Applying the non-relativistic standard model extension to hydrogen

— Undergraduate Honors Thesis —

THEODORE J. YODER

ADvised BY DR. GREG ADKINS

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Abstract

During its 40 year lifetime, the standard model of particle physics has come to be well established experimentally. However, straightforward extensions of the standard model can be valuable guides for observations of potentially non-standard phenomena. The standard model extension (SME) naturally generalizes the standard model to include Lorentz and CPT violation. A number of new terms in the SME Lagrangian serve to incorporate these symmetry violations in a renormalizable effective field theory. Each term is controlled in magnitude by an SME tensor, which is a parameter in the theory. Determining these parameters, which so far are believed to be nearly if not exactly zero, is the object of experimental searches for Lorentz or CPT violation that use the SME as a guide.

Our ultimate goal in this work is the calculation of the SME corrections to the free hydrogen energy levels through order SME-$\alpha^2$. Starting from the extended Dirac equation, we find the non-relativistic SME Hamiltonian for fermions to first order in the SME parameters and second order in momentum using the standard Foldy-Wouthuysen procedure. The SME Hamiltonian is that of the SM, augmented by additive terms involving the SME parameters. We performed a perturbative calculation with the SME-extended, non-relativistic effective hamiltonian to find the modified energy levels of hydrogen. This calculation was carried out for all eigenstates of total angular momentum in free hydrogen.
1. INTRODUCTION

The standard model extension (SME) was introduced by Colladay and Kostelecký in 1997 with the purpose of including Lorentz violation in conventional quantum field theory in the most general way possible. No such violation has yet been detected, but a theory of these violations organizes the experimental searches. Suffice it to say, a detection of Lorentz violation, essentially a violation of special relativity, would be a very important discovery.

Systems that respect Lorentz symmetry may be rotated in 3-dimensional space or boosted (a change from one constant velocity to another constant velocity) without changing the workings within the system. At a higher level of abstraction, Lorentz symmetry may be part of the equations of a theory but not its solutions. In this case the symmetry is said to be spontaneously broken. The entire spectrum of solutions must certainly be Lorentz symmetric, but any particular solution might not be. So, nature makes a spontaneous, random choice as to which solution is physically realized. For example, the electric force exhibits fundamental spherical symmetry, yet, due to this force, molecules like water and carbon dioxide form that are certainly not spherically symmetric. Alan Kostelecký’s website provides a very readable introduction to Lorentz violation under the FAQ section.

Spontaneous symmetry breaking, in which nature does not exhibit an underlying symmetry explicitly, is an attractive mechanism to explain any suspected breaking of Lorentz symmetry because the symmetry is broken only on a practical level. Moreover, there is evidence that string theories predict such spontaneous symmetry breaking. Indeed, since all string theories require more than 4 dimensions to be realistic (most popularly either 10 or 11 spacetime dimensions), Lorentz symmetry must be broken. Clearly, we see only 4 of these dimensions as macroscopic. Therefore, some of the string theory dimensions must definitely be physically different from the rest.

Notice that the standard model extension does not attempt an explanation for Lorentz symmetry violation. Instead, the SME provides a general accounting of possible Lorentz violating effects and is therefore a phenomenological theory. The SME postulates Lorentz violation in order to explore its effect in a variety of physical systems. In the SME, the extent of Lorentz violation in all its forms is also tunable by many parameters. When all these are zero, there is no Lorentz violation and the standard model is recovered. That is, the SME is a generalization of the standard model.

Another symmetry that is violated by the SME is CPT (charge, parity, and time). The CPT transformation switches particles and their antiparticles (electrons become positrons, positrons become electrons, etc.), reverses all spatial directions (the positive x-direction becomes the negative x-direction, etc.), and reverses time (forward in time becomes backward). The CPT symmetry present in the standard model states that the combination of all three of these operations leaves physical laws unchanged. There is a strong theoretical reason to believe in CPT symmetry. The CPT theorem, discovered by Gehart Lüders and Wolfgang Pauli in the 1950s, states that Lorentz symmetry within the general framework of quantum field theory implies CPT symmetry. Since Lorentz symmetry is such an intuitive notion and its violation has not been observed, many physicists are convinced by the CPT theorem that CPT is also an exact symmetry. On the other hand, only violations of C, P, and CP symmetries are experimentally known. This is typically taken to mean T is violated, since the tripartite CPT symmetry is assumed. However, independent observation of T violation, to cancel the observed CP violation, has not yet been seen experimentally.

The SME is, at its most general, an infinite collection of Lorentz violating corrections to field theory. However, if one considers only renormalizable terms, a finite subset is obtained called the minimal SME, which we work with here and refer to as simply the SME, for brevity. In the minimal extension to quantum electrodynamics (QED), the quantum description of electromagnetism, the Lorentz violation for fermions is achieved through addition of CPT-even and CPT-odd terms to the Dirac equation, controlled in magnitude by a set of eight SME vectors and tensors. As a contrapositive of the CPT theorem, Greenberg has shown that CPT violation in field theories (under minor assumptions) implies Lorentz violation. Just as Lorentz violation is generally represented in the full SME, CPT violation is also represented generally by a subset of the SME terms. Violation of CPT is present in the minimal SME, as well.

Kostelecký and Lane extracted the nonrelativistic Hamiltonian, to linear order in the (minimal) SME parameters, for a free massive fermion from the SME lagrangian, a result that we reproduce here with the addition of an electromagnetic four-vector potential (i.e. the fermion is no longer free). They also reported the extended Dirac equation. Lehnert finds the SME Hamiltonian to all orders in the SME parameters and investigates some discrete symmetries of the single-particle dispersion relation in the SME.

A concise summary of the SME and some resulting energy corrections at lowest order in hydrogen are provided by Bluhm et al. and Russell gives much the same discussion. Lehnert and Bluhm provide more involved reviews. Kharlanov and Zhukovsky give a detailed discussion of the effect of a single symmetry violating SME vector ($b^\mu$) on the structure of hydrogen.

Even the most sensitive modern experiments have not yet detected Lorentz violation and so the SME parameters must be incredibly small. Part of the hope of detection, however, is due to curious behavior of the SME effects. The parameters in the SME violate Lorentz symmetry because they are anisotropic. The SME vectors, for example, single out a preferred direction in space. Though the parameters are fixed in inertial frames, the Earth is not inertial.
With respect to the Earth the SME parameters will be seen to vary as we orbit the Sun and rotate. The Sun is, more or less, inertial on a human timescale and bounds on the SME are often given for parameters in a Sun-centered reference frame, in which they are constant.\textsuperscript{8} The Earth frame parameters must be used for calculations involving experiments on Earth, however, and due to yearly or even daily variations in the SME parameters, measured values in the experiments may change. Picking out such periodic effects from the constant background is one technique for detecting the SME.\textsuperscript{5}

Another advantage for experimental detection is the ubiquity of the SME effects. Unsurprisingly, a fundamental property like Lorentz violation in quantum field theory would influence many diverse phenomena. Of course, choosing experiments that will yield amazing accuracy, enough to detect the presumably small Lorentz violation, is the challenge. Still, even in attempting to observe just the changes to the physics of the electron, many techniques have been and continue to be employed, including rotating Michelson-Morley interferometers,\textsuperscript{14} comparisons of atomic clocks,\textsuperscript{15} radiation from astrophysical sources,\textsuperscript{16} torsion pendulum studies,\textsuperscript{17} and observations of the transitions in atomic hydrogen.\textsuperscript{18} The comprehensive list of experimental bounds on the size of the SME parameters for not just electrons, but photons, neutrinos, protons, etc. is kept up to date by Kostelecký.\textsuperscript{8} Here, the primary interest is hydrogen and, therefore, the electron and proton sectors.

Our objective in this work is a comprehensive, structured calculation of the energy perturbations in free hydrogen due to the standard model extension (for the electron and proton) at orders \( O(SME), O(SME \cdot \alpha) \), and \( O(SME \cdot \alpha^2) \), where \( \alpha \) is the fine structure constant. This subsumes the lowest order corrections \( O(SME) \) which were presented before\textsuperscript{11,19,20} while adding the higher order shifts. We also do not limit our calculation to \( S \) states, but instead obtain energy corrections for the general eigenstates of total angular momentum. Our procedure should also make it clear how to go about obtaining even higher order corrections.

Finally, we also discuss the ways in which our equations, when combined with appropriate experimental data, would put bounds on the size of Lorentz and CPT violation. For the most part, bounds can be found by exploiting the fact that the Earth is non-inertial to hopefully observe changes in the hydrogen spectrum with time of year.\textsuperscript{15} We also briefly discuss the effect of an external magnetic field on SME hydrogen. The presence of a magnetic field changes the hydrogen eigenstates, which in turn makes the SME corrections visible at higher order.\textsuperscript{11}

\subsection*{2. Obtaining Schrödinger’s Equation from the Dirac Equation}

The Dirac equation, which describes the wave function for a spin \( 1/2 \) fermion (e.g. electron, proton, etc.), in the SME can be made to look like that of the standard model. In the SME, the Dirac equation is\textsuperscript{10}

\begin{equation}
(i \Gamma^\nu D_\nu - M) \psi(\vec{r}) = 0,
\end{equation}

where \( \psi(\vec{r}) \) is a wave function with four components. There is a component to \( \psi(\vec{r}) \) for both spins (up or down) of the particle and both spins of the antiparticle. Here \( iD_\nu = i\partial_\nu - qA_\nu \), where \( A_\nu \) is an electric potential four-vector, \( q \) is the particle’s charge, and \( m \) is its mass. In the standard model, \( \Gamma^\nu = \gamma^\nu \) and \( M = m \). However, in the SME, \( \Gamma^\nu \) and \( M \) are also augmented with SME terms:\textsuperscript{10}

\begin{align}
\Gamma^\nu &= \gamma^\nu + e^{\mu\nu}\gamma_\mu + d^{\mu\nu}\gamma_5\gamma_\mu + e^\nu + if^\nu\gamma_5 + \frac{1}{2}g^{\lambda\mu\nu}\sigma_{\lambda\mu} \quad \text{(2.2)} \\
M &= m + a^{\mu}\gamma_\mu + b^{\mu}\gamma_5\gamma_\mu + \frac{1}{2}H^{\mu\nu}\sigma_{\mu\nu}. \quad \text{(2.3)}
\end{align}

See appendix A for more information regarding our definitions of the Dirac matrices \( \gamma^\mu, \gamma_5, \) and \( \sigma^{\mu\nu} \). In the above equations, \( a^{\mu}, b^{\mu}, e^{\mu\nu}, d^{\mu\nu}, e^\nu, f^\nu, g^{\lambda\mu\nu}, \) and \( H^{\mu\nu} \) are the (minimal) electron SME parameters, which are all assumed to be small, as evidenced by experiment. Each of these parameters is a real vector or tensor. The parameters in equations (2.2) and (2.3) are considered to be those of the lab frame. These parameters are fixed for inertial frames, but from the point of view of a lab frame on Earth they could very well vary periodically with the sidereal day and year.\textsuperscript{9} This variation of the parameters with time means the Dirac equation, and therefore the Hamiltonian, will be time varying, as well. However, the timescale of that variation (24 hrs.) is much longer than the timescale of the atomic transitions (0.122 s for 2S-1S in hydrogen) we are considering. In the adiabatic approximation, the Hamiltonian is constant in time. That is, we will not be doing time-dependent perturbation theory when the time comes to calculate corrections to the hydrogen energy levels.

While all these SME parameters are Lorentz violating, the CPT-odd parameters \( a^{\mu}, b^{\mu}, e^\nu, f^\nu, \) and \( g^{\lambda\mu\nu} \) also govern CPT violation.\textsuperscript{21} Because \( \sigma_{\mu\nu} = -\sigma_{\nu\mu} \), we may choose \( g^{\lambda\mu\nu} \) to be antisymmetric in its first two indices and \( H^{\mu\nu} \) to be antisymmetric. Additionally, \( e^{\mu\nu} \) and \( d^{\mu\nu} \) can be taken to be traceless \( (e^{\mu}_{\mu} = d^{\mu}_{\mu} = 0) \).\textsuperscript{9} Since the Dirac equation (2.1) is a description of fermions in general, the SME parameters may also depend on the type of particle...
from which we read off the Hamiltonian as the operator $H$ order in $\epsilon$ by keeping $H$ defines the Hamiltonian, SME dependence. Of course, since the SME corrections are evidently small, we will restrict our calculations to linear SME. When an expression contains terms linear in the SME parameters we say it and declare all SME parameters order SME. When an expression contains terms linear in the SME parameters we say it as a Hamiltonian.

We will be calculating a correction to the standard model Hamiltonian to first order in the SME parameters. Thus, the usual approach to the Dirac equation is to put Eq. (2.1) in the form which defines the Hamiltonian,

$$i\hbar \partial_t \psi(\vec{r}) = H \psi(\vec{r}),$$  \hspace{1cm} \text{(2.4)}

from which we read off the Hamiltonian as the operator $H$. Rearranging Eq. (2.1), we find

$$i\hbar \partial_t \psi(\vec{r}) = (\Gamma^0)^{-1}(-i\Gamma^\mu D_\mu + M + q\Gamma^0 A_0)\psi(\vec{r})$$  \hspace{1cm} \text{(2.5)}

which suggests $H' = (\Gamma^0)^{-1}(\vec{\Gamma} \cdot \vec{\pi} + M) + q A_0$ if $\vec{\pi} = \vec{p} - q\vec{A}$. However, this is not generally hermitian as can be seen by keeping $e^\nu$ nonzero while all other SME parameters, and the four-vector potential, vanish. In this instance, to first order in $e^\nu$, we find $(\Gamma^0)^{-1} = (\gamma^0 + e^0)^{-1} = (\gamma^0 - e^0)$. So

$$(H')^\dagger = (\vec{p} \cdot (-\vec{\gamma} + \vec{e}) + m)(\gamma^0 - e^0)$$  \hspace{1cm} \text{(2.6)}

Evidently, we cannot use $H'$ as a Hamiltonian.

