{E}, \vec{B}, \vec{p}, \vec{\sigma}$ can be shown to contribute only at higher order, and thus can be neglected. Corrections coming from Eq. (149) are obtained by rederiving the Breit-Pauli Hamiltonian $H_{SD}$ using these modified electromagnetic vertices and photon propagator, with the result

$$
\begin{aligned}
\delta_3 H = \pi\,Z\,\alpha & (F_1' + 2\,F_2' + F_V') i\,[\sigma_1(p_1'', p_1) + \sigma_2(p_2'', p_2)] \\
& - \pi\,\alpha(2\,F_1' + 2\,F_2' + F_V') i\,[\sigma_1(p_1', p_1) + \sigma_2(p_2', p_2)] \\
& - 2\,\pi\,\alpha(2\,F_1' + F_2' + F_V') i\,[\sigma_1(p_2', p_2) + \sigma_2(p_1', p_1)] \\
& + \pi\,\alpha(2\,F_1' + 2\,F_2' + F_V')\,\sigma_1(j,q)\,\sigma_1(j,q)\,,
\end{aligned} \tag{150}
$$

where by $p''$ we denote momentum scattered off the Coulomb potential of a nucleus. There is also a low-energy contribution which is calculated in a way similar to this in Eq. (145), namely

$$\delta E_L = \alpha \int_\Lambda^\infty \frac{d^d k}{(2\,\pi)^d\, 2\,k}\, P_{ij}(k) \times \delta \left\langle \phi \middle| p_1^i\, \frac{1}{E-H-k}\, p_1^j \middle| \phi \right\rangle + (1 \to 2). \tag{151}$$

The resulting effective Hamiltonian is

$$\begin{aligned}\delta_4 H = \alpha^2 & \left[\frac{5}{9} + \frac{1}{3\,\epsilon} + \frac{2}{3}\,\ln[(Z\,\alpha)^{-2}]\right] \\ & \times\left[\frac{i\,Z}{2}\,\sigma_1(p_1'', p_1) + \frac{i\,Z}{2}\,\sigma_2(p_2'', p_2) \right.\\ & -i\,\sigma_1(p_1', p_1) - i\,\sigma_2(p_2', p_2) - 2\,i\,\sigma_2(p_1', p_1) \\ & \left. -2\,i\,\sigma_1(p_2', p_2) + \sigma_1(j,q)\,\sigma_2(j,q)\right]. \end{aligned}\tag{152}$$

The complete radiative correction is the sum of Eqs. (150) and (152), $H_R = \delta_3 H + \delta_4 H$. Using symmetry $1 \leftrightarrow 2$ it takes the form

$$\begin{aligned}H_R = Z\,\alpha^2 & \left[\frac{91}{180} + \frac{2}{3}\,\ln[(Z\,\alpha)^{-2}]\right] i\,\sigma_1(p_1'', p_1) \\ & +\alpha^2\left[\frac{73}{180} + \frac{2}{3}\,\ln[(Z\,\alpha)^{-2}]\right]\,\sigma_1(j,q)\,\sigma_2(j,q) \\ & -\alpha^2\left[\frac{21}{10} + 4\,\ln[(Z\,\alpha)^{-2}]\right]\, i\,\sigma_1(p_1', p_1). \end{aligned}\tag{153}$$

It is convenient to consider the sum of Eqs. (148) and (153), as several logarithmic terms cancel out. In coordinate space, using atomic units, $H_Q = H_E + H_R$ takes the form

$$\begin{aligned}H_Q = Z\,\alpha^7 & \left(\frac{91}{180} + \frac{2}{3}\,\ln[(Z\,\alpha)^{-2}]\right) i\,\vec{p}_1 \times \delta^3(r_1)\,\vec{p}_1 \cdot \vec{\sigma}_1 \\ & +\alpha^7\left(-\frac{83}{60} + \frac{\ln\alpha}{2}\right)\,(\vec{\sigma}_1 \cdot \vec{\nabla})\,(\vec{\sigma}_2 \cdot \vec{\nabla})\delta^3(r) \\ & -\alpha^7\,\frac{15}{8\,\pi}\,\frac{1}{r^7}\,(\vec{\sigma}_1 \cdot \vec{r})\,(\vec{\sigma}_2 \cdot \vec{r}) \\ & +\alpha^7\,\left(\frac{69}{10} + 3\,\ln\alpha\right)\, i\,\vec{p}_1 \times \delta^3(r)\,\vec{p}_1 \cdot \vec{\sigma}_1 \\ & -\alpha^7\,\frac{3}{4\,\pi}\, i\,\vec{p}_1 \times \frac{1}{r^3}\,\vec{p}_1 \cdot \vec{\sigma}_1, \end{aligned}\tag{154}$$

where the singular $\int dr/r$ integral is defined with an implicit lower cut-off $\epsilon$ and a term $\ln\epsilon + \gamma$ is subtracted out. The logarithmic terms in the above equation agree with Refs. [46,34]. Numerical results for the nonlogarithmic terms are presented in Table 4.

Table 4. Operators due to exchange diagrams, slope of formfactors and the vacuum polarization, in atomic units with a prefactor $m\,\alpha^7/\pi$

| Operator | $\nu_{01}$[kHz] | $\nu_{12}$[kHz] |
|---|---|---|
| $Q_1 = \frac{91\,\pi}{180}\,Z\,i\,\vec{p}_1 \times \delta^3(r_1)\,\vec{p}_1 \cdot \vec{\sigma}_1$ | 2.854 | 5.709 |
| $Q_2 = -\frac{83\,\pi}{60}\,\vec{\sigma}_1 \cdot \vec{\nabla}\,\vec{\sigma}_2 \cdot \vec{\nabla}\delta^3(r)$ | 10.886 | −4.355 |
| $Q_3 = -\frac{15}{8}\,\frac{1}{r^7}\,\vec{r}\cdot\vec{\sigma}_1\,\vec{r}\cdot\vec{\sigma}_2$ | 4.132 | −1.653 |
| $Q_4 = \frac{69\,\pi}{10}\,i\vec{p}_1 \times \delta^3(r)\vec{p}_1 \cdot \vec{\sigma}_1$ | 5.186 | 10.372 |
| $Q_5 = -\frac{3\,i}{4}\,\vec{p}_1 \times \frac{1}{r^3}\,\vec{p}_1 \cdot \vec{\sigma}_1$ | −1.328 | −2.656 |
| $E_Q = \sum_{i=1,5} Q_i$ | 21.731 | 7.418 |