The solution to this problem is to redefine the field $\psi(\vec{r})$ to $\chi(\vec{r})$, using $\psi(\vec{r}) = A\chi(\vec{r})$ for some operator $A$. We let $A = (\gamma^0\Gamma^0)^{-1/2}$ and show that this leaves us with a hermitian Hamiltonian. \hspace{1cm} \text{(2.7)}

Note that $A$ is hermitian because $\gamma^0\Gamma^0 = (\Gamma^0)^\dagger\gamma^0$. Starting from Eq. (2.5) and applying $\psi(\vec{r}) = A\chi(\vec{r})$, we find

$$i\hbar \partial_t \chi(\vec{r}) = A^{-1} H' A \chi(\vec{r}),$$

so that the new candidate Hamiltonian is $H = A^{-1} H' A$. Using $A^{-1} = A(\gamma^0\Gamma^0)$, this takes the form

$$H = A\gamma^0(\vec{\Gamma} \cdot \vec{\pi} + M)A + qA^0.$$  \hspace{1cm} \text{(2.8)}

Using the identities $\gamma^0\Gamma^\nu = (\Gamma^\nu)^\dagger\gamma^0$ and $\gamma^0 M = M^\dagger\gamma^0$ resulting from our definitions (2.2) and (2.3) and the fundamental anticommutation relations of the gamma matrices, we see that $H$ is indeed hermitian:

$$H^\dagger = A^\dagger ( (\Gamma^0)^i \pi^i + M^i ) A^0 \gamma^0 A^\dagger + qA^0$$  \hspace{1cm} \text{(2.9)}

We will be calculating a correction to the standard model Hamiltonian to first order in the SME parameters. Thus, it is convenient to have an expression for $H_E$, the perturbation in the standard model Hamiltonian $H_{SM}$ that is first order in the SME parameters. Similarly, we write $\Gamma^\nu = \gamma^\nu + \Gamma_E^\nu$ and $M = M + M_E$. Noting that $A = I - \frac{1}{2}\gamma^0\Gamma_E^0$ and using Eq. (2.8), we find

$$H_E = \gamma^0(\Gamma_E^0 \pi^i + M_E) - \frac{1}{2}\gamma^0\Gamma_E^0 \gamma^0(\gamma^i \pi^i + m) - \frac{1}{2}(\gamma^i \pi^i + m)\Gamma_E^0.$$  \hspace{1cm} \text{(2.10)}

Notice the last two terms are adjoints of one another and $H_E$ is hermitian. The standard model piece of the
Hamiltonian is well known, but is displayed here for completeness

\[ H_{SM} = \gamma^0 (\gamma^i \pi^i + m) + qA^0 \]  

so that \( H = H_{SM} + H_E + O(\text{SME}^2) \).

We can further expand \( H_E \) to display more explicitly its dependence on the SME parameters using Eq. (2.2) and Eq. (2.3). Since we are keeping only terms linear in the SME, we may consider each SME parameter separately. We show the calculation involving \( e^\nu \) as an example.

With \( e^\nu \) the only nonzero SME parameter, \( \Gamma_\nu^E = e^\nu \) and \( M_E = 0 \). Accordingly, from Eq. (2.10) we find

\[ H_E(e) = \gamma^0 e^i \pi^i - \frac{1}{2} \gamma^0 e^0 \gamma^0 (\gamma^i \pi^i + m) - \frac{1}{2} (-\gamma^i \pi^i + m) e^0 = \gamma^0 e^i \pi^i - m e^0. \]  

(2.12)

The same process with the other seven SME parameters will give the first-order dependence of \( H_E \) on those parameters. In the end, we find agreement with Kostelecky and Lane’s result, their equation (7).

In the notation that we use, we write

\[ H = m\gamma_0 + \mathcal{E} + \mathcal{O}, \]  

(2.13)

where both \( \mathcal{E} \) and \( \mathcal{O} \) decompose into standard model and extension parts,

\[ \mathcal{E} = qA_0 + \delta_E \]  

(2.14)

\[ \mathcal{O} = \gamma_0 \gamma^i \pi^i + \mathcal{O}_E. \]  

(2.15)

The \( \mathcal{E} \) term consists of all terms in the Hamiltonian (excluding \( m\gamma_0 \)) which have an even 2 \( \times \) 2 matrix structure and the \( \mathcal{O} \) term consists of all terms with the structure of an odd 2 \( \times \) 2 matrix. That is,

\[ \mathcal{E} = \begin{pmatrix} A & 0 \\ 0 & B \end{pmatrix}, \]  

(2.16)

\[ \mathcal{O} = \begin{pmatrix} 0 & C \\ C^\dagger & 0 \end{pmatrix}, \]  

where \( A, B, \) and \( C \) are 2 \( \times \) 2 matrices with \( A \) and \( B \) hermitian. So really Eq. (2.13) is just an organizational decomposition that could be done for any Hamiltonian. For our purposes, Eq. (2.13) is useful for application of the Foldy-Wouthuysen procedure, which is coming soon.

Of course, \( \mathcal{E} \) and \( \mathcal{O} \) have particular forms in the SME. We define \( \Sigma^i = \gamma_5 \gamma_0 \gamma^i \left( \begin{array}{cc} \sigma^i & 0 \\ 0 & \sigma^i \end{array} \right) \), in terms of the Pauli matrices \( \sigma^i \). The set \( \{ \Sigma^i \} \) forms a basis for even, hermitian, 4 \( \times \) 4 matrices such as \( \delta \), while the set \( \{ \gamma_5, \gamma_5 \gamma^i, i\gamma_0 \gamma_5, i\gamma^i \} \) serves as a basis for odd, hermitian, 4 \( \times \) 4 matrices like \( \mathcal{O} \). All matrices in these sets are themselves hermitian. We therefore expect that there exist real coefficients, linear in the SME parameters, \( \epsilon_0, \epsilon^i, \mathcal{E}_0, \) and \( \mathcal{E}^i \) such that

\[ \delta_E = \epsilon_0 + \epsilon^i \Sigma^i + \mathcal{E}_0 \gamma_0 + \mathcal{E}^i \gamma_0 \Sigma^i. \]  

(2.17)

Likewise, there must be real coefficients \( \omega_0, \omega^i, \Omega_0, \) and \( \Omega^i \), which are linear in the SME parameters, such that

\[ \mathcal{O}_E = \omega_0 \gamma_5 + \omega^i \gamma_0 \gamma^i + i\Omega_0 \gamma_0 \gamma_5 + i\Omega^i \gamma^i. \]  

(2.18)

In general, each omega and epsilon coefficient has dependence on \( \pi^i \) as well, making them partly differential operators. We find, from explicit calculations like the \( e^\nu \) example above and subsequent rearrangement, the values of these eight coefficients in terms of the SME parameters:

\[ \epsilon_0 = (a_0 - mc_0) + (c^{0i} + c^{ij}) \pi^i, \]  

\[ \epsilon^i = (b^i - \frac{1}{2} m e_{hhk} g_{hkk} + (d^{ij} + d_{00} \delta^{ij}) \pi^j, \]  

\[ \mathcal{E}_0 = -mc_0 + \epsilon^i \pi^i, \]  

\[ \mathcal{E}^i = \left( \frac{1}{2} e_{hhk} H^{hk} - md^{00} \right) + \left( e^{hhj} g_{hkk} + \epsilon^{ijk} g^{kk00} \right) \pi^j, \]  

\[ \omega_0 = -b_0 - (d^{00} - d^{ij}) \pi^j, \]  

\[ \omega^i = a^i + (e^{ij} - c_{00} \delta^{ij}) \pi^j, \]  

\[ \Omega_0 = f^i \pi^j, \]  

\[ \Omega^i = H^{0j} + (g^{0j} + g^{j0}) \pi^j. \]  

(2.19)
3. FOLDY-WOUTHUYSEN PROCEDURE

A. FW Overview

The Foldy-Wouthuysen (FW) procedure is a general and essentially mechanized procedure for transforming a Hamiltonian $H$ into block diagonal even form

$$H_{FW} = \begin{pmatrix} h_{e-} & 0 \\ 0 & h_{e+} \end{pmatrix}, \tag{3.1}$$

where $h_{e-}$ and $h_{e+}$ are then the particle and anti-particle $2 \times 2$ Hamiltonians, respectively. The procedure consists of an infinite succession of unitary transformations applied to the wave function $\psi(\vec{r})$. The result is $H_{FW}$ as a power series in what is roughly the particle’s velocity, $|\vec{p}|/m$. We seek to verify Kostelecký and Lane’s non-relativistic Hamiltonian that was calculated using a more inventive and less standard procedure.

The typical expansion for electromagnetic phenomena is in powers of $\alpha = e^2 \approx 1/137$ using Gaussian units, not $|\vec{p}|/m$ as in the FW procedure. However, these quantities are essentially equivalent in hydrogen, as we will now argue. Hydrogen’s distance scale [$L = a = 1/m\alpha \approx 0.529 \text{Å}$, roughly the size of the atom in its ground state. Essentially, we mean by this that expectation values of anything with units of distance are of order $a$ in hydrogen. Likewise, the hydrogen time scale is $T = a/c = a$ and the relevant mass scale is $M = \hbar/c = ma$ and we conclude $|\vec{p}|/m = O(\alpha)$, justifying the FW expansion.

Note that for relativistic systems $|\vec{p}|/m \sim c = 1$ so that $|\vec{p}|/m$ is not a small number whose powers define a useful expansion. This is why our procedure leads to a non-relativistic Hamiltonian. Kostelecký and Lane produce the relativistic Hamiltonian that we confirm reduces to our result in the low speed limit.

Another unit of interest is that of magnetic field, which is often dominated by an artificial external field. In Gaussian units, a large magnetic field for present technology is of order $10^5$ Gauss. However, in our hydrogen units, the fundamental unit of magnetic field is $B = [M^{1/2}L^{-1/2}T^{-1}] = \sqrt{\hbar/m} = 1.9 \times 10^{14}$ G. This is $10^8 \approx \alpha^{-4}$ larger than any currently produceable lab magnetic field. Thus, we treat any magnetic field we find present in the Hamiltonian to be fourth order in $\alpha$. Note that since $\vec{B} = \nabla \times \vec{A} = i\vec{p} \times \vec{A}$ and $\vec{p} = O(\alpha)$, then $\vec{A} = O(\alpha^3)$.

B. FW Result

We now begin the FW procedure as described by Holstein. Given $H$ in the form of Eq. (2.13), we select the unitary matrix $U = e^{iS}$, in which $S$, defined as

$$S = -i \frac{1}{2m} \gamma_0 O, \tag{3.2}$$

is hermitian. Since $i\partial_0 \psi(\vec{r}) = H\psi(\vec{r})$ initially, after applying $U$ in the sense that our new wave function is $\psi'(\vec{r}) = U\psi(\vec{r})$, we find

$$i\partial_0 \psi'(\vec{r}) = \left[ UHU^{-1} - iU \frac{d}{dt} U^{-1} \right] \psi'(\vec{r}), \tag{3.3}$$

so that the new Hamiltonian is

$$H' = UHU^{-1} - iU \frac{d}{dt} U^{-1}. \tag{3.4}$$

Making explicit the dependence of $H'$ on $S$, we have

$$H' = H + i[S,H] + \frac{i^2}{2!} [S,[S,H]] + \ldots \tag{3.5}$$

$$- (S + \frac{i}{2!} [S,S] + \frac{i^2}{3!} [S,[S,S]] + \ldots).$$
We see that our choice of \( S \) creates a \(-\mathcal{O}\) from the term \( i[S, H] \) to cancel with \( \mathcal{O} \) from the term \( H \). Thus, the odd part of the Hamiltonian is pushed back to \( O(1/m) \). We write

\[
H' = \gamma_0 m + \mathcal{O}' + \mathcal{O}.
\]  

(3.6)

Making explicit the dependence of \( \mathcal{O}' \) and \( \mathcal{O}' \) on \( \mathcal{E} \) and \( \mathcal{O} \) by plugging Eq. (B.10) into Eq. (3.5), we find

\[
\mathcal{E}' = \mathcal{E} + \frac{1}{2m} \gamma_0 \mathcal{O}^2 - \frac{1}{8m^2} \left[ \mathcal{O}, [\mathcal{O}, \mathcal{E}] + i\dot{\mathcal{O}} \right] - \frac{1}{8m^3} \gamma_0 \mathcal{O}^4 + O\left( \frac{1}{m^4} \right).
\]  

(3.7)

\[
\mathcal{O}' = \frac{1}{2m} \gamma_0 \left[ [\mathcal{O}, \mathcal{E}] + i\dot{\mathcal{O}} \right] - \frac{1}{3m^2} \mathcal{O}^3 - \frac{1}{48m^3} \gamma_0 \left[ \mathcal{O}, \left[ \mathcal{O}, [\mathcal{O}, \mathcal{E}] + i\dot{\mathcal{O}} \right] \right] + O\left( \frac{1}{m^4} \right).
\]  

(3.8)

Accordingly, corrections to \( \mathcal{E} \) are at order \( 1/m \).

Another iteration of this procedure yields \( H'' \) from \( H' \) in Eq. (3.6) using \( S = -i \frac{1}{2m} \gamma_0 \mathcal{O}' \). Since Eq. (3.6) has the same form as Eq. (2.13), both \( \mathcal{E}'' \) and \( \mathcal{O}'' \) have the same dependence on \( \mathcal{E}' \) and \( \mathcal{O}' \) as \( \mathcal{E}' \) and \( \mathcal{O}' \) have on \( \mathcal{E} \) and \( \mathcal{O} \). That is, equations (3.7) and (3.8) hold if \( \mathcal{O} \) is replaced by \( \mathcal{O}^{(n)} \), \( \mathcal{E} \) by \( \mathcal{E}^{(n)} \), \( \mathcal{O}' \) by \( \mathcal{O}^{(n+1)} \), and \( \mathcal{E}' \) by \( \mathcal{E}^{(n+1)} \).

After \( n \) iterations of the unitary transformation, \( H^{(n)} = \gamma_0 m + \mathcal{E}^{(n)} + \mathcal{O}^{(n)} \). The odd part \( \mathcal{O}^{(n)} \) is of order \( 1/m^n \) the even part is \( \mathcal{E}^{(n)} = \mathcal{E}^{(n-1)} + O(1/m^{2n-1}) \). Calculating the block diagonal Hamiltonian \( H_{FW} \) to order \( 1/m^3 \), we find

\[
H_{FW} = H^{(4)} = \gamma_0 m + \mathcal{E}'' + O\left( \frac{1}{m^4} \right)
\]  

(3.9)

Calculation to order \( 1/m^2 \) suffices for our purposes of calculating energy level corrections for hydrogen to order \( O(\text{SME} \cdot \alpha^2) \). A term with a factor of \( 1/m^2 \) must have three factors of mass in the numerator. Each would normally result in a factor of \( \alpha \), however, massive SME parameters (e.g. \( \alpha^v, \beta^v \), and \( H^{uv} \)) do not, by our accounting of order, contribute an \( \alpha \). Thus, we could hope for a \( O(\text{SME} \cdot \alpha^2) \) contribution at most from the \( O(1/m^2) \) terms. Accordingly, no such contribution is expected to appear from the \( O(1/m^3) \) terms, where the smallest order in \( \alpha \) is \( O(\text{SME} \cdot \alpha^3) \).

In the SME, \( \mathcal{E} \) and \( \mathcal{O} \) have the forms (2.17) and (2.18). Calculating \( H^{(4)} \) for these is a matter of commutator algebra. We carry out the calculation to first order in the SME parameters and second order in \( \alpha \) and consider the magnetic field \( B \) to be constant, uniform, and of order \( \alpha^3 \) so that \( A \) is order \( \alpha^3 \). We find,

\[
\frac{1}{2m} \gamma_0 \mathcal{O}^2 = \gamma_0 \frac{\pi^2}{2m} - \gamma_0 \frac{q}{2m} \vec{B} \cdot \vec{S} 
\]  

(3.10)

\[
- \gamma_0 \frac{p^i}{m} a^i - \gamma_0 \frac{p^i \Sigma^j}{m} (\delta^{ij} b_0 + \gamma_0 \varepsilon^{ijk} H^k 0) - \gamma_0 \frac{p^i p^j}{m} (\varepsilon^{ij} + c_0 \delta^{ij}) 
\]

\[
- \gamma_0 \frac{p^i p^j \Sigma^k}{m} (\delta^{jk} (d^{00} + a^{00}) + \gamma_0 \varepsilon^{jkl} (g^{h0l} + g^{h0l}))
\]

and

\[
- \frac{1}{8m^2} [\mathcal{O}, [\mathcal{O}, \mathcal{E}] + i\dot{\mathcal{O}}] = - \frac{iq}{8m^2} \vec{\sigma} \cdot (\nabla \times \vec{E}) - \frac{q}{4m^2} \vec{\sigma} \cdot (\dot{\vec{E}} \times \vec{p}) - \frac{q}{8m^2} \vec{E} \times \vec{p}
\]  

(3.11)

\[
+ \gamma_0 \frac{p^i p^j}{2m} (c_0 \delta^{ij}) - \gamma_0 \frac{p^i p^j \Sigma^k}{2m^2} \left( \varepsilon^{i\rho \varepsilon^{jkl} (b^\rho - \frac{1}{2} m \varepsilon^{k\rho \sigma} g^{h0\sigma}) + \gamma_0 \delta^{ij} \frac{1}{2} \varepsilon^{i\rho \varepsilon^{jkl} (H^{0\rho} - md^{0\rho})} \right).
\]

The \( 1/m^3 \) part of Eq. (3.9) does not contribute to order \( O(\text{SME} \cdot \alpha^2) \) but does make the first relativistic correction
\[ -\gamma_0 p^4 / 8 m^3. \] Remembering \( \mathcal{E} \) is also to be included in \( H_{FW} \), we find \( h_{e^-} \), the upper left block of \( H_{FW} \), to be

\[
h_{e^-} = h_{SM} + h_E = \left[ \left( m + \frac{\pi^2}{2m} - \frac{p^4}{8 m^3} \right) + q A_0 - \frac{q}{2m} \vec{B} \cdot \vec{\sigma} - \frac{iq}{8 m^2} \vec{\sigma} \cdot (\vec{\nabla} \times \vec{E}) - \frac{q}{4 m^2} \vec{\sigma} \cdot (\vec{E} \times \vec{p}) - \frac{q}{8 m^2} \vec{\nabla} \cdot \vec{E} + O(\alpha^2) \right]
\]

\[
+ \left[ (a_0 - mc_0 - mc_{00}) + \left( b^i - md^0 - \frac{1}{2} \varepsilon_{ijk} (m g_{jk} - H_{kk}) \sigma^i + (c^i + m(c^0 + e^0i) + me^i) \frac{p^i}{m} \right)
\]

\[
- b_0 \delta^{ij} - \varepsilon^{ijk} H_{kk} + m(d^{ij} + d_{00} \delta^{ij}) + \frac{1}{2} m \varepsilon^{ijkl} g_{kk} \sigma^i + m \varepsilon^{ijkl} g_{k00} \frac{p^i \sigma^j}{m} - (c^i + \frac{1}{2} c_{00} \delta^{ij}) \frac{p^i p^j}{m^2} \right]
\]

\[
+ \left( -\frac{1}{2} (\varepsilon^{ijkl} b^{k} - \varepsilon^{ijk} b^{j}) - \delta^{ij} (md^{0} + \frac{1}{2} m d^{00} + \frac{1}{4} \varepsilon^{ipl} H_{pl}) - m \varepsilon^{ijk} (g_{k0i} + \frac{1}{2} g^{k0i}) \right) \frac{p^i p^j \sigma^k}{m^2} + O(\text{SME} \cdot \alpha^3) \right].
\]

This equation stands in agreement with Kostelecký and Lane’s equation (26).\(^9\) We will additionally split the standard model part of the Hamiltonian,

\[
h_{SM} = h_0 + h_{FS} + h_L + h_{HFS}.
\]

The first part is the traditional unperturbed Hamiltonian including just the Coulomb potential,

\[
h_0 = m + \frac{p^2}{2m} + q A_0,
\]

which yields energies of order \( O(\alpha^2) \). The second is the fine structure at order \( O(\alpha^4) \),

\[
h_{FS} = \left( \frac{\pi^2 - p^2}{2m} - \frac{p^4}{8 m^3} - \frac{q}{4 m^2} \vec{\sigma} \cdot (\vec{E} \times \vec{p}) - \frac{q}{8 m^2} \vec{\nabla} \cdot \vec{E} \right).
\]

The Lamb shift contribution \( h_L \) is at order \( O(\alpha^5) \), while that of the hyperfine splitting \( h_{HFS} \), the interaction of the electron’s angular momentum with the magnetic field induced by the proton spin, is at order \( O(\alpha^4 m / m_p) \), where \( m_p \) is the proton’s mass. From now on we will assume the absence of any external electric or magnetic field. This assumption of free hydrogen will aid us in calculating the energy perturbations due to the SME both by freeing us to choose a convenient quantization axis and by keeping the hydrogen eigenstates simple. Note that there is no Zeeman contribution, \( \vec{B} \cdot \vec{\sigma} \) due to this assumption.

## 4. CALCULATING ENERGY PERTURBATIONS

### A. Perturbation Theory and Setup

We wish to calculate the effect of the perturbing Hamiltonian \( h_E \) from (3.12) on the energy levels of free hydrogen. The simplest states we might consider using are the eigenstates of \( L_z \) and \( S_z \), the electron orbital and spin angular momentum, \(|nlm sm_s\rangle = |nl\rangle |Y_l^m\rangle |m_s\rangle \). The orbital part of this state is contained in the spherical harmonic \(|Y_l^m\rangle \). The spherical harmonics are functions of the polar angles \( \theta \) and \( \phi \) and have many nice identities. Perhaps most importantly, they are orthonormal \langle Y_{l_1}^{m_1}|Y_{l_2}^{m_2}\rangle = \delta_{l_1 l_2} \delta_{m_1 m_2} \). The spin of the electron has eigenstates \(|sm_s\rangle = |\frac{1}{2} m_s\rangle = |m_s\rangle \), where \( s = \frac{1}{2} \) is the electron’s total spin and \( m_s \) is its z-component. We often drop \( s \) since it is always \( \frac{1}{2} \). Also, \( m_s \) equals either positive or negative one half, states which we will sometimes write as \(|\uparrow\rangle \) and \(|\downarrow\rangle \), respectively. Likewise, when we consider proton spin, it can assume the states \(|\uparrow_p\rangle \) or \(|\downarrow_p\rangle \).

The simple states \(|nlm sm_s\rangle \) are very easy to calculate with and because they are complete, we can make any more complicated state from some linear combination of them. However, they are actually not good states to use to calculate the effect of \( h_E \), because \(|nlm sm_s\rangle \) is not an eigenstate of \( h_{SM} \). The correct way to approach this problem is to use the eigenstates \(|\psi_N\rangle \) of \( h_{SM} \) for some set of quantum numbers \( N \) and calculate first order energy corrections due to the perturbation \( h_E \) using degenerate perturbation theory. We begin with a review of non-degenerate versus degenerate perturbation theory and the influence of the standard model perturbations, namely, the fine structure, Lamb, and hyperfine structure. We conclude by finding the necessary set of quantum numbers \( N \).
The simple states $|nlm_{s}\rangle$ are eigenstates of $h_0$, which is $O(a^2)$. At this order, the energy levels are degenerate in $l$, $m_l$, $s$, and $m_s$. The fact that these are degenerate states has a crucial impact on calculating perturbed states. Consider, for example, adding a perturbation $h'$ that couples $m_s = 1/2$ to $m_s = -1/2$. That is the matrix element $(m_s = 1/2|h'|m_s = -1/2)$ is nonzero. In the basis, $|m_s = \pm \frac{1}{2}\rangle \equiv |\pm\rangle$, $h'$ looks like

$$h' = \begin{pmatrix} ae & bc \\ b^*\epsilon & cc \end{pmatrix}. \quad (4.1)$$

Here $\epsilon$ marks the size of the perturbation and $a, c \in \mathbb{R}$ while $b \in \mathbb{C}$. Overall, since $|nlm_{s}\rangle$ are eigenstates of $h_0$,

$$h_0 + h' = \begin{pmatrix} E_+ + ae & bc \\ b^*\epsilon & E_- + cc \end{pmatrix}. \quad (4.2)$$

Moreover, due to the degeneracy of $h_0$ in $m_s$, we know $E_+ = E_-$. The eigenstates of $h_0 + h'$ have, of course, changed from those of $h_0$. The eigenstates (without normalization) of the complete Hamiltonian are now

$$|\phi_+\rangle = \frac{(a-c) + \sqrt{(a-c)^2 + 4b^2}}{2b}|+\rangle + |-\rangle, \quad (4.3)$$

$$|\phi_-\rangle = \frac{(a-c) - \sqrt{(a-c)^2 + 4b^2}}{2b}|+\rangle + |-\rangle. \quad (4.4)$$

Notice that $\epsilon$ has disappeared! It does not matter how small the perturbation is, if the states are originally degenerate, even a very small perturbation will make a large $O(1)$ change to the eigenstates. Of course, the energy perturbation is still of order $\epsilon$,

$$E'_+ = E_+ + \frac{\epsilon}{2} \left((a + c) + \sqrt{(a-c)^2 + 4b^2}\right), \quad (4.5)$$

$$E'_- = E_- + \frac{\epsilon}{2} \left((a + c) - \sqrt{(a-c)^2 + 4b^2}\right). \quad (4.6)$$

Compare this to the situation in which $E_+ \neq E_-$. Then it is easy enough to find that the new eigenstates satisfy,

$$|\phi_+\rangle = |+\rangle + O(\epsilon), \quad (4.7)$$

$$|\phi_-\rangle = |-\rangle + O(\epsilon). \quad (4.8)$$

The new eigenstates are only slightly different from the old. If $O(\epsilon^2)$ corrections can be ignored, using the old eigenstates is good enough for the calculation of matrix elements. Also, the eigenvalues

$$E'_+ = E_+ + ac + O(\epsilon^2), \quad (4.9)$$

$$E'_- = E_- + cc + O(\epsilon^2) \quad (4.10)$$

are independent of $b$ to first order in $\epsilon$. Note that the order $\epsilon$ corrections are the diagonal matrix elements of $(4.2)$. If the states are originally non-degenerate and $O(\epsilon^2)$ can be ignored, we may just calculate the diagonal of $h'$ to find energy corrections.

Of course, $h_0$ and $h'$ here are shown as $2 \times 2$ matrices but the conclusions drawn are, in fact, general. Once degeneracies have been broken at an order higher than that of interest (e.g. SME), we can simply calculate diagonal matrix elements to find the energy corrections and do not even have to worry about changes to the eigenstates, at least, to first order in SME. This is non-degenerate perturbation theory. However, if degeneracies remain, the full matrix must be calculated and diagonalized (degenerate perturbation theory).

Once we add $h_{FS}$ to $h_0$, the eigenstates become, even at lowest order, those of $J^2$ and $J_z$, the magnitude and $z$-component of the total (electronic) angular momentum $\vec{J} = \vec{L} + \vec{S}$. We denote these states $|nljm_{j}m_{s}\rangle$. They are related to $|nlm_{s}\rangle$ by the Clebsch-Gordan coefficients

$$|nljm_{j}m_{s}\rangle = \sum_{m_{l},m_{s}} |lm_{l}; sm_{s}|jm_{j}\rangle|nlm_{s}\rangle \quad (4.11)$$

$$= \pm \alpha_{\pm}(l, m_{j})|nY_{l}^{m_{j},-1/2}\rangle|\uparrow_{s}\rangle + \alpha_{\mp}(l, m_{j})|nY_{l}^{m_{j},+1/2}\rangle|\downarrow_{s}\rangle,$$
where the \( \pm \) is chosen according to \( j = l \pm 1/2 \) and

\[
\alpha_\pm(l, m_j) = \sqrt{\frac{l \pm m_j + 1/2}{2l + 1}}. \tag{4.12}
\]

The energies of these states to the order of fine structure \( O(\alpha^4) \) are\(^{23}\)

\[
E_{FS} = \langle nljm_s|m_0 + h_{FS}|nljm_s \rangle = -\frac{ma^2}{2n^2} + \left( \frac{3}{8} - \frac{n}{(2j + 1)} \right) \frac{ma^4}{n^4}. \tag{4.13}
\]

Thus, we see that the degeneracy in \( j \) has been broken by the fine structure. This makes higher order calculations easier; we will not have to consider all matrix elements in \( j \)-space of a perturbing Hamiltonian, just those on the diagonal.