The remaining contribution to $H^{(7)}$ involves the anomalous magnetic moment (amm) correction to the spin dependent operators. They do not lead to any divergences, and therefore can be calculated without dimensional regularization. The amm corrections to the second order contribution have already been included in $\nu_A^{(4)}$, as discussed in Section 4.1. The amm part of $H^{(7)}$ is calculated with the help of a NRQED Hamiltonian which is obtained by a Foldy-Wouthuysen transformation of the Dirac Hamiltonian including the magnetic moment anomaly [43],

$$\begin{aligned}
H_{FW} = {}& \frac{\vec{\pi}^2}{2} + e\,A^0 - \frac{e}{2}\,(1+a_e)\,\vec{\sigma}\cdot\vec{B} - \frac{\vec{\pi}^4}{8} \\
& -\frac{e}{8}\,(1+2\,a_e)\,[\vec{\nabla}\cdot\vec{E} + \vec{\sigma}\cdot(\vec{E}\times\vec{\pi} - \vec{\pi}\times\vec{E})] \\
& +\frac{e}{8}\big(\{\vec{\sigma}\cdot\vec{B},\vec{\pi}^2\} + a_e\,\{\vec{\pi}\cdot\vec{B},\vec{\pi}\cdot\vec{\sigma}\}\big) \\
& -\frac{(3+4\,a_e)}{64}\,\{\vec{p}^2, e\,\vec{E}\times\vec{p}\cdot\vec{\sigma}\}.
\end{aligned} \tag{155}$$

All the $m\,\alpha^6$ operators obtained by Douglas and Kroll (DK) in [27], derived in this chapter using time dependent perturbation theory, can also be obtained using this Hamiltonian, as shown in Ref. [16]. The anomalous magnetic moment operators can be derived in a very similar way. They differ from the DK operators only by multiplicative factors, as shown in Table 5. There is a one to one correspondence with the listing of DK operators given in Table I of Ref. [38] with 3 exceptions. The operator $H_8$ from our Table 5 cancels out in the DK calculation, as mentioned after Eq. (132). The other two exceptions are related to the different spin structure of the next to last term in Eq. (155), which leads to the operators $H_{16}$ and $H_{17}$ in our Table 5.

Table 5. Operators due to magnetic moment anomaly in atomic units with the prefactor $m\,\alpha^7/\pi$

| Operator | $\nu_{01}$[kHz] | $\nu_{12}$[kHz] |
|---|---|---|
| $H_1 = -\frac{Z}{4}\,p_1^2\,\frac{\vec{r}_1}{r_1^3}\times\vec{p}_1\cdot\vec{\sigma}_1$ | 3.239 | 6.478 |
| $H_2 = -\frac{3\,Z}{4}\,\frac{\vec{r}_1}{r_1^3}\times\frac{\vec{r}}{r^3}\cdot\vec{\sigma}_1\,(\vec{r}\cdot\vec{p}_2)$ | 0.267 | 0.534 |
| $H_3 = \frac{3\,Z}{4}\,\frac{\vec{r}}{r^3}\cdot\vec{\sigma}_1\,\frac{\vec{r}_1}{r_1^3}\cdot\vec{\sigma}_2$ | 0.332 | −0.133 |
| $H_4 = \frac{1}{2\,r^4}\,\vec{r}\times\vec{p}_2\cdot\vec{\sigma}_1$ | 0.749 | 1.498 |
| $H_5 = -\frac{3}{4\,r^6}\,\vec{r}\cdot\vec{\sigma}_1\,\vec{r}\cdot\vec{\sigma}_2$ | 2.638 | −1.055 |
| $H_6 = \frac{1}{4}\,p_1^2\,\frac{\vec{r}}{r^3}\times\vec{p}_1\cdot\vec{\sigma}_1$ | −0.807 | −1.614 |
| $H_7 = -\frac{1}{4}\,p_1^2\,\frac{\vec{r}}{r^3}\times\vec{p}_2\cdot\vec{\sigma}_1$ | −1.237 | −2.474 |
| $H_8 = -\frac{Z}{4\,r}\,\frac{\vec{r}_1}{r_1^3}\times\vec{p}_2\cdot\vec{\sigma}_1$ | −0.460 | −0.920 |
| $H_9 = -\frac{i}{2}\,p_1^2\,\frac{1}{r^3}\,\vec{r}\cdot\vec{p}_2\,\vec{r}\times\vec{p}_1\cdot\vec{\sigma}_1$ | 0.093 | 0.187 |
| $H_{10} = \frac{3\,i}{4\,r^5}\,\vec{r}\times(\vec{r}\cdot\vec{p}_2)\,\vec{p}_1\cdot\vec{\sigma}_1$ | −0.376 | −0.752 |
| $H_{11} = -\frac{3}{8\,r^5}\,\vec{r}\times(\vec{r}\times\vec{p}_1\cdot\vec{\sigma}_1)\,\vec{p}_2\cdot\vec{\sigma}_2$ | −0.193 | 0.077 |
| $H_{12} = -\frac{1}{8\,r^3}\,\vec{p}_1\cdot\vec{\sigma}_2\,\vec{p}_2\cdot\vec{\sigma}_1$ | −0.447 | 0.179 |
| $H_{13} = \frac{21}{16}\,p_1^2\,\frac{1}{r^5}\,\vec{r}\cdot\vec{\sigma}_1\,\vec{r}\cdot\vec{\sigma}_2$ | −14.908 | 5.963 |
| $H_{14} = -\frac{3\,i}{8}\,p_1^2\,\frac{\vec{r}}{r^3}\cdot\vec{\sigma}_1\,\vec{p}_1\cdot\vec{\sigma}_2$ | 4.411 | −1.764 |
| $H_{15} = \frac{i}{8}\,p_1^2\,\frac{1}{r^3}\,\big(\vec{r}\cdot\vec{\sigma}_2\,\vec{p}_2\cdot\vec{\sigma}_1 + (\vec{r}\cdot\vec{\sigma}_1)$ | | |
| $\times(\vec{p}_2\cdot\vec{\sigma}_2) - \frac{3}{r^2}\,\vec{r}\cdot\vec{\sigma}_1\,\vec{r}\cdot\vec{\sigma}_2\,\vec{r}\cdot\vec{p}_2\big)$ | 4.618 | −1.847 |
| $H_{16} = -\frac{1}{4}\,\vec{p}_1\cdot\vec{\sigma}_1\,\vec{p}_1\times\frac{\vec{r}}{r^3}\cdot\vec{p}_2$ | −0.483 | −0.967 |
| $H_{17} = \frac{1}{8}\,\vec{p}_1\cdot\vec{\sigma}_1\,\big(-\vec{p}_1\cdot\vec{\sigma}_2\,\frac{1}{r^3}$ | | |
| $+3\vec{p}_1\cdot\vec{r}\,\frac{\vec{r}}{r^5}\cdot\vec{\sigma}_2\big)$ | −1.643 | 0.657 |
| $E_H = \sum_{i=1,17}\langle H_i\rangle$ | −4.208 | 4.047 |