Consideration of the Lamb shift \( h_L \) breaks the degeneracy in \( l \) at order \( \alpha^5 \), without changing the eigenstates. The next correction, hyperfine splitting, takes the proton spin into consideration. The simplest states including the proton spin which are also eigenstates of \( h_{FS} \) would be \( |nljm_i\rangle \), where \( m_i \) is the proton’s spin z-component. However, it happens this is not an eigenstate of \( h_{HFS} \). The solution is much the same as that to the fine structure. We add the proton spin \( \vec{I} \) to the total electronic angular momentum \( \vec{J} \) to get the total angular momentum \( \vec{F} = \vec{J} + \vec{I} = (\vec{L} + \vec{S}) + \vec{I} \).

The states \( |nljm_f\rangle \) labeled by the total angular momentum number \( f \) are eigenstates of \( h_{HFS} \). They are constructed similarly to the total electronic momentum states,

\[
|nljm_f\rangle = \pm' \alpha_\pm'(j, m_f)|nlj, m_f - 1/2 \rangle |\uparrow_p \rangle + \alpha_\mp'(j, m_f)|nlj, m_f + 1/2 \rangle |\downarrow_p \rangle, \tag{4.14}
\]

where \( \pm' \) refers to \( f = j \pm' 1/2 \). The perturbation \( h_{HFS} \) breaks the degeneracy in \( f \) at order \( \alpha^4 m/m_p \), with \( m \) the electron mass and \( m_p \) the proton’s. These states \( |nljm_f\rangle \) are eigenstates of \( h_{SM} \).

For later reference, combination of Eqs. (4.11) and (4.14) to express \( |nljm_f\rangle \) in terms of the spherical harmonics and the electron and proton spinors, yields

\[
|nljm_f\rangle = \pm' \pm \left[ \alpha_\pm'(j, m_f)\alpha_\pm(l, m_f - 1/2) \right] |nY_l^{m_f - 1} \rangle |\uparrow_p \rangle
\]

\[
+ \left[ \alpha_\mp'(j, m_f)\alpha_\pm(l, m_f + 1/2) \right] |nY_l^{m_f} \rangle |\downarrow_p \rangle
\]

\[
+ \left[ \alpha_\mp'(j, m_f)\alpha_\mp(l, m_f + 1/2) \right] |nY_l^{m_f + 1} \rangle |\downarrow_p \rangle.
\]

in terms of \( \alpha_\pm(\cdot, \cdot) \) introduced in Eq. (4.12). Here the sign choices are determined by \( f = j \pm' 1/2 \) and \( j = l \pm 1/2 \). This change of basis is convenient since the spherical harmonics are often convenient functions to work with. Plus, \( |nY_L^M \rangle \) is the lowest order hydrogen wave function (from solving Schrödinger’s equation with just the Coulomb potential), which is much more familiar.

We use the total angular momentum states \( |\psi_N\rangle = |nljm_f\rangle \) to calculate the energy corrections due to the SME. The set of quantum numbers in the label \( N \) is \( \{n, l, j, m_f\} \). Only one degeneracy remains, that of \( m_f \). We will find that the SME corrections break this final degeneracy and also, through judicious choice of our \( z \)-axis, breaks it without change to the eigenstates \( |\psi_N\rangle \). Our ultimate goal then is an expression for \( E_{SM} = \langle nljm_f|H_E|nljm_f \rangle \) to first order in the SME parameters and second order in \( \alpha \). We refer to the SME energy corrections at the zeroth, first, and second orders in \( \alpha \) as \( E_{SM}^0 \), \( E_{SM}^1 \) and \( E_{SM}^2 \), respectively.

### B. \( O(\text{SME}) \) Energy Contributions

Referencing Eq. (3.12), the lowest order contributions involving the electron’s SME parameters is from the term

\[
h_{E,e}^0 = \Lambda_0 + \Lambda^i\sigma^i = (a_0 - mc_0 - mc_{00}) + \left( b^i - ma^{00} - \frac{1}{2}e^{ihk}(mg^{h00} - H^{hk}) \right) \sigma^i. \tag{4.16}
\]
We seek the matrix elements $\langle nljm_f'|h_{E,e}^0|nljm_f\rangle$, where we must consider even unequal values of $m'_f$ and $m_f$ since $h_{SM}$ leaves $m_f$ a degenerate quantum number.

Of course, the constant part $\Lambda_0$ of $h_{E,e}^0$ leaves only elements with $m'_f = m_f$ nonzero. The term involving $\sigma^i$ is less straightforward. Consider, as an example, the specific situation $f = 1, j = 3/2$, and $l = 1$. Now in terms of the basis $|n1\frac{3}{2}1m_f\rangle$ we write the matrix $h_{E,e}^0$. By use of equations (4.11) and (4.14) we find

$$
|n1\frac{3}{2}1m_f\rangle = - \sqrt{2} \langle 1|Y_{i-1}^{m_f}+1|\uparrow_p\rangle - \frac{2 - m_f}{\sqrt{12}} \langle 1|Y_{i-1}^{m_f}|\downarrow_p\rangle
$$

(4.17)

In Eq. (4.16), $\vec{\sigma} = 2\vec{S}_e$ is the vector of electronic spin Pauli matrices and as such acts only on the electron spinors $|\uparrow_e\rangle$ and $|\downarrow_e\rangle$. The catalogued behavior of each $\sigma^i$ is

$$
\sigma^1 |\uparrow_e\rangle = |\downarrow_e\rangle, \quad \sigma^1 |\downarrow_e\rangle = |\uparrow_e\rangle,
\sigma^2 |\uparrow_e\rangle = i |\downarrow_e\rangle, \quad \sigma^2 |\downarrow_e\rangle = -i |\uparrow_e\rangle,
\sigma^3 |\uparrow_e\rangle = |\uparrow_e\rangle, \quad \sigma^3 |\downarrow_e\rangle = -|\downarrow_e\rangle.
$$

(4.18)

Using Eqs. (4.17) and (4.18), we can find the matrix elements $\langle n1\frac{3}{2}1m_f'|h_{E,e}^0|n1\frac{3}{2}1m_f\rangle$ with $m'_f, m_f \in \{1, 0, -1\}$. For example, when $m'_f = m_f$,

$$
\langle n1\frac{3}{2}1m_f'|h_{E,e}^0|n1\frac{3}{2}1m_f\rangle = \langle m_f|\Lambda_0|m_f\rangle + \vec{\Lambda} \cdot \langle m_f|\vec{\sigma}|m_f\rangle
$$

(4.19)

$$
= \Lambda_0 + \frac{A^3}{12} \langle m_f|m_f\rangle
$$

$$
= \Lambda_0 + \frac{A^3}{12} \left( (2 - m_f)(1 + m_f) - (2 - m_f)^2 + (2 + m_f)^2 - (2 + m_f)(1 - m_f) \right)
$$

Continuing like this for other values of $m'_f$ and $m_f$, the entire matrix $h_{E,e}^0$ is found to be

$$
\begin{pmatrix}
\Lambda_0 + \frac{5}{6} A^3 & \frac{5}{6\sqrt{2}} (A^1 - i A^2) & 0 \\
\frac{5}{6\sqrt{2}} (A^1 + i A^2) & \Lambda_0 & \frac{5}{6\sqrt{2}} (A^1 - i A^2) \\
0 & \frac{5}{6\sqrt{2}} (A^1 + i A^2) & \Lambda_0 - \frac{5}{6} A^3
\end{pmatrix}.
$$

(4.20)

Note that, in general for any set of $l, j, f$, the matrix $h_{E,e}^0$ has nonzero elements only in the main diagonal and the two adjacent diagonals. The eigenvalues of $h_{E,e}^0(1, 3/2, 1)$ are $\Lambda_0$ and $\Lambda_0 + \frac{5}{6} |\vec{\Lambda}|$. This is, in fact, a general phenomenon; the eigenvalues, as physically observable quantities, depend only on the magnitude of $\vec{\Lambda}$. Though, the eigenstates are generally dependent on the individual components of $\vec{\Lambda}$ and, thus, also depend on our choice of coordinate system.

This should not be a surprise; the vector $\vec{\Lambda}$ from Eq. (4.16) has some direction in physical space. Changing the alignment of our apparatus with respect to this vector should not change the observed energy levels. This is analogous to the effect of an applied magnetic field; the Zeeman term $\vec{B} \cdot \vec{\sigma}$ in Eq. (3.12) has the same form, in fact. We assume no external applied magnetic field, but we do have the external vector $\vec{\Lambda}$.

We would be justified in aligning our $z$-axis with $\Lambda$ so that

$$
\begin{align*}
h_{E,e}^0 &= \Lambda_0 + |\vec{\Lambda}| \sigma^3 = \Lambda + \Lambda^3 \sigma^3.
\end{align*}
$$

(4.21)

This would be a good plan; since $\sigma^3$ is diagonal in the basis $|nljm_f\rangle$ with respect to $m_f$, the degeneracy in $m_f$ would be broken in a trivial manner so that $|nljm_f\rangle$ would remain our eigenstates. This can be seen from the example Eq. (4.20) where the off-diagonals vanish when $\Lambda^1 = \Lambda^2 = 0$.

However, there is a part of the lowest order Hamiltonian we have neglected. The proton in hydrogen is also affected by the SME. Since the proton is also a fermion, Eq. (3.12) is also the proton’s SME Hamiltonian (with the mass equal
to the proton mass). The \( p \)-subscripted \( \tilde{\alpha}_p \) vector and scalar \( \Lambda^0_p \) are exactly analogous to those of the electron,

\[
h^0_{E,p} = \Lambda^0_p + \Lambda^i_p \sigma^i = (a^0_p - m_p c^0_p - m_p c^0_{p'}) + \left( b^i_p - m_p d^0_p - \frac{1}{2} \sigma^{hk}(m_p g_{hk}^0 - H^0_p) \right) \sigma^i_p, \tag{4.22}
\]

involving the proton SME parameters \( a^\mu_p, b^\mu_p \), etc. The Hamiltonian with all fermion contributions for hydrogen at \( O(\text{SME}) \) is then

\[
h^0_E = h^0_{E,e} + h^0_{E,p} = (\Lambda^0_e + \Lambda^0_p) + \left( \tilde{\alpha}_e \cdot \vec{\sigma}_e + \tilde{\alpha}_p \cdot \vec{\sigma}_p \right). \tag{4.23}
\]

Now we have two vectors \( \tilde{\alpha}_e \) and \( \tilde{\alpha}_p \) that would make candidates for a \( z \)-axis, but we cannot have both!

The solution to this problem involves application of the Wigner-Eckart theorem, described in Appendix B. Both \( \vec{\sigma}_e \) and \( \vec{\sigma}_p \) satisfy the set of commutation relations

\[
[F_i, \sigma_j] = i \varepsilon_{ijk} \sigma_k \tag{4.24}
\]

and so both \( \sigma_e^i \) and \( \sigma_p^i \) have matrix elements proportional to the matrix elements of the total angular momentum \( F^i \), with a proportionality constant independent of \( m_f, m_f' \), and \( i \) (Appendix B). That is,

\[
\langle nljfm'|\sigma^i|nljfm_f \rangle = C(n, l, j, f) \langle nljfm_f'|F^i|nljfm_f \rangle. \tag{4.25}
\]

We can find the proportionality functions \( C_e(n, l, j, f) = c_e \) for the electron’s Pauli operator and \( C_p(n, l, j, f) = c_p \) for the proton’s by comparing the expectation values \( \langle nljfm'|\sigma_p^i|nljfm_f \rangle \) and \( \langle nljfm'|\sigma_e^i|nljfm_f \rangle \) with \( \langle nljfm_f'|F^3|nljfm_f \rangle = m_f \). For example, in the protonic case,

\[
\sigma_p^0|nljfm_f \rangle = \pm' \alpha_{\pm'}(j, m_f)|nlj, m_f - 1/2 \rangle |\uparrow_p \rangle - \alpha_{\pm'}(j, m_f)|nlj, m_f + 1/2 \rangle |\downarrow_p \rangle \tag{4.26}
\]

provided the linear composition from Eq. (4.14). So

\[
\langle nljfm_f'|\sigma_p^0|nljfm_f \rangle = \alpha_{\pm'}(j, m_f)^2 - \alpha_{\pm'}(j, m_f)^2 = \pm' \frac{2m_f}{2j + 1}
\]

\[
= \pm' \frac{2}{2j + 1} \langle nljfm_f'|F^3|nljfm_f \rangle. \tag{4.27}
\]

Which leads us to conclude

\[
c_p = \pm' \frac{2}{2j + 1}. \tag{4.28}
\]

The similar calculation for the electron yields

\[
c_e = \pm \frac{2(2j + 1 + 2l + 1)}{(2l + 1)(2j + 1)}. \tag{4.29}
\]

Accordingly,

\[
\langle nljfm_f'|h^0_E|nljfm_f \rangle = (\Lambda^0_e + \Lambda^0_p)\delta_{m_f m_f'} + \left( c_e \tilde{\alpha}_e + c_p \tilde{\alpha}_p \right) \cdot \langle nljfm_f'|F^3|nljfm_f \rangle). \tag{4.30}
\]

Now we have a single vector with which to align our \( z \)-axis. Let

\[
\hat{z} = \frac{(c_e \tilde{\alpha}_e + c_p \tilde{\alpha}_p)}{|c_e \tilde{\alpha}_e + c_p \tilde{\alpha}_p|} \tag{4.31}
\]

be the \( z \) unit vector. Note that \( \hat{z} \) depends on \( l, j, \) and \( f \). When considering an \( S \) state we will be using a different coordinate system than we will when considering a \( P \) state, for example. Our states \( |nljfm_f \rangle \) are also affected by this prescription. The quantum number \( m_f \) is the projection of \( f \) on our chosen \( z \)-axis, Eq. (4.31). Notice that Eq. (4.31)
also implies
\[ |c_e \vec{\Lambda}_e + c_p \vec{\Lambda}_p| = \left( c_e \vec{\Lambda}_e \cdot \hat{z} + c_p \vec{\Lambda}_p \cdot \hat{z} \right). \tag{4.32} \]

We will now let the index 3 on a vector represent its projection on our z-axis. So
\[ |c_e \vec{\Lambda}_e + c_p \vec{\Lambda}_p| = (c_e \Lambda_e^3 + c_p \Lambda_p^3). \tag{4.33} \]

The left side emphasizes that we are really finding the magnitude of a vector and it is not coordinate system dependent. On the right, we have imposed our coordinate system. We will typically use the notation on the right for its ostensible simplicity. However, remember the z-axis is \( l, j \), and \( f \) dependent and so an index of 3 would depend on the context. For example, \( b^3 \) with \( l = 0 \) is not the same projection of \( \vec{b} \) as \( b^3 \) when \( l = 1 \).

Returning to Eq. (4.30) we have
\[ \langle nljm'| h_E^0 |nljm \rangle = (\Lambda_e^0 + \Lambda_p^0) \delta_{m_f m_f'} + |c_e \vec{\Lambda}_e + c_p \vec{\Lambda}_p| \cdot \langle nljm'| \vec{F} |nljm \rangle \]
\[ = (\Lambda_e^0 + \Lambda_p^0) \delta_{m_f m_f'} + (c_e \Lambda_e^3 + c_p \Lambda_p^3) m_f \delta_{m_f m_f'}. \tag{4.34} \]

Assuming \((c_e \Lambda_e^3 + c_p \Lambda_p^3) \neq 0\), the degeneracy in \( m_f \) is broken. Because the matrix \( h_E^0 \) is diagonal in the basis \(|m_f\rangle \) (with \( m_f \) quantized along the z-axis \( (4.31) \)), the total angular momentum states \(|nljm\rangle \) remain our eigenstates of the Hamiltonian \((h_{SM} + h_E^0)\). Finally, the energy shift of state \(|nljm\rangle \) due to \( h_E^0 \) is
\[ E_{SME}^0 = (\Lambda_e^0 + \Lambda_p^0) + |c_e \vec{\Lambda}_e + c_p \vec{\Lambda}_p| m_f \]
\[ = (\Lambda_e^0 + \Lambda_p^0) + (c_e \Lambda_e^3 + c_p \Lambda_p^3) m_f \]
\[ = (\Lambda_e^0 - m e_e^0 - m c_e^0) + (b_3^0 - m d_3^0 - m g_{120}^e + H_0^{12}) \left( \pm \frac{2m_f(2j + 1)}{(2l + 1)(2j + 1)} \right) \]
\[ + (\Lambda_p^0 - m e_p^0 - m c_p^0) + (b_3^0 - m d_3^0 - m g_{120}^p + H_0^{12}) \left( \pm \frac{2m_f}{2j + 1} \right). \tag{4.35} \]

If the energy splitting between \( m_f = 0, \pm 1 \) were detectable, the magnitude of the vector \( \vec{\Lambda} = c_e \vec{\Lambda}_e + c_p \vec{\Lambda}_p \) could be determined. This magnitude is a combination of a variety of the more fundamental SME parameters \( b^i, H^{ij}, \text{etc.} \).

Notice that the emission from hydrogen’s 2S to 1S transition (a two-photon process\(^{23} \)) is actually unaffected by the energy shifts in Eq. (4.35). Selection rules in hydrogen forbid the 2S-1S transition unless \( \Delta f = 0 \) and \( \Delta m_f = 0 \).\(^{24} \)

Thus, \( m_f \) does not change and neither does the sign choice \( \pm' \) in Eq. (4.35). The sign choice \( \pm \) is unchanged because \( l = 0 \) in S orbitals and thus it must be the case that \( j = 1/2 \). Therefore, \( E_{SME}^0(1S) = E_{SME}^0(2S) \). The first correction from the SME to the 2S-1S transition in hydrogen will occur at \( O(\text{SME} \cdot \alpha^2) \), consistent with Bluhm et. al.\(^{11} \)

C. \( O(\text{SME} \cdot \alpha) \) Energy Contributions

We now continue on to higher order corrections, namely those at order SME \( \cdot \alpha \). Looking at Eq. (3.12), we see that the Hamiltonian at this order takes the form
\[ h_E^i = (\Lambda^i + \Lambda^{ik} \sigma^k) p^i \tag{4.36} \]
for \( \Lambda^i \) and \( \Lambda^{ik} \) linear in SME parameters.

We focus on the \( \Lambda^i \) term first. Our objective is the calculation of
\[ \Lambda^i \langle nljm|p^i|nljm\rangle. \tag{4.37} \]

It would definitely be strange if this expectation value were not zero, since then components of the momentum would have nonzero average values. The electron would on average be moving away from the proton! We can prove this expectation value is zero using the concept of parity.

The parity operator \( P \) is defined by its effect on functions of the space coordinates \( x = r \sin \theta \cos \phi, y = r \sin \theta \sin \phi, \)
and \( z = r \cos \theta \),

\[
P f(x, y, z) = f(-x, -y, -z) \quad (4.38)
\]

\[
P f(r, \theta, \phi) = f(r, \pi - \theta, \pi + \phi). \quad (4.39)
\]

Therefore, \( P \) flips all spatial directions, like a mirror does for a single dimension. In addition, \( P \) is its own inverse since reversing space \textit{twice} is the same as doing nothing. In general then \( P^2 = I \) for identity operator \( I \).

The important theorem which makes \( P \) a useful operator in our situation is as follows: Given an operator \( Q \) such that \( [P, Q] = 0 \) and the simultaneous eigenstates \( |\chi_n\rangle \) of \( P \) and \( Q \), if \( \{P, W\} = 0 \) for another hermitian operator \( W \), then \( \langle \chi_n | W | \chi_n \rangle = 0 \).

**Proof:** Say \( [P, Q] = 0 \) for some hermitian operator \( Q \). The operator \( Q \) has an orthonormal basis in which it is diagonal, say for basis states \( |\chi_n\rangle \). So \( Q|\chi_n\rangle = \lambda_n|\chi_n\rangle \) for \( \lambda_n \in \mathbb{R} \). This implies

\[
Q(P|\chi_n\rangle) = \lambda_n(P|\chi_n\rangle).
\]

Now, \( P|\chi_n\rangle = P|\chi_m\rangle \) if and only if \( n = m \) since \( P^2 = I \). Thus, \( P|\chi_n\rangle \) is a set of basis vectors and, by virtue of being eigenvectors of the hermitian operator \( Q \), are orthonormal. So

\[
\delta_{mn} = (P|\chi_{\text{m}}\rangle)^\dagger(P|\chi_{\text{n}}\rangle) = \langle \chi_{\text{m}} | P^\dagger P | \chi_{\text{n}} \rangle.
\]

From this equation, we conclude \( P^\dagger P = I \) in this basis. Since \( P^2 = I \), as well, that implies \( P = P^\dagger \). So \( P \) is both hermitian and unitary. Now that \( P \) has been revealed to be hermitian, it too is diagonalizable. We might as well have \( |\chi_n\rangle \) be the simultaneous diagonalizing basis for \( P \) and \( Q \), which exists because they are commuting, hermitian operators. Then the real eigenvalues of \( P \) are undoubtedly \( \pm 1 \) for each eigenvector \( |\chi_n\rangle \).

Introduce the operator \( W \), which anti-commutes with \( P \). Then, for \( P|\chi_n\rangle = \pm|\chi_n\rangle \) with the choice of sign dependent on \( n \),

\[
\langle \chi_n | W | \chi_n \rangle = \pm \langle \chi_n | WP | \chi_n \rangle = \mp \langle \chi_n | WP | \chi_n \rangle = -\langle \chi_n | WP | \chi_n \rangle.
\]

Since the expectation value of \( W \) equals its opposite, it must vanish, concluding the proof.

The operator \( Q \) in our hydrogen situation is the standard model Hamiltonian \( h_{SM} \). We have \( [P, h_{SM}] = 0 \) as required. Also, we have simultaneous eigenstates of \( Q \) and \( P \), though it may not be immediately obvious. The effect of parity on a spherical harmonic is \( P|Y^M_L\rangle = (-1)^L|Y^M_L\rangle \) (since remember \( Y^M_L \) is a function of \( \theta \) and \( \phi \), which parity redefines). The effect of parity on the spatial component \( |nL\rangle \) of the hydrogen eigenstates is that of the identity. So \( P|nlm_m m_m\rangle = (-1)^l|nlm_m m_m\rangle \) and therefore the orbital angular momentum states with electron and proton spin appended are eigenstates of \( P \). The eigenvalues of \( P \) depend only on \( l \) so, in fact, \( |nljm_{\text{m}} m_{\text{m}}\rangle \) and \( |nljm_{\text{f}} m_{\text{f}}\rangle \) are also eigenstates of \( P \). Therefore, \( |nljm_{\text{f}} m_{\text{f}}\rangle \), the total angular momentum states, are the simultaneous eigenstates of \( h_{SM} \) and \( P \) we want.

Finally, since \( \{P, p_i'\} = 0 \) for any \( i = 1, 2, 3 \) we conclude that Eq. (4.37) is in fact 0, using the parity theorem. Likewise, \( \{P, p_i' \sigma^j\} = 0 \) and so the expectation of \( H_{\text{p}} \) in Eq. (4.36), which is \( E_{\text{SM}}^p \), is entirely zero. There is no SME contribution to the hydrogen energy levels at order SME-\( \alpha \). Any operators at order SME-\( \alpha^k \) for free hydrogen that are either \( k \) factors of momentum \( p^k \) or with a spin operator \( p^k \sigma \), will vanish for odd integer \( k \).

**D. \( O(\text{SME-} \alpha^2) \) Energy Contributions**

Here we seek to calculate the expectation values of the Hamiltonian with form

\[
h_{\text{E}}^p = (\Lambda^{ij} + \Lambda^{ijk} \sigma^k) p^i p^j.
\]

These expectation values can be calculated using the method of spherical tensors and the Wigner-Eckart theorem, which is summarized in Appendix B.

The first step is the decomposition of \( p^i p^j \) into the trace and symmetric, traceless parts,

\[
p^i p^j = \frac{1}{3} \delta^{ij} p^2 + \left( p^i p^j - \frac{1}{3} \delta^{ij} p^2 \right) = t^{ij} + s^{ij}.
\]

just as was done in Eq. (B.7). The (rank 2) spherical tensor components of \( s^{ij} \) are shown in general in Eq. (B.10).
With reference to the notation used there, we are presently using \( \mathbf{u} = \mathbf{r} = \mathbf{p} \), the momentum vector.

The expectation value of \( t^{ij} \) is easily done. With \( T \) representing kinetic energy and \( V \) representing potential, the virial theorem in three dimensions states that

\[
2\langle T \rangle = \langle \mathbf{p} \cdot \nabla V \rangle. \tag{4.45}
\]

Ultimately, we are calculating to order \( \alpha^2 \) since \( p^2 \) is of that order. So \( T = p^2/2m + p^2/2m_p = p^2/\mu \) and \( V = -e^2/r \) in hydrogen. We are using

\[
\mu = \frac{m m_p}{m + m_p} \tag{4.46}
\]
as the reduced mass of the electron and proton. Therefore, the virial theorem (4.45) reduces to \( 2\langle T \rangle + \langle V \rangle = 0 \). Since also, \( E_{SM} = \langle T + V \rangle \), then \( \langle p^2 \rangle/2\mu = \langle T \rangle = -E_{SM} \) and \( \langle V \rangle = 2E_{SM} \). Now, because of our simple, lowest order choices for \( T \) and \( V \), \( E_{SM} \) is simply \( E_n = -\mu\alpha^2/2n^2 \), the lowest order energy levels. That is,

\[
\langle t^{ij} \rangle = \frac{1}{3} \delta^{ij} \langle p^2 \rangle = -\frac{1}{3} \delta^{ij} 2\mu E_n = \frac{1}{3} \delta^{ij} \left( \frac{\mu \alpha^2}{n^2} \right)^2. \tag{4.47}
\]

This expectation value is the same whether in the basis of states \( |nlm_i m_i \rangle \) or \( |nljm_j \rangle \). We will actually use the former states in the following calculation due to the ease of working with the spherical harmonics \( Y_{l}^{m} \). Eventually, we do need the expectation values in the total angular momentum \( \ell \) states, and so we will make use of Eq. (4.15).

The Wigner-Eckart theorem is the key to calculating the expectation value of \( s^{ij} \) in the state \( |nlm_i m_i \rangle \). We first seek the expectation value of the single spherical tensor component \( S_0^2 = (3p_z^2 - p^2)/\sqrt{6} \), of which the expectation value of \( p_z^2 \) is the obstacle. We propose doing this calculation using the momentum space wave functions of hydrogen in spherical coordinates \( p = |\mathbf{p}|, \Theta \in [0, \pi], \) and \( \Phi \in [0, 2\pi) \). This function \( \phi_{nlm_i} \) can be decomposed into radial and angular components just like the spacial wave function,

\[
|nlm_i \rangle = |\phi_{nlm_i}(p, \Theta, \Phi)\rangle = |P_{nl}(p)\rangle |Y_{l}^{m_i}(\Theta, \Phi)\rangle. \tag{4.48}
\]
The spherical harmonic \( Y_{l}^{m_i}(\Theta, \Phi) \) captures all angular dependence, just as in space. The explicit form of \( P_{nl}(p) \) makes use of the Gegenbauer polynomials.\(^{25}\) Since \( p_z = p \cos(\Theta) \),

\[
\langle nlm_i | p_z^2 | nlm_i \rangle = \int_0^\infty [P_{nl}^2 P_{nl}^*] p^2 dp \int_0^{2\pi} \int_0^\pi [(Y_{l}^{m_i})^* \cos^2(\Theta) Y_{l}^{m_i}] \sin(\Theta) d\Theta d\Phi
\]

\[
= \langle P_{nl}(p^2) | P_{nl}(\Theta, \Phi) Y_{l}^{m_i} | Y_{l}^{m_i} \rangle. \tag{4.49}
\]
The first integral is exactly the expectation value of \( p_z^2 \), which we found in our calculation of \( \langle t^{ij} \rangle \), Eq. (4.47). The angular integrals can be done using the recursion relations for the spherical harmonics.\(^{26}\)

\[
\cos \Theta Y_{L}^{M} = \sqrt{(L - M + 1)(L + M + 1)/(2L + 2L + 3)} Y_{L+1}^{M} + \sqrt{(L - M)(L + M)/(2L - 1)(2L + 1)} Y_{L-1}^{M} \tag{4.50}
\]
\[
e^{i\Phi} \sin(\Theta) Y_{L}^{M} = -\sqrt{(L + M + 1)(L + M + 2)/(2L + 1)(2L + 3)} Y_{L+1}^{M} + \sqrt{(L - M)(L - M - 1)/(2L - 1)(2L + 1)} Y_{L-1}^{M} \tag{4.51}
\]
\[
e^{-i\Phi} \sin(\Theta) Y_{L}^{M} = \sqrt{(L - M + 1)(L - M + 2)/(2L + 1)(2L + 3)} Y_{L-1}^{M} - \sqrt{(L + M)(L + M - 1)/(2L - 1)(2L + 1)} Y_{L+1}^{M}. \tag{4.52}
\]

We will use these relations several times in the following calculations. They make concrete the interpretation of \( \mathbf{p} \) as a spherical tensor. Currently, we use (4.50)-(4.52) to write \( \cos^2(\Theta) Y_{L}^{M} \) as a linear combination of \( Y_{L-2}^{M}, Y_{L}^{M}, \) and
\[ Y_{L+2}^M. \] The angular integral is then completed using the orthonormality of the spherical harmonics. We find,

\[ B(l, m_l) \equiv \langle Y^m_l | \cos^2(\Theta) | Y_l^m \rangle = \frac{(l - m_l + 1)(l + m_l + 1)}{(2l + 1)(2l + 3)} + \frac{(l - m_l)(l + m_l)}{(2l - 1)(2l + 1)}. \] (4.53)

Now, with all the pieces evaluated, we return to the calculation of the expectation of \([S_0^q]^2\) for \(q = -2, -1, 0, 1, 2\). The theorem states,

\[ \langle nlm | S_0^q | nlm \rangle = \langle nl || S^2 || nl \rangle \langle lmi; 2q | lmi \rangle, \] (4.55)

for any such \(q\). Now the second factor on the right is a Clebsch-Gordan coefficient, and we know that it will vanish unless \(q = 0\), which is the case we have done explicitly. The Wigner-Eckart theorem makes the guarantee that all the other spherical tensor components \(S_j^q\) have zero expectations.