Apart from the $H_i$ and $Q_i$ operators, second order contributions and low energy Bethe-logarithmic type corrections contribute to the fine structure. These contributions have been obtained in [45]. The second order contribution, beyond the anomalous magnetic moment terms is the second term in the general formula (139)

$$E_S = 2\left\langle\phi\middle|H_{SD}\,\frac{1}{(E-H)'}\,H^{(5)}\middle|\phi\right\rangle, \tag{156}$$

where $H_{SD}$ is the leading relativistic spin-dependent correction given in Eq. (91) with $a_e = 0$ and $H^{(5)}$ is the spin-independent effective Hamiltonian at order $m\,\alpha^5$,

$$H^{(5)} = -\frac{7}{6\,\pi}\,\frac{\alpha^2}{r^3} + \frac{38\,Z\,\alpha^2}{45}\,\left[\delta^3(r_1)+\delta^3(r_2)\right] + \frac{4\,Z\,\alpha^2}{3}\,\ln(Z\,\alpha)^{-2}\,\left[\delta^3(r_1)+\delta^3(r_2)\right]. \tag{157}$$

The low energy contribution $E_L$ comes from photon momenta $k<\Lambda$. We derive from the low energy form of the electromagnetic interaction Hamiltonian

$$H_I = \sum_a -e\,\vec r_a\cdot\vec E - \frac{e}{2\,m}\,\sigma_a^i\,r_a^j\,B^i_{,j} - \frac{e}{4\,m^2}\,\vec\sigma_a\cdot\vec E_a\times\vec p_a \tag{158}$$

instead of the general nonrelativistic Hamiltonian in Eq. (B.9). This is because of the high degree of cancellation between various terms, which is more visible using Eq. (158). Specifically, the contribution from the second and the third terms cancel out between themselves and only the first term leads to $E_L$,

$$E_L = \frac{2}{3}\,\alpha\int_0^\Lambda \frac{d^3k}{(2\,\pi)^3\,2\,k}\,k^2\,\delta\left\langle\phi\left|(\vec r_1+\vec r_2)\,\frac{1}{E-H-k}\,(\vec r_1+\vec r_2)\right|\phi\right\rangle, \tag{159}$$

where $\delta\langle\ldots\rangle$ denotes the correction to the matrix element $\langle\ldots\rangle$ due to $H_{SD}$. Using the relation

$$[H,\vec r_1+\vec r_2] = -\frac{i}{m}(\vec p_1+\vec p_2) + \frac{1}{4\,m^2}\,[\vec p_1\times\vec\sigma_1+\vec p_2\times\vec\sigma_2, H_0-E_0] \tag{160}$$

$E_L$ is transformed to

$$E_L = -\frac{2\,\alpha}{3\,\pi}\,\delta\left\langle\phi\right|(\vec p_1+\vec p_2)\,(H-E)\ln\left[\frac{2(H-E)}{(Z\,\alpha)^2}\right](\vec p_1+\vec p_2)\left|\phi\right\rangle + \frac{i\,Z^2\,\alpha^3}{3\,\pi}\left\langle\phi\right|\left(\frac{\vec r_1}{r_1^3}+\frac{\vec r_2}{r_2^3}\right) \times\frac{(\vec\sigma_1+\vec\sigma_2)}{2}\ln\left[\frac{2(H-E)}{(Z\,\alpha)^2}\right]\cdot\left(\frac{\vec r_1}{r_1^3}+\frac{\vec r_2}{r_2^3}\right)\left|\phi\right\rangle. \tag{161}$$

Numerical results for all these contributions are presented in Table 6.