We are now ready to find the components of the cartesian tensor \(s^ij\), through use of Eq. (B.13). The expectations

\[ \langle nlm | s^{11} | nlm \rangle = \langle nlm | s^{22} | nlm \rangle = \frac{1}{\sqrt{6}} \langle S_0^2 \rangle - \langle p^2 \rangle = -\frac{1}{\sqrt{6}} \langle S_0^2 \rangle = -\frac{\mu^2 \alpha^2}{2n^2} \left( B(l, m_l) - \frac{1}{3} \right) \] (4.56)

\[ \langle nlm | s^{33} | nlm \rangle = \frac{2}{\sqrt{6}} \langle S_0^2 \rangle = \frac{\mu^2 \alpha^2}{n^2} \left( B(l, m_l) - \frac{1}{3} \right) \] (4.57)

follow because the expectation of \(S_j^q\) is zero unless \(q = 0\). Returning to Eq. (4.44), we can find the expectation value of \(p^i p^j\) in general. Combination of equations (4.47), (4.56), and (4.57) yields,

\[ \langle nlm | p^i p^j | nlm \rangle = \langle nlm | p^2 p^2 | nlm \rangle = \frac{\mu^2 \alpha^2}{2n^2} (1 - B(l, m_l)) \] (4.58)

\[ \langle nlm | p^3 p^3 | nlm \rangle = \frac{\mu^2 \alpha^2}{n^2} B(l, m_l). \]

Again, \(\langle nlm | p^i p^j | nlm \rangle = 0\) when \(i \neq j\).

Finally, we can use the Clebsch-Gordan coefficients to find the expectation value of \(p^i p^j\) in the states labeled by the total angular momentum number \(f\) from the previous equation. Making use of Eq. (4.15), the result is the expectation value of \(p^i p^j\) in the states \(\langle nljm | \rangle\) with sign choices determined by \(f = j \pm 1/2\),

\[ \langle nljm | p^i p^j | nljm \rangle = [\left(1 + \frac{1 + 4m_f^2}{4j(j + 1)} \right) \delta_{ij} \delta_{j1} + \delta_{i2} \delta_{j2} \frac{2m_f^2}{j(j + 1)(2j + 1)}] \left(1 - \frac{1 + 4m_f^2}{4j(j + 1)} \right) \delta_{i3} \delta_{j3} \frac{\mu^2 \alpha^2}{n^2}. \] (4.59)

This is consistent with \(\langle p^2 \rangle = (\mu \alpha / n)^2\).

We are not done with order SME-\(\alpha^2\), however. We must also calculate the expectation values of \(p^i p^j \sigma^k\) in the total angular momentum states. Since \(\sigma\) here refers to the electron spin, the desired expectation reduces through use of Eq. (4.14) to

\[ \langle nljm | p^i p^j \sigma^k | nljm \rangle = \alpha_x \langle j, m_f \rangle^2 \langle nljm_- | p^i p^j \sigma^k | nljm_- \rangle + \alpha_x \langle j, m_f \rangle^2 \langle nljm_+ | p^i p^j \sigma^k | nljm_+ \rangle \] (4.60)

where \(m_- = m_f - 1/2\) and \(m_+ = m_f + 1/2\) are the two possible values of \(m_j\). This will turn out to be a nice form for
calculation, since it reduces the problem to the calculation of the expectations of \( p^i p^j \sigma^k \) in the total electronic angular momentum states \(|n{l}m_j\rangle\). Just like in the previous paragraph, the sign choices are made according to \( f = j \pm 1/2 \).

In later equations, sign choices indicated by \( \pm \) are determined by \( j = l \pm 1/2 \).

We may further break the problem into two situations, that in which \( k = 3 \) and that in which \( k = 1 \) or \( 2 \). In the former case, we note that Eq. (4.11) implies

\[
\langle n{l}m_j| p^i p^j \sigma^k |n{l}m_j\rangle = \alpha_\pm (l, m_j)\langle nY^{m_j-1/2}_l| p^i p^j |nY^{m_j+1/2}_l\rangle - \alpha_\mp (l, m_j)\langle nY^{m_j+1/2}_l| p^i p^j |nY^{m_j-1/2}_l\rangle,
\]

where \( j = l \pm 1/2 \). All the quantities on the right are known given equations (4.12) and (4.58), our calculation of the \( p^i p^j \) expectations. Thus, all quantities on the right side of (4.60) are known (for \( k = 3 \)). Though doing the algebra is unenviable, we can find

\[
\langle n{l}m_j| p^i p^j \sigma^3 |n{l}m_j\rangle = \frac{\pm 4m_f (2j + 1 \mp 1)}{(2l - 1)(2l + 1)} \left[ \frac{1 - 4m_f^2}{2(2j + 1 \mp 1)^2} \right] \delta_{\nu \ell} \delta_{j_1} + \frac{1 - 4m_f^2}{2(2j + 1 \mp 1)^2} \delta_{\nu j} \delta_{j_3} \right] \frac{\mu^2 \alpha^2}{n^2}.
\]

When \( k = 1 \) or \( 2 \) in the expression \( p^i p^j \sigma^k \) we have

\[
\begin{align*}
\langle n{l}m_j| p^i p^j \sigma^1 |n{l}m_j\rangle & = \pm \alpha_\pm (l, m_j) \alpha_- (l, m_j) \left( \langle nY^{m_j-1/2}_l| p^i p^j |nY^{m_j+1/2}_l\rangle + \langle nY^{m_j+1/2}_l| p^i p^j |nY^{m_j-1/2}_l\rangle \right) \tag{4.63} \\
\langle n{l}m_j| p^i p^j \sigma^2 |n{l}m_j\rangle & = \pm \alpha_\pm (l, m_j) \alpha_- (l, m_j) \left( \langle nY^{m_j-1/2}_l| p^i p^j |nY^{m_j+1/2}_l\rangle - \langle nY^{m_j+1/2}_l| p^i p^j |nY^{m_j-1/2}_l\rangle \right)
\end{align*}
\]

The remaining challenge is the calculation of matrix elements with form \( \langle nY^{M-1}_L| p^i p^j |nY^M_L\rangle \). Again we turn to the Wigner-Eckart theorem. We employ the decomposition of \( p^i p^j \) into its trace and its traceless, symmetric parts \( p^i p^j = t^{ij} + s^{ij} \) as in Eq. (4.44). This time the matrix element of \( t^{ij} \) vanishes

\[
\langle nY^{M-1}_L| t^{ij} |nY^M_L\rangle = \frac{1}{3} \delta^{ij} \langle nY^{M-1}_L| p^2 |nY^M_L\rangle = \langle nL| p^2 |nL\rangle \langle Y^{M-1}_L| Y^M_L\rangle = 0.
\]

Consider the spherical tensor \( S^2_q \) corresponding to the cartesian tensor \( s^{ij} \). The Wigner-Eckart theorem says \( \langle nY^{M-1}_L| S^2_q |nY^M_L\rangle \) is proportional to the Clebsch-Gordan coefficient \( \langle LM; 2q|LM - 1 \rangle \). In this case, only when \( q \) equals \(-1\) does this coefficient not vanish. So the only nonzero matrix element of \( S^2_q \) is that of \( S^2_{-1} \), which we calculate now.

According to Eq. (B.10),

\[
S^2_{-1} = \frac{1}{2} \left[ p_x (p_x - ip_y) + (p_x - ip_y) p_x \right] = p_x (p_x - ip_y) = p^2 e^{-i\Phi} \sin(\Theta) \cos(\Theta),
\]

where the last form is written in terms of the spherical angular momentum space coordinates. The expectation value, done in momentum space, is

\[
\langle nY^{M-1}_L| S^2_{-1} |nY^M_L\rangle = \langle nL| p^2 |nL\rangle \langle Y^{M-1}_L| e^{-i\Phi} \sin(\Theta) \cos(\Theta) |Y^M_L\rangle = \frac{\mu^2 \alpha^2}{n^2} C(L, M),
\]

where \( C(L, M) \) is found using the relations (4.50) and (4.52) and orthonormality of the spherical harmonics to be

\[
C(L, M) = -\frac{(2M - 1)}{(2L - 1)(2L + 3)} \sqrt{(L + 1/2)^2 - (M - 1/2)^2}.
\]
Having evaluated the matrix element of $S^2_{1,1}$, using (B.13) we can find the cartesian components $\langle p'p' \rangle = \langle s^{ij} \rangle$ to be zero except for the four components

$$
\langle nY_L^{-1}|p^3p^3|nY_L^M \rangle = \langle nY_L^{-1}|p^3p^3|nY_L^M \rangle = \sqrt{\frac{(L+1/2)^2 - (M-1/2)^2}{2L+1}} C(L, M) \frac{\mu^2\alpha^2}{2n^2}
$$

(4.68)

$$
\langle nY_L^{-1}|p^3p^3|nY_L^M \rangle = \langle nY_L^{-1}|p^3p^3|nY_L^M \rangle = i\sqrt{\frac{(L+1/2)^2 - (M-1/2)^2}{2L+1}} C(L, M) \frac{\mu^2\alpha^2}{2n^2}.
$$

(4.69)

The fact that the matrix element of $p^1p^3$ is real and that of $p^2p^3$ is purely imaginary implies (with reference to Eq. (4.60) and also Eq. (4.63)) that

$$
\langle nljm_f|p^1p^3\sigma^1|nljm_f \rangle = \langle nljm_f|p^1p^3\sigma^2|nljm_f \rangle = 0.
$$

(4.70)

Therefore, the only nonzero expectation values (in either the basis $|nljm_j \rangle$ or $|nljm_f \rangle$) are $\langle p^1p^3\sigma^1 \rangle$ and $\langle p^2p^3\sigma^2 \rangle$ up to commuting the momenta. The expectation value of $p'p'^k$ for $k = 1, 2$ can therefore be written succinctly as

$$
\langle nljm_f|p'p'^k|nljm_f \rangle = \frac{\mp 2m_f(2j + 1 \mp')}{(2l+1)(2l+3)(2j+1)} \times \left[ \delta_{ik}\delta_{j3} + \delta_{i3}\delta_{jk} \right] \frac{\mu^2\alpha^2}{n^2},
$$

(4.71)

where $f = j \pm' 1/2$ and $j = l \pm 1/2$.

From equations (4.62) and (4.71) we note the special cases,

$$
\langle nljm_f|\vec{p}\cdot\vec{p}'\sigma^k|nljm_f \rangle = \langle \sigma^k \rangle = \frac{m^2\alpha^2}{n^2} = \left( \pm \frac{2m_f(2j + 1 \mp')}{(2l+1)(2j+1)} \right) \frac{\mu^2\alpha^2}{n^2}\delta_{k3},
$$

(4.72)

$$
\langle nljm_f|p^l\vec{p}\cdot\vec{p}'|nljm_f \rangle = \frac{2m_f(2j + 1 \mp)(2j + 1 \mp')}{(2l-1)(2l+1)(2l+3)(2j+1)} \frac{\mu^2\alpha^2}{n^2}\delta_{i3}.
$$

(4.73)

Equations (4.59), (4.62), and (4.71) express the expectation values of all terms needed to calculate $E_{\text{SME}}^2$, the expectation value of $h_E^2$ from Eq. (4.74).

The order SME $\alpha^2$ energy is the expectation value of

$$
h_E^2 = H_1 + H_2
$$

$$
= - (\epsilon^{ij} + \frac{1}{2}\epsilon^{00}\delta^{ij}) \frac{p^i p^j}{m} - (\epsilon^{ij} \epsilon^{3jk} \vec{p}^2 + \delta^{ijk} \Delta^i + \epsilon^{ijk}\Gamma^{hi}) \frac{p^i p^j \sigma^k}{m^2}
$$

(4.74)

with the notation

$$
\Xi^p = \frac{1}{2} \delta^{p^2},
$$

(4.75)

$$
\Delta^i = m_0 \delta^{hi} + \frac{1}{2} m_0 \delta^{io} + \frac{1}{4} \epsilon^{ipl} H^{pl},
$$

(4.76)

$$
\Gamma^{hi} = m_0 (g^{hi} + \frac{1}{2} \delta^{hi}).
$$

(4.77)

Do we also need to include the SME correction to the proton as was done in the O(SME) correction (4.35)? We do not, because each term in $h_E^2$ is divided by at least one $m$, the mass of the fermion in question. The protonic version of Eq. (4.74) would be at least $m/m_p \sim 10^{-3}$ times smaller than the electronic version. Since we are calculating only to order $O(\text{SME} \cdot \alpha^2)$, we do not need to include the second order proton correction. It is dwarfed, assuming the proton’s SME parameters are not magnitudes larger than the electron’s, by the electronic contribution at order SME $\alpha^2$. Moreover, including the protonic contribution at $O(\text{SME} \cdot \alpha^2 \cdot \mu/m_p)$ would oblige us to include electronic corrections to the energies at $O(\text{SME} \cdot \alpha^3)$.