## 9. Conclusions

Since all relevant contributions to helium fine structure splitting have now been treated, we are at a position to present our final theoretical predictions following Ref. [14]. We begin with a discussion of the small interval $\nu_{12}$, as its treatment is unambiguous. By this we mean that unlike $\nu_{01}$, which can

Table 6. Summary of contributions to helium fine structure, $E^{(4)}$ and $E^{(6)}$ including nuclear recoil corrections and the electron anomalous magnetic moment at the level of the Breit-Pauli Hamiltonian; $\alpha^{-1} = 137.03599911(46)$, $m/m_\alpha = 1.37093355575(61)10^{-4}$, Ry $c = 3.289841960360(22)\ 10^{15}$ Hz. Not indicated is the uncertainty due to $\alpha$, which is 0.20 kHz for $\nu_{01}$. The last row includes the most recent experimental values.

| | $\nu_{01}$[kHz] | $\nu_{12}$[kHz] | Ref. |
|---|---|---|---|
| $E_Q$ | 21.73 | 7.42 | |
| $E_H$ | $-4.21$ | 4.05 | |
| $E_S$ | 11.37(02) | $-1.25(01)$ | 45 |
| $E_L$ | $-29.76(16)$ | $-12.51(27)$ | 45 |
| $E^{(7)}$ | $-0.87(16)$ | $-2.30(27)$ | |
| $E^{(7)}_{\log}$ | 82.59 | $-10.09$ | 46 |
| $E^{(6)}$ | $-1557.50(06)$ | $-6544.32(12)$ | 32,53,36,37 |
| $E^{(4)}$ | 29 618 418.79(01) | 2 297 717.84 | 32,36 |
| total | 29 616 943.01(17) | 2 291 161.13(30) | |
| Drake | 29 616 946.42(18) | 2 291 154.62(31) | 32 |
| exp. | 29 616 951.66(70) | 2 291 175.59(51) | 31,49,48,51,50 |

either be used to determine $\alpha$ or else be directly compared with experiment using the $g-2$ value of $\alpha$, only the latter approach is available for $\nu_{12}$. As shown in the above Table, the essentially $\alpha$-independent theory predictions disagree both with each other and with experiment. A notable feature of the experimental situation is the fact that two independent groups, using very different techniques, published results consistent with one another within experimental error at the same time [50], [49]. We have quoted a later determination [31] of even greater accuracy, which is also in agreement with the earlier measurements, so we regard the experiment determination as non-controversial. The difference in theory comes primarily from $\nu^{(5)}$, so we defer its discussion to the large interval treatment.

We begin the treatment of the large interval by first assuming $\alpha$ is known, using the $g-2$ result of Eq. (8). From Table 6 we see that our theory is significantly discrepant. Drake's results are discrepant with ours, but in somewhat better agreement with experiment.

However, the main point of this chapter is the determination of $\alpha$ from helium fine structure. As shown in Eq. (73), the value of the fine structure constant as determined by our theory is strongly discrepant, which is of course the same discrepancy as noted above. Again, because Drake's result was less discrepant, the value of $\alpha$ coming from his theory is

$$\alpha^{-1}(\text{He fs}) = 137.036987(2), \tag{162}$$

with the error corresponding to his estimate of 1 kHz theoretical uncertainty. In terms of $\delta\nu_{01}$, the difference of the two calculations is that Ref. [14], described in this chapter, has -1.475 78 MHz and Ref. [32] has -1.472 37 MHz, with the difference coming solely from $\nu_{01}^5$. While the difference of 3.4 kHz is significant, we note that it is smaller than the 8.6 and 5.2 kHz respective differences of the two theories from experiment. This discrepancy is far worse for the small interval for both theories. It is clearly premature to quote either value as a definitive helium fine structure determination. We now turn to a discussion of this quite unsatisfactory situation.

There are a number of possible sources of the discrepancy. A problem that was quite important in the early days of helium fine structure was the quality of the nonrelativistic wave functions, determined with variational techniques, so we begin by discussing the numerical error expected from the wave functions used here. A central parameter used to gauge the quality of a wave function is the nonrelativistic energy. Our wave function, consisting of 1500 explicitly correlated exponential functions reproduces the nonrelativistic $2P$ energy with 21 significant digits, consistent with the result of Drake in [32]. Matrix elements determined with this wave function are not as accurate as the nonrelativistic energy, but they are sufficiently accurate for evaluating the leading fine structure operators, and again our results agree with the independent calculation of Drake [32]. For example, $E^{(4)}$ agrees to 0.01 kHz and $E^{(6)}$ to 0.1 kHz. In fact almost all numerical calculations have been performed by us and by Drake independently with one exception; we have not obtained recoil correction to the second order matrix element with Breit operators in $E^{(6)}$.

A much more important issue is the complexity of the derivation of the operators that contribute in order $m\,\alpha^7$, specifically $H_i$ and $Q_i$. We purposely derived $H_i$ in a way very similar way to the derivation of the D-K operators to avoid error. We note that the $Q_i$ operators were obtained from the one-loop scattering amplitude in an almost automatic way, in contrast to the former very lengthy derivation of Zhang [15,54,55], with which we are in disagreement (see the summary of Zhang results in Ref. [32]). In previous papers by the present authors [45,37] we have pointed out several computational mistakes and inconsistencies in Zhang's calculations, and therefore we consider the result of Drake, given in Table 6, to be incomplete. While it is possible that we have made a mistake somewhere, the other probable explanation of the discrepancy with experiments is the neglect of higher order terms, specifically those of order $m\,\alpha^8$. An indication of their importance is the recoil correction to the second order contribution, obtained by

Drake in [32]. In spite of the small electron-alpha particle mass ratio, this correction is very significant; for example $\delta\nu_{01} = -10.81$ kHz. The mass ratio $m/m_\alpha \approx 0.00014$ is not much different from $\alpha^2 \approx 0.000053$, and for this reason it is possible that iteration of the Breit-Pauli Hamiltonian to third order could give a significant contribution. However, we expect that most $m\,\alpha^8$ operators should be negligible, as $E^{(7)}$ is already at the few kHz level, so that an additional power of $\alpha$ will make these operators contribute well below the experimental accuracy. However, while it is important to consider higher order corrections, we feel that it is vital to have an independent calculation of the terms already considered in this chapter carried out.