For exactly the same reason of relative orders of magnitude, we will approximate any reduced masses $\mu$ coming
from expectation values of momenta by the electron mass \( m \). Recall

\[
\mu = \frac{m m_p}{m + m_p} = m \left[ 1 - \frac{m}{m_p} + \left( \frac{m}{m_p} \right)^2 - \left( \frac{m}{m_p} \right)^3 + \ldots \right].
\] (4.78)

For example, \( \langle p^i p^j \rangle / m \propto \alpha^2 \mu^2 / m = m(1 - (m/m_p) + \ldots )^2 \alpha^2 \approx m\alpha^2 \) to our order of interest.

The first expectation \( \langle \mathcal{H}_1 \rangle \), which is quadratic in \( \vec{p} \) but with no \( \sigma^k \), is done using Eq. (4.59), the expectation value of \( p^ip^j \). We find

\[
\langle \mathcal{H}_1 \rangle = - \left[ \left( 1 + \frac{1 + 4m^2_j}{4j(j + 1)} \right) \pm \frac{2m^2_j}{j(j + 1)(2j + 1)} \right] mc^{11} + mc^{22} \] \[+ \left( 1 - \frac{1 + 4m^2_j}{4j(j + 1)} \right) \pm \frac{2m^2_j}{j(j + 1)(2j + 1)} \right] mc^{33} + mc_{00} \right] \frac{\alpha^2}{\hbar^2}.
\] (4.79)

The second term \( \mathcal{H}_2 \) requires some more effort. To start, the levi-civita product \( \varepsilon^{ik} \varepsilon^{jk} \) equals \( \delta^{ij} \delta^{pk} - \delta^{ik} \delta^{pj} \).

This leaves us with the expectation value

\[
\Xi \varepsilon^{ik} \varepsilon^{jk} \langle p^i p^j \sigma^k \rangle = \Xi^k \langle \vec{p} \cdot \vec{p} \sigma^k \rangle - \Xi^l \langle p^l \vec{p} \cdot \vec{\sigma} \rangle = \Xi^3 \left( \langle \vec{p} \cdot \vec{p} \sigma^3 \rangle - \langle p^3 \vec{p} \cdot \vec{\sigma} \rangle \right),
\] (4.80)

which simply requires application of equations (4.72) and (4.73). The \( \Delta^i \) term evaluates similarly,

\[
\Delta^i \delta^{jk} \langle p^i p^j \sigma^k \rangle = \Delta^i \langle p^i \vec{p} \cdot \vec{\sigma} \rangle = \Delta^i \langle p^3 \vec{p} \cdot \vec{\sigma} \rangle.
\] (4.81)

The final term involving \( \Gamma^{hi} \) becomes, through summation on \( i, j, k, \) and \( h \),

\[
\Gamma^{hi} \varepsilon^{jk} \langle p^i p^j \sigma^k \rangle = \Gamma^{3i} \langle p^i p^j \sigma^2 \rangle - \Gamma^{3i} \langle p^i p^j \sigma^1 \rangle + \Gamma^{1i} \langle p^i p^j \sigma^3 \rangle - \Gamma^{1i} \langle p^i p^j \sigma^1 \rangle + \Gamma^{2i} \langle p^i p^j \sigma^1 \rangle - \Gamma^{2i} \langle p^i p^j \sigma^3 \rangle
\]
\[
= \Gamma^{12} \langle p^i p^j \sigma^3 \rangle - \Gamma^{12} \langle p^i p^j \sigma^2 \rangle + \Gamma^{21} \langle p^i p^j \sigma^1 \rangle - \Gamma^{21} \langle p^i p^j \sigma^3 \rangle
\]
\[
= (\Gamma^{12} - \Gamma^{21}) \langle p^1 p^3 \sigma^1 \rangle + (\Gamma^{21} - \Gamma^{12}) \langle p^1 p^3 \sigma^3 \rangle
\]
\[
= \left( \langle p^1 p^3 \sigma^3 \rangle - \langle p^1 p^3 \sigma^1 \rangle \right) (\Gamma^{12} - \Gamma^{21}).
\] (4.82)

Evaluating each of the expectation values, we find that

\[
\langle \mathcal{H}_2 \rangle = \frac{\mp m_j (2j + 1 \mp 1)}{(2 l - 1)(2 l + 1)(2 l + 3)(2 l + 1)} \left[ \Xi^3 (2 l + 1 \mp 1) (2 l + 1 \mp 2) \mp 2 \Delta^3 (2 l + 1 \mp 1) \right]
\]
\[
\mp (\Gamma^{12} - \Gamma^{21}) (2 l \mp 1) (2 l + 1 \mp 2) \right] \frac{\alpha^2}{\hbar^2}.
\] (4.83)

The sum of equations (4.79) and (4.83) is the energy level corrections in hydrogen at order SME \( \alpha^2 \),

\[
E_{\text{SME}}^2 = \langle \mathcal{H}_1 \rangle + \langle \mathcal{H}_2 \rangle.
\] (4.84)

When we applied the order SME corrections to the 2S-1S hydrogen transition we found that, though the energies of both states were affected, they were shifted by the same amount. The 2S-1S transition is subject to the selection rules \( \Delta f = 0 \) and \( \Delta m_f = 0 \), and, necessarily, \( l = 0 \) and \( j = 1/2 \) in both of these states. The only changing quantum number in the transition is therefore \( n \), which is involved in the \( O(\text{SME} \cdot \alpha^2) \) corrections, while it was not involved in the \( O(\text{SME}) \) corrections. Its presence accounts for the nonzero \( O(\text{SME} \cdot \alpha^2) \) correction to the 2S-1S transition. By using our expressions for \( \langle \mathcal{H}_1 \rangle \) and \( \langle \mathcal{H}_2 \rangle \) above, we find that the S-states with principal number \( n \), have a second order correction,

\[
E_{\text{SME}}^2(nS) = - \frac{\alpha^2}{3 \hbar^2} \left( \frac{5}{2} mc_{00} + m_f (\Gamma^{12} - \Gamma^{21}) + m_f \Delta^3 + 2m_f \Xi^3 \right).
\] (4.85)
Therefore, the energy released by the transition 2S-1S is corrected by
\[ \delta E_{\text{SME}}^2(2S \rightarrow 1S) = \frac{\alpha^2}{4} \left( \frac{5}{2} m c_0^0 + m_f (\Gamma_1^{12} - \Gamma_2^{21}) + m_f \Delta_3 + 2 m_f \Xi_3 \right) \]
\[ = \frac{5}{8} m c_0^0 \alpha^2 + \frac{1}{4} m_f \left[ h^3 + \frac{1}{2} \mathcal{H}^{12} + m \left( g^{102} - g^{201} + g^{120} + d^{03} + \frac{1}{2} d^{30} \right) \right] \alpha^2. \] 

\[ (4.86) \]

5. CONCLUSIONS

A. Bounding the SME Parameters

First, note that our consideration of the 2S-1S transition frequencies below Eq. (4.35) and in Eq. (4.86) as special cases of our more general results (4.35), (4.79), and (4.83) is not arbitrary. The 2S-1S transition is forbidden as a one photon transition and is realized only by the emission of two photons. As a consequence, the 2S state in hydrogen has an unusually long lifetime, around 0.122 s, before transitioning to the 1S state. This is many orders of magnitude larger than the nanosecond lifetimes of most other states. Accordingly, the energy of the 2S-1S transition can be determined with remarkable accuracy. By the energy-time uncertainty relation, fundamentally the best accuracy we can hope for from a single measurement of the energy emission is
\[ \frac{\hbar}{2} \approx 2.7 \times 10^{-15} \text{ eV}. \] 

In terms of frequency \((f = E/\hbar)\), the accuracy available is 0.65 Hz. To put that accuracy in perspective, the energy released by the 2S-1S transition is 10.2 eV or 2.466 \times 10^{15} \text{ Hz} so that 0.65 Hz represents roughly one part in 4 \times 10^5. In reality, we can hope for even greater accuracy, since many measurements of the 2S-1S transition may be made. Though the width of the 2S-1S peak in the spectrum will ideally be 0.65 Hz, the central value may be determined more accurately than that. In any case, the current error on the measurement of the 2S-1S transition in hydrogen is a mere 34 Hz (out of \sim 10^{15} \text{ Hz}, recall) obtained by a group at the Max-Planck-Institut für Quantenoptik (MPQ).

To detect effects as small as those the SME may cause, this accuracy is invaluable. The better approach is to investigate differences in the outcomes of independent experiments and simply use the theory to interpret the result in terms of the SME parameters. For example, one type of experiment may find the value of the electron mass to be significantly different than that found with a different experiment. If the SME affects each experiment through different parameters, it could provide an explanation for the discrepancy. The size of the discrepancy would in turn bound the size of the SME parameters.

The two experiments need not even be very different in construction. Since the SME parameters are time dependent according to a non-inertial frame like the Earth, even the same experiment conducted at two (or more) different times during the year would provide two experiments affected differently by the SME. Our calculation makes use of the SME parameters in the Earth frame. Converting these Earth frame parameters through a Lorentz boost (involving the Earth’s velocity, which is time dependent according to the Sun) to the SME parameters in a Sun frame would make explicit the time dependence of, for example, Eq. (4.86). The SME Sun parameters are roughly time independent on the timescale between experiments in recent history; the Sun orbits the galactic center with period on the order of 100 million years. A difference in the 2S-1S transition frequency at two times of year could be explained by the SME and a bound placed on a combination of SME parameters, the combination present in Eq. (4.86) with an appropriate boost applied. Altschul used this technique and the result of two hydrogen spectroscopy experiments to place a bound on a linear combination of parameters \(c_{TJ} \) and \(c_{JT} \), where \(T \) is time in his chosen Sun frame and \(J = X, Y, Z \) are the spatial dimensions in the Sun frame. In a sense, an inconsistency, like that described above, between one experiment moving with respect to its twin is Lorentz violation at its most exemplary.

Another two experiments that could be compared, and which need not be moving with respect to one another, are the following. Observe the energy \(\epsilon_0 \) of the 2S-1S transition for states with total spin number \(f = 1 \) and z-projection \(m_f = 0 \). Also, observe the energy \(\epsilon_{\pm 1} \) of the 2S-1S transition with \(f = 1 \) and \(m_f = \pm 1 \). The energy difference should be zero for SM hydrogen (with no external magnetic field). However, free SME hydrogen will show a difference at
of order SME-$\alpha^2$, 
\[
\epsilon_{\pm 1} - \epsilon_0 = \pm \frac{1}{4} \left[ b^3 + \frac{1}{2} H^{12} + m \left( g^{102} - g^{201} + g^{120} + d^{03} + \frac{1}{2} d^{30} \right) \right] \alpha^2 
\]  
(5.2)

using Eq. (4.86). Of course, each of the SME parameters above is evaluated in the Earth frame at the time of the experiment. The time dependence of the quantity $\epsilon_{\pm 1} - \epsilon_0$, due to the Earth’s non-inertial motion, may provide even further sensitivity in the manner discussed in the previous paragraph.

B. SME Hydrogen in an External Magnetic Field

Although we calculated the corrections to the energies of hydrogen without the presence of an external magnetic field, considering such a field has both a practical and theoretical value. Practically, eliminating even the Earth’s magnetic field from an experiment either through cancellation or shielding is an added complication. The Earth’s magnetic field is, at its largest, $10^{-4}$ T. With the Bohr magneton $\mu_B = 5.8 \times 10^{-5}$ eV/T in mind as a natural conversion factor, the Earth’s magnetic field makes energy differences on the order of $5 \times 10^{-9}$ eV to hydrogen energy levels. As a comparison to the SME, the bound on Altschul’s combination of $c_{aTJ}$ and $m_e c_{IT}$ parameters times $\alpha^2$, the order at which $c_{00}$ contributes, is also on the order of $10^{-9}$ eV. Looking for better bounds on the SME parameters $\epsilon_{\mu\nu}$ in hydrogen is obviously problematic without practical elimination or theoretical consideration of external magnetic fields.

The picture of external magnetic fields is actually brighter on the theoretical side. It turns out that the presence of an external field lowers the order of the biggest SME contribution to the $2S-1S$ transition from $O(\alpha^5)$ to $O(\alpha^3)$. With only $S$ states ($l = 0$) in mind, consider the hyperfine and Zeeman Hamiltonians as a small perturbation on the Bohr hydrogen with fine structure. The Zeeman contribution is

\[
h_{Z} \propto (g_e \vec{\sigma}_e - g_p \vec{\sigma}_p) \cdot \vec{B},
\]  
(5.3)

where $g_e \approx 2$ and $g_p \approx 5.59$ are the gyromagnetic ratios of the electron and proton, respectively. The hyperfine contribution is

\[
h_{HFS} \propto \frac{1}{n^3} \vec{\sigma}_e \cdot \vec{\sigma}_p.
\]  
(5.4)

The eigenstates of hydrogen $nS$ states in a magnetic field, found as eigenstates of the hyperfine plus the Zeeman Hamiltonians, are

\[
\begin{align*}
|a\rangle_n &= |nl\rangle (\cos \theta_n | \uparrow e \uparrow p \rangle - \sin \theta_n | \uparrow e \downarrow p \rangle),
|b\rangle_n &= |nl\rangle | \uparrow e \uparrow p \rangle,
|c\rangle_n &= |nl\rangle (\sin \theta_n | \downarrow e \uparrow p \rangle + \cos \theta_n | \uparrow e \downarrow p \rangle),
|d\rangle_n &= |nl\rangle | \downarrow e \downarrow p \rangle.
\end{align*}
\]  
(5.5)

Here $\theta_n$ has dependence on the principal quantum number $n$ as determined by the equation

\[
\tan 2\theta_n \approx \frac{51 m T}{n^3 B_{\text{ext}}}.
\]  
(5.6)

with magnitude of the external field $B_{\text{ext}}$. Importantly, the order SME corrections to the transitions $2S_a - 1S_a$ and $2S_e - 1S_e$ (say $\epsilon_a^0$ and $\epsilon_e^0$, respectively) will be nonzero. From Eq. (3.12) and the easy to calculate expectations values of $\vec{\sigma}$ in the basis states (5.5). We find, for example, $\epsilon_e^0 = (\cos 2\theta_2 - \cos 2\theta_1) \left( b^3_e - b^3_p + H^{12}_e - H^{12}_p - m_e d^{30}_e + m_p d^{30}_p - m_e g^{120}_e + m_p g^{120}_p \right)$,  

where the z-axis is determined by the magnetic field, so that, for example, $b^3$ is the projection of $\vec{b}$ on the applied magnetic field $\vec{B}$.