## References

1. A. Sommerfeld, Ann. der Phys. **51**, 1-94, 125-167 (1916).
2. J.C. Baird, J. Brandenberger, K.-I. Gondaira, and H. Metcalf, Phys. Rev. A **5**, 564 (1972).
3. P.J. Mohr and B.N. Taylor, Rev. Mod. Phys. **77**, 1 (2005).
4. D. Hanneke, S. Fogwell, and G. Gabrielse, Phys. Rev. Lett. 100, 120801 (2008)
5. T. Aoyama, M. Hayakawa, T. Kinoshita and M. Nio, Phys. Rev Lett. **99**, 110406 (2007).
6. P. Cladé, E. de Mirandes, M. Cadoret, S. Guellati-Khélifa, C. Schwob, F. Nez, L. Julien, and F. Biraben, Phys. Rev. A **74**, 052109 (2006).
7. A. Wicht, J.M. Hensley, E. Sarajlic, and S. Chu, Phys. Scripta **T102**, 82 (2002).
8. K. Pachucki, Ann. Phys. (N.Y.) **226**, 1 (1993).
9. K. Pachucki, Phys. Rev. Lett. **72**, 3154 (1994).
10. K. Melnikov and T. van Ritbergen, Phys. Rev. Lett. **84**, 1673 (2000).
11. U.D. Jentschura, P.J. Mohr, and G. Soff, Phys. Rev. Lett. **82**, 53 (1999).
12. U.D. Jentschura and K. Pachucki, Phys. Rev. Lett. **91**, 113005 (2003).
13. V.A. Yerokhin, P. Indelicato, and V.M. Shabaev, Phys. Rev. A **71**, 040101(R), (2005).
14. K. Pachucki, Phys. Rev. Lett. **97**, 013002 (2006).
15. T. Zhang, Phys, Rev. A **53**, 3896 (1996).
16. K. Pachucki, Phys. Rev. A **71**, 012503 (2005).
17. Considerable effort has gone into attempts to generalize the Dirac equation to helium, but the proper treatment of negative energy states requires a field theoretic treatment, as discussed by G.E. Brown and D.G. Ravenhall, Proc. R. Soc. London, Ser. A **208**, 552 (1951).
18. K. Pachucki, Phys. Rev. A **56**, 297 (1997).
19. A. Czarnecki, K. Melnikov, and A. Yelkhovksy, Phys. Rev. Lett. **82**, 311 (1999).
20. J. Sapirstein and D. Yennie, in *Quantum Electrodynamics*, ed. T. Kinoshita,

World Scientific (Singapore) (1991).
21. W.A. Barker and F.N. Glover, Phys. Rev. **99**, 317 (1955).
22. V.M. Shabaev, Teor. Mat.Fiz. **63**, 394 (1985). [Translated in Theor. Math. Phys. **63**, 588 (1985).]
23. A.N. Artemyev, V.M. Shabaev, and V.A. Yerokhin, Phys. Rev. A **52**, 1884 (1995).
24. A.N. Artemyev, V.M. Shabaev, and V.A. Yerokhin, J. Phys. B **28**, 5201 (1995).
25. G.S. Adkins, S. Morrison, and J. Sapirstein, Phys. Rev. A **76**, 042508 (2007).
26. Baranger, H. Bethe, and R.P. Feynman, Phys. Rev. **92**, 482 (1953).
27. M. Douglas and N.M. Kroll, Ann. Phys. NY **82**, 89 (1974).
28. U. Jentschura and K. Pachucki, Phys. Rev. A **54**, 1853 (1996).
29. C. Schwartz, Phys. Rev. **5**, A1181 (1964).
30. K. Pachucki, Phys. Rev. A. **74**, 022512 (2006).
31. T. Zelevinsky, D. Farkas, and G. Gabrielse, Phys. Rev. Lett. **95**, 203001 (2005).
32. G.W.F. Drake, Can. J. Phys. **80**, 1195 (2002).
33. V. Korobov, Phys. Rev. A **61**, 064503 (2000).
34. K. Pachucki, J. Phys. B **32**, 137 (1999).
35. M.L. Lewis and P.H. Serafino, Phys. Rev. A **18**, 867 (1978).
36. K. Pachucki and J. Sapirstein, J. Phys. B. **35**, 1783 (2002).
37. K. Pachucki and J. Sapirstein, J. Phys. B **36**, 803 (2003).
38. J. Daley, M. Douglas, L. Hambro, and N.M. Kroll, Phys. Rev. Lett. **29**, 12 (1972).
39. T. Zhang, Phys. Rev. A **56**, 270(1997).
40. T. Zhang, Phys. Rev. A **54**, 1252 (1996).
41. A. Yelkhovsky, Phys. Rev. A **64**, 062104 (2001).
42. V. Korobov and A. Yelkhovsky, Phys. Rev. Lett **87**, 193003 (2001).
43. U. Jentschura, A. Czarnecki and K. Pachucki, Phys. Rev. A **72**, 062102 (2005).
44. A. Czarnecki, U. Jentschura, and K. Pachucki, Phys. Rev. Lett. **95**, 180404 (2005).
45. K. Pachucki and J. Sapirstein, J. Phys. B **33**, 5297 (2000).
46. T. Zhang, Z-C. Yan and G.W.F. Drake, Phys. Rev. Lett. **77**, 1715 (1996).
47. T. Zhang, Phys. Rev. A **53**, 3896 (1996).
48. M.C. George, L.D. Lombardi, and E.A. Hessels, Phys. Rev. Lett. **87**, 173002 (2001).
49. C.H. Storey, M.C. George, and E.A. Hessels, Phys. Rev. Lett. **84**, 3274 (2000).
50. J. Castillega, D. Livingston, A. Sandars and D. Shiner, Phys. Rev. Lett. **84**, 4321 (2000).
51. F. Minardi, G. Bianchini, P. Cancio Pastor, G. Giusfredi, F. S. Pavone, and M. Inguscio, Phys. Rev. Lett. **82**, 1112 (1999).
52. G. Giusfriedi, P. de Natale, D. Mazzotti. P.C. Pastor, C. de Mauro, L. Fallani, G. Hagel, V. Krachmalnicoff, and M. Inguscio, Can. J. Phys. **83**, 301 (2005).
53. Z-C. Yan and G.W.F. Drake, Phys. Rev. Lett. **74**, 4791 (1995).
54. T. Zhang, Phys, Rev. A **54**, 1252 (1996).

55. T. Zhang and G. W. F. Drake, Phys. Rev. A **54**, 4882 (1996).
56. P. Clade *et al.*, Phys. Rev. Lett. **96**, 033001 (2006).
57. C. Itzykson and J. B. Zuber, *Quantum Field Theory*, McGraw–Hill, New York (1990).

## Appendix A. Dimensionally regularized QED of bound states

We take the dimension of space to be $d = 3 - 2\,\epsilon$. The surface area of a $d$-dimensional unit sphere can be obtained by considering the integral

$$\mathrm{I} = \int d^d k\, e^{-\vec{k}^2}. \tag{A.1}$$

In Cartesian coordinates it is a product of $d$ one-dimensional integrals

$$\mathrm{I} = \left[\int dk\, e^{-k^2}\right]^d = \pi^{d/2}, \tag{A.2}$$

while in spherical coordinates it is

$$\mathrm{I} = \int d\Omega_d \int_0^\infty dk\, k^{d-1}\, e^{-k^2} = \Omega_d\, \frac{1}{2}\, \Gamma(d/2). \tag{A.3}$$

From comparison of Eq. (A.2) and (A.3) one obtains

$$\Omega_d = \frac{2\,\pi^{d/2}}{\Gamma(d/2)}\,. \tag{A.4}$$

The $d$-dimensional Laplacian is $\nabla^2 = \partial^i\,\partial^i$. For spherically symmetric functions $f$ and $g$

$$\begin{aligned}\int d^d r\, \nabla^2(f)\, g &= -\int d^d r\, \nabla(f)\cdot\nabla(g) = -\Omega_d \int dr\, r^{d-1}\, \partial_r f\, \partial_r g \\ &= \Omega_d \int dr\, \partial_r(r^{d-1}\,\partial_r f)\, g = \int d^d r\, r^{1-d}\, \partial_r(r^{d-1}\,\partial_r f)\, g,\end{aligned} \tag{A.5}$$

so the Laplacian takes the form

$$\nabla^2 = r^{1-d}\partial_r\, r^{d-1}\partial_r. \tag{A.6}$$

The photon propagator, and thus Coulomb interaction preserves its form in the momentum representation, while in the coordinate representation it is

$$\mathcal{V}(r) = \int \frac{d^d k}{(2\,\pi)^d}\, \frac{4\,\pi}{k^2}\, e^{i\,\vec{k}\cdot\vec{r}} = \pi^{\epsilon-1/2}\,\Gamma(1/2-\epsilon)\, r^{2\,\epsilon-1} \equiv \frac{C_1}{r^{1-2\,\epsilon}}. \tag{A.7}$$

An alternative derivation of $\mathcal{V}(r)$ which does not require a Fourier transform is the following. Consider the equation

$$\nabla^2 \mathcal{V}(r) = -4\,\pi \delta^d(r). \tag{A.8}$$

If one assumes that $\mathcal{V}(r)$ is of the form $\mathcal{V}(r) = C\,r^\gamma$, then for $r \neq 0$

$$r^{1-d} \partial_r\, r^{d-1} \partial_r (C\,r^\gamma) = 0, \tag{A.9}$$

and therefore $\gamma = 2-d = 2\,\epsilon-1$. The coefficient $C$ is obtained by considering the integral with a trial function $f$

$$\begin{aligned} 4\,\pi\, f(0) &= -\int d^d r\, \nabla^2(\mathcal{V})\, f = \int d^d r\, \nabla(\mathcal{V}) \cdot \nabla(f) \\ &= \lim_{\varepsilon \to 0} \int_\varepsilon dr\, r^{d-1}\, \Omega_d\, \partial_r(\mathcal{V})\, \partial_r(f) \\ &= \lim_{\varepsilon \to 0} \left[ r^{d-1}\, \Omega_d\, \partial_r(\mathcal{V})\, f \bigg|_{r=\varepsilon} - \int_\varepsilon dr\, \Omega_d\, \partial_r(r^{d-1}\, \partial_r(\mathcal{V}))\, f \right] \\ &= \lim_{\varepsilon \to 0}\, \Omega_d\, \varepsilon^{d-1}\, \partial_\varepsilon (C\, \varepsilon^{2-d})\, f(\varepsilon) \\ &= \Omega_d\, (2-d)\, C\, f(0). \end{aligned} \tag{A.10}$$

Therefore

$$C \equiv C_1 = \frac{4\,\pi}{(d-2)\,\Omega_d} = \pi^{\epsilon - 1/2}\, \Gamma(1/2 - \epsilon). \tag{A.11}$$

We are now ready to consider quantum mechanics in $d$-dimensions. The nonrelativistic Hamiltonian of a hydrogen-like system is

$$H_0 = \frac{\vec{p}^{\,2}}{2} - Z\, \frac{C_1}{r^{1-2\,\varepsilon}}\,, \tag{A.12}$$

and of a helium-like system

$$H_0 = \frac{\vec{p_1}^{\,2}}{2} + \frac{\vec{p_2}^{\,2}}{2} - Z\, \frac{C_1}{r_1^{1-2\,\epsilon}} - Z\, \frac{C_1}{r_2^{1-2\,\epsilon}} + \frac{C_1}{r^{1-2\,\epsilon}}. \tag{A.13}$$

We denote the solution of the stationary Schrödinger equation $H_0\, \phi = E_0\, \phi$ by $\phi$, but do not need to refer to its explicit (and unknown) form in $d$-dimensions. Instead, we will use only the generalized cusp condition to eliminate various singularities from matrix elements with relativistic operators. Specifically, we expect that for small $r$

$$\phi(r) \approx \phi(0)\, (1 - C\, r^\gamma), \tag{A.14}$$

with the coefficients $C$ and $\gamma$ to be obtained from the two-electron Schrödinger equation around $r = 0$

$$[-\nabla^2 + \mathcal{V}(r)] \phi(0)\, (1 - C\, r^\gamma) \approx E\, \phi(0)\, (1 - C\, r^\gamma). \tag{A.15}$$

From the cancellation of small $r$ singularities on the left hand side of above equation, one obtains

$$\gamma = 1 + 2\,\epsilon, \tag{A.16}$$

$$C \equiv C_2 = \frac{1}{4}\,\pi^{\epsilon-1/2}\,\Gamma(-1/2-\epsilon). \tag{A.17}$$

Therefore the two-electron wave function around $r = 0$ behaves as

$$\phi(\vec r_1, \vec r_2) \approx \phi(r_{12} = 0)\,\bigl(1 - C_2\, r_{12}^{1+2\,\epsilon}\bigr). \tag{A.18}$$

Apart from the Coulomb potential $\mathcal{V}(r)$ in coordinate space, we need additional functions which appear in the calculations of relativistic operators, namely

$$\mathcal{V}_2(r) = \int \frac{d^d k}{(2\,\pi)^d}\,\frac{4\,\pi}{k^4}\,e^{i\,\vec k\cdot\vec r}, \tag{A.19}$$

$$\mathcal{V}_3(r) = \int \frac{d^d k}{(2\,\pi)^d}\,\frac{4\,\pi}{k^6}\,e^{i\,\vec k\cdot\vec r}. \tag{A.20}$$

They can be obtained from the differential equations

$$-\nabla^2 \mathcal{V}_2(r) = \mathcal{V}(r), \tag{A.21}$$

$$-\nabla^2 \mathcal{V}_3(r) = \mathcal{V}_2(r), \tag{A.22}$$

$$\tag{A.23}$$

with the results

$$\mathcal{V}_2(r) = C_2\, r^{1+2\,\epsilon}, \tag{A.24}$$

$$\mathcal{V}_2(r) = C_3\, r^{3+2\,\epsilon}, \tag{A.25}$$

$$\tag{A.26}$$

with $C_2$ defined in Eq. (A.17) and

$$C_3 = \frac{1}{32}\,\pi^{\epsilon-1/2}\,\Gamma(-3/2-\epsilon). \tag{A.27}$$

Using $\mathcal{V}_i$ we calculate various integrals involving the photon propagator in Coulomb gauge, namely

$$\begin{aligned} &\int \frac{d^d k}{(2\,\pi)^d}\,\frac{4\,\pi}{k^4}\,P_{ij}(k)\,e^{i\,\vec k\cdot\vec r} = \delta^{ij}\mathcal{V}_2 + \partial^i\partial^j\,\mathcal{V}_3 \\ &= \pi^{\epsilon-1/2}\,r^{-1+2\,\epsilon}\left[\frac{3}{16}\,\delta^{ij}\,\Gamma(-1/2-\epsilon)\,r^2 + \frac{1}{8}\,\Gamma(1/2-\epsilon)\,r^i\,r^j\right] \\ &\equiv \left[\frac{1}{8\,r}(r^i\,r^j - 3\,\delta^{ij}\,r^2)\right]_\epsilon, \end{aligned} \tag{A.28}$$

$$\int \frac{d^d k}{(2\,\pi)^d}\,\frac{4\,\pi}{k^2}\,P_{ij}(k)e^{i\,\vec{k}\cdot\vec{r}} = \delta^{ij}\mathcal{V} + \partial^i\partial^j\,\mathcal{V}_2$$
$$= \pi^{\epsilon-1/2}\,r^{-3+2\,\epsilon}\left[\frac{1}{2}\,\delta^{ij}\,\Gamma(1/2-\epsilon)\,r^2 + \Gamma(3/2-\epsilon)\,r^i\,r^j\right]$$
$$\equiv \left[\frac{1}{2\,r^3}(\delta^{ij}\,r^2 + r^i\,r^j)\right]_\epsilon, \qquad \text{(A.29)}$$

and

$$\int \frac{d^d k}{(2\,\pi)^d}\,4\,\pi\,P_{ij}(k)\,e^{i\,\vec{k}\cdot\vec{r}} = \frac{(d-1)}{d}\delta^{ij}4\,\pi\,\delta^d(r) + \left(\partial^i\partial^j - \frac{\delta^{ij}}{d}\,\partial^2\right)\mathcal{V}$$
$$= \frac{(d-1)}{d}\delta^{ij}4\,\pi\,\delta^d(r) + \pi^{\epsilon-1/2}\,r^{-5+2\,\epsilon}\left[-2\,\delta^{ij}\,\Gamma(3/2-\epsilon)\,r^2 + 4\,\Gamma(5/2-\epsilon)\,r^i\,r^j\right]$$
$$= \left[\frac{2}{3}\,\delta^{ij}\,4\,\pi\,\delta^3(r) + \frac{1}{r^5}\,(3\,r^i\,r^j - \delta^{ij}\,r^2)\right]_\epsilon \equiv \delta^{ij}_\perp. \qquad \text{(A.30)}$$

## Appendix B. Foldy-Wouthuysen transformation in *d*-dimensions

The Foldy-Wouthuysen (FW) transformation [57] is the nonrelativistic expansion of the Dirac Hamiltonian in an external electromagnetic field. Following Ref. [30] we extend this transformation to the case where the dimension $d$ of space is arbitrary. The Dirac Hamiltonian in an external electromagnetic field is

$$H = \vec{\alpha}\cdot\vec{\pi} + \beta\,m + e\,A^0\,, \qquad \text{(B.1)}$$

where $\vec{\pi} = \vec{p} - e\,\vec{A}$,

$$\alpha^i = \begin{pmatrix} 0 & \sigma^i \\ \sigma^i & 0 \end{pmatrix},\;\; \beta = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix}, \qquad \text{(B.2)}$$

and

$$\{\sigma^i, \sigma^j\} = 2\,\delta^{ij}\,I. \qquad \text{(B.3)}$$

The FW transformation $S$ [57] leads to a new Hamiltonian

$$H_{\rm FW} = e^{i\,S}\,(H - i\,\partial_t)\,e^{-i\,S}\,, \qquad \text{(B.4)}$$

which decouples the upper and lower components of the Dirac wave function up to a specified order in the $1/m$ expansion. Here we calculate the FW Hamiltonian up to terms which contribute to $m\,\alpha^6$ correction to the energy.

We use a convenient form of Foldy-Wouthuysen operator $S$, which can be written as

$$S = -\frac{i}{2\,m}\biggl\{\beta\,\vec{\alpha}\cdot\vec{\pi} - \frac{1}{3\,m^2}\,\beta\,(\vec{\alpha}\cdot\vec{\pi})^3 + \frac{1}{2\,m}\,[\vec{\alpha}\cdot\vec{\pi}\,,\,e\,A^0 - i\,\partial_t] + \frac{\beta}{5\,m^4}\,(\vec{\alpha}\cdot\vec{\pi})^5 - \frac{\beta\,e}{4\,m^2}\,\vec{\alpha}\cdot\dot{\vec{E}} + \frac{i\,e}{24\,m^3}\,[\vec{\alpha}\cdot\vec{\pi},[\vec{\alpha}\cdot\vec{\pi},\vec{\alpha}\cdot\vec{E}]] - \frac{i\,e}{3\,m^3}\,\bigl\{(\vec{\alpha}\cdot\vec{\pi})^2\,,\,\vec{\alpha}\cdot\vec{E}\bigr\}\biggr\} \tag{B.5}$$

The F.W. Hamiltonian is expanded in a power series in $S$

$$H_{\rm FW} = \sum_{j=0}^{6}\mathcal{H}^{(j)} + \ldots \tag{B.6}$$

where

$$\begin{aligned}
\mathcal{H}^{(0)} &= H,\\
\mathcal{H}^{(1)} &= [i\,S\,,\mathcal{H}^{(0)} - i\,\partial_t],\\
\mathcal{H}^{(j)} &= \frac{1}{j}\,[i\,S\,,\mathcal{H}^{(j-1)}]\ \text{for}\ j>1,
\end{aligned} \tag{B.7}$$

and higher order terms in this expansion, denoted by dots, are neglected. The calculation of subsequent commutators is rather tedious but the result is simply

$$H_{\rm FW} = e\,A^0 + \frac{(\vec{\sigma}\cdot\vec{\pi})^2}{2\,m} - \frac{(\vec{\sigma}\cdot\vec{\pi})^4}{8\,m^3} + \frac{(\vec{\sigma}\cdot\vec{\pi})^6}{16\,m^5} - \frac{i\,e}{8\,m^2}\,[\vec{\sigma}\cdot\vec{\pi},\vec{\sigma}\cdot\vec{E}] - \frac{e}{16\,m^3}\,\bigl\{\vec{\pi}\,,\,\partial_t\vec{E}\bigr\} - \frac{i\,e}{128\,m^4}\,[\vec{\sigma}\cdot\vec{\pi},[\vec{\sigma}\cdot\vec{\pi},[\vec{\sigma}\cdot\vec{\pi},\vec{\sigma}\cdot\vec{E}]]] + \frac{i\,e}{16\,m^4}\,\Bigl\{(\vec{\sigma}\cdot\vec{\pi})^2\,,\,[\vec{\sigma}\cdot\vec{\pi},\vec{\sigma}\cdot\vec{E}]\Bigr\}\,. \tag{B.8}$$

There is some arbitrariness in the operator $S$, which means that $H_{\rm FW}$ is not unique. The standard approach [57], which relies on subsequent use of FW-transformations, differs from this one in $d = 3$ by the transformation $S$ with an additional even operator.

We aim to obtain a Hamiltonian suitable for further calculations of $m\,\alpha^7$ contributions to energy levels of an arbitrary light atom. For this one can neglect the vector potential $\vec{A}$ in all the terms having $m^4$ and $m^5$ in the denominator. Moreover, less obviously, one can neglect terms with $\vec{\sigma}\cdot\vec{A}\,\vec{\sigma}\cdot\dot{\vec{E}}$ and $\vec{B}^2$. This is because they are of second order in electromagnetic fields which additionally contain derivatives, and thus contribute only at higher orders. After these simplifications, $H_{\rm FW}$ takes the form

$$\begin{aligned} H_{\rm FW} = e\,A^0 + \frac{\pi^2}{2\,m} - \frac{e}{4\,m}\,\sigma^{ij}\,B^{ij} - \frac{\pi^4}{8\,m^3} - \frac{e}{8\,m^2}\Big(\vec{\nabla}\cdot\vec{E} + \sigma^{ij}\,\big\{E^i\,,\,\pi^j\big\}\Big) \\ + \frac{e}{16\,m^3}\big\{\sigma^{ij}B^{ij}\,,\,p^2\big\} - \frac{e}{16\,m^3}\,\big\{\vec{p},\,\partial_t\vec{E}\big\} + \frac{3\,e}{32\,m^4}\,\big\{\sigma^{ij}\,E^i\,p^j\,,\,p^2\big\} \\ + \frac{e}{128\,m^4}\,[p^2,[p^2,A^0]] - \frac{3\,e}{64\,m^4}\,\big\{p^2\,,\,\nabla^2 A^0\big\} + \frac{p^6}{16\,m^5}, \end{aligned} \tag{B.9}$$

where

$$\sigma^{ij} = \frac{1}{2\,i}\,[\sigma^i\,,\,\sigma^j], \tag{B.10}$$

$$B^{ij} = \partial^i\,A^j - \partial^j\,A^i, \tag{B.11}$$

$$E^i = -\nabla^i A^0 - \partial_t A^i. \tag{B.12}$$