Since the Earth rotates and revolves a magnetic field fixed in the lab frame will change direction with, most prominently, a daily period, resulting in a daily periodicity of $\epsilon_e^0$ that may be detectable. The magnetic field here serves to make the SME corrections appear at order SME rather than at the smaller order SME-$\alpha^2$. Also, the detection method need not rely on the difference between Lorentz boosts of the SME parameters, which are small.
since the Earth moving at only around $10^{-4}$ of the speed of light. Unfortunately, this elevation of the SME effects to greater orders of magnitude comes with a tradeoff. As pointed out by Bluhm et al., inhomogeneity in the applied external field will result in broadening of the emission spectrum and decreased accuracy, up to 1 MHz error for a 10 mT field at 100 µK.\textsuperscript{11}

\section*{C. Other SME Effects in Hydrogen}

There are other effects due to the SME that we have not included in our calculations, but are worth mentioning. First, higher order SME corrections to energy levels certainly could be calculated for hydrogen. Without external fields and without vacuum polarization effects, for $k = 0, 1, \ldots$ an order SME-$\alpha^k$ correction (that would add into Eq. (3.12)) will take the form

$$H_{\text{SME}}^{k} = p^{i_1}p^{i_2}\cdots p^{i_k} (A^{i_1i_2\cdots i_k} + B^{i_1i_2\cdots i_k j} \sigma^j), \quad (5.8)$$

where $A^{i_1\cdots i_k}$ and $B^{i_1\cdots i_k j}$ are tensors linear in the SME parameters. For odd $k$, the fact that the states $|nljm_i\rangle$ are either even or odd under parity results in the disappearance of the expectation value of $H_{\text{SME}}^{k}$, just as in section 4C for $k = 1$. Of course, vacuum polarization, analogous to the sources of Lamb shift corrections, could make contributions at $O(\text{SME} \cdot \alpha^k)$ for odd $k$.

With the addition of an external field with vector potential $\vec{A} = O(\alpha^3)$ and scalar potential $A^0 = O(\alpha^2)$, more terms appear in the Hamiltonian (3.12) at orders SME-$\alpha^3$ and higher. Recall that magnetic fields producible in the lab are of order $\alpha^4$ according to the argument in section 3A. So, for example, at $O(\text{SME} \cdot \alpha^4)$, among other new terms, comes the magnetic field dependence,

$$H_{\text{SME}}^{B} = \left( b^k + \frac{1}{2} mc^{ihk} g^{i\hbar} + mc^{ikj} g^{i\hbar} - \sigma^j (mc^{kj} + mc^{ijk} f^i) \right) \frac{qB^k}{2m^2}. \quad (5.9)$$

Here $\vec{B}$ includes both internal and external magnetic fields. Since external magnetic fields are known and usually manipulatable in hydrogen spectroscopy experiments, such a term provides a degree of control over the components of the SME vectors that are contributing, assuming such a small correction could be reliably detected in the future.

Also, in our calculations we have considered only the electron and proton SME parameters to be nonzero. In addition, photons, the force carriers of the electromagnetism holding hydrogen together, may also be affected by the SME.\textsuperscript{6,28} There is reason to believe that these effects will come into play at $O(\text{SME} \cdot \alpha^2)$ and so supplement Eq. (4.86) to correct the $2S - 1S$ transition. On the other hand, astrophysical experiments provide excellent sensitivity to these photon parameters and have not detected a nonzero SME photon parameter beyond the 1$\sigma$ confidence level. The primary boon in these experiments is that the light under consideration has traveled cosmological distances, over which some SME effects, such as vacuum birefringence and dispersion, can accumulate.\textsuperscript{28}

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\section*{APPENDIX A: DIRAC GAMMA MATRICES}

In this appendix, we make clear the conventions we used for the gamma matrices and illustrate some of their algebra. In $2 \times 2$ block form the gamma matrices are $(i = 1, 2, 3)$

$$\gamma^0 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad (A.1)$$

$$\gamma^i = \begin{pmatrix} 0 & -\sigma^i \\ \sigma^i & 0 \end{pmatrix}, \quad (A.2)$$
These satisfy the anticommutation relation \( \{ \gamma^\mu, \gamma^\nu \} = 2 \eta^{\mu\nu} \), where \( \eta^{\mu\nu} \) is the Minkowski metric with trace -2. We also make use of the Pauli matrices, which are \( 2 \times 2 \) and both hermitian and unitary,

\[
\sigma^0 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \quad \sigma^1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \\
\sigma^2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma^3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.
\] (A.3)

Since the Pauli matrices are hermitian, \( (\gamma^i)^\dagger = -\gamma^i \). Combined with the Dirac commutation relation, commutation of \( \gamma^i \) with \( \gamma^0 \) is the same as taking the adjoint of \( \gamma^i \); that is, \( \gamma^0 \gamma^i = (\gamma^i)^\dagger \gamma^0 \). Finally, we make the definitions

\[
\gamma_5 = i\gamma^0\gamma^1\gamma^2\gamma^3 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix},
\] (A.4)

\[
\sigma^{\mu\nu} = i\frac{2}{\eta^{\mu\nu}}[\gamma^\mu, \gamma^\nu],
\] (A.5)

\[
\Sigma^\mu = \gamma_5\gamma^\mu = \begin{pmatrix} \sigma^\mu & 0 \\ 0 & \sigma^\mu \end{pmatrix}.
\] (A.6)

A complete set of matrices for \( 4 \times 4 \), hermitian matrices that appear even when written as a \( 2 \times 2 \) matrix of \( 2 \times 2 \) blocks is

\[
\{ \Sigma^0 = \sigma_0 \otimes \sigma_0, \Sigma^i = \sigma_0 \otimes \sigma^i, \gamma_0 = \sigma^3 \otimes \sigma_0, \gamma_0 \Sigma^i = \sigma^3 \otimes \sigma^i \}. \] (A.7)

Likewise, the complete set used to build \( 4 \times 4 \), hermitian, block odd matrices is

\[
\{ \gamma_5 = \sigma^1 \otimes \sigma_0, \gamma_0 \gamma^i = \sigma^1 \otimes \sigma^i; -i\gamma_0 \gamma_5 = \sigma^2 \otimes \sigma_0, -i\gamma^i = \sigma^2 \otimes \sigma^i \}. \] (A.8)

Since matrix multiplication separates over the outer product, \( (A_1 \otimes A_2)(B_1 \otimes B_2) = (A_1 B_1) \otimes (A_2 B_2) \), exploitation of the known rules for multiplying sigma matrices \( (i,j) = 1,2,3 \)

\[
\sigma^i \sigma^j = \delta^{ij} \sigma_0 + i\varepsilon^{ijk} \sigma^k
\] (A.9)

can be used to calculate the products of the gamma matrices and the associated matrices \( \sigma^{\mu\nu} \) and \( \Sigma^\mu \). As an example,

\[
(-i\gamma^i)(-i\gamma^j) = (\sigma^2 \otimes \sigma^i)(\sigma^2 \otimes \sigma^j)
\]

\[
= (\sigma^2 \sigma^2) \otimes (\sigma^i \sigma^j)
\]

\[
= \sigma_0 \otimes (\delta^{ij} \sigma_0 + i\varepsilon^{ijk} \sigma^k)
\]

\[
= \delta^{ij} \Sigma_0 + i\varepsilon^{ijk} \Sigma^k.
\] (A.10)

As with adding integers, odd times odd or even times even gives an even matrix, while an odd times even or even times odd gives an odd matrix.

**APPENDIX B: SPHERICAL TENSORS AND THE WIGNER-ECKART THEOREM**

The rank 1, spherical tensor components of a cartesian vector \( \vec{v} \) with spherical direction \((\theta, \phi)\) are

\[
V_0^1 = v_3 = |\vec{v}| \cos \theta
\] (B.1)

\[
V_{\pm 1}^1 = \mp \frac{1}{\sqrt{2}}(v_1 \pm iv_2) = \frac{1}{\sqrt{2}}|\vec{v}| \sin \theta e^{\pm i\phi}.
\] (B.2)
The superscript signifies a rank 1 tensor and the capital letters that these are spherical components. These emulate the spherical harmonics with \( l = 1 \), which are

\[
Y^0_1 = \sqrt{\frac{3}{4\pi}} \cos \theta, \quad (B.3)
\]

\[
Y^\pm_1 = \mp \sqrt{\frac{3}{8\pi}} \sin \theta e^{\pm i\phi}. \quad (B.4)
\]

A vector \( \vec{v} \) written with spherical components can act like an object with angular momentum number \( l = 1 \) as we will see. For example, with \( \vec{v} = \vec{p} \), the momentum vector, equations (B.1) and (B.2) give the spherical momentum tensor \( P^1 \).

How can we tell that a tensor \( S^k_q \) is a spherical tensor acting like it has angular momentum \( k \) in a particular system? A sufficient condition is that the commutation relations of \( S^k_q \) with the angular momentum operator \( \vec{L} \) of the system satisfy

\[
[L_0, S^k_q] = [L_z, S^k_q] = q S^k_q \quad \text{(B.5)}
\]

\[
[L_\pm, S^k_q] = [L_\pm \mp iL_y, S^k_q] = \sqrt{(k \mp q)(k \pm q + 1)} S^k_{q \pm 1}.
\]

These commutators define the components of a spherical tensor \( S^k_q \) for any \( k \), as we did explicitly for \( k = 1 \) in Eq. (B.1). For \( k = 1 \), these commutation relations are equivalent to the familiar

\[
[L_i, s_j] = i \varepsilon_{ijk} s_k \quad \text{(B.6)}
\]

where \( \vec{L} \) and \( \vec{s} \) are the cartesian vectors corresponding to \( L_q \) and \( S^1_q \) in Eq. (B.5). For example, note that \( \vec{\sigma} \) satisfies Eq. (B.6) with the total angular momentum operator \( \vec{F} = \vec{L} + \frac{1}{2} \vec{\sigma} \), since \( \vec{\sigma} \) commutes with \( \vec{L} \) and \( \vec{\sigma} \) satisfies the Pauli commutation relations \( [\sigma_i^p, \sigma_j^q] = 2i \varepsilon_{ijk} \sigma_k^p \). Likewise, \( \vec{\sigma} \) also commutes with \( \vec{F} \) in the way described by Eq. (B.6).

Consider also a tensor \( v^{ij} = u^i w^j \) with rank 2. We also want to express this product in terms of spherical tensors. Inspired by the addition of angular momentum we expect three parts, an \( l = 0 \) rank 0 tensor, an \( l = 1 \) rank 1 tensor, and an \( l = 2 \) rank 2 tensor. This is realized by the decomposition

\[
v^{ij} = \frac{1}{3} \delta^{ij} u^k w^k + \frac{1}{2} (u^i w^j - u^j w^i) + \left( \frac{1}{2} (u^i w^j + u^j w^i) - \frac{1}{3} \delta^{ij} u^k w^k \right)
\]

\[
= t^{ij} + a^{ij} + s^{ij} \quad (B.7)
\]

in which \( t \) contains the trace of \( v \), \( a \) is the antisymmetric part of \( v \), and \( s \) is the symmetric, traceless part. Note that the tensor \( t \) has only one independent element; it is rank 0. Likewise, \( a \) has 3 independent components and \( s \) has 5; they are the rank 1 and rank 2 spherical tensors, respectively, that we seek. The spherical component of \( t \) is

\[
T^0_0 = -\frac{1}{\sqrt{3}} u^k w^k. \quad (B.8)
\]

The spherical components of \( a \) are

\[
A^0_0 = \frac{1}{\sqrt{2}} \left( U^1_{+1} W^1_{-1} - U^1_{-1} W^1_{+1} \right) \quad (B.9)
\]

\[
A^1_{\pm 1} = \pm \frac{1}{\sqrt{2}} \left( U^1_0 W^1_{\pm 1} - U^1_{\pm 1} W^1_0 \right),
\]

where \( U^1_q \) and \( W^1_q \) are the spherical components of \( \vec{u} \) and \( \vec{w} \) defined as they were in equations (B.1) and (B.2) for \( \vec{v} \).
The spherical components of $s$ are \(^{29}\)

$$
S_0^2 = \frac{1}{\sqrt{6}} (U_{+1}^1 W_{-1}^1 + U_{-1}^1 W_{+1}^1 + 2U_0^1 W_0^1) \\
S_{\pm 1}^2 = \frac{1}{\sqrt{2}} (U_0^1 W_{\pm 1}^1 + U_{\pm 1}^1 W_0^1) \\
S_{\pm 2}^2 = U_{\pm 1}^1 W_{\pm 1}^1.
$$

We will also have need of the inverse relations, expressing $t^{ij}$, $a^{ij}$, and $s^{ij}$ in terms of their spherical components. For $t^{ij}$ this is simple

$$
t^{ij} = -\frac{1}{\sqrt{3}} \delta^{ij} T_0^0. \quad (B.11)
$$

For $a^{ij}$ and $s^{ij}$ it becomes a matter of using the definitions of $U_{q}^1$ and $W_{q}^1$ and finding the combinations of $u^i$ and $w^i$ that make up $a^{ij}$ and $s^{ij}$ by their definitions in Eq. (B.7). For $a^{ij}$ this process yields

$$
a^{23} = \frac{1}{2i} (A_{+1}^1 - A_{-1}^1) \\
a^{31} = \frac{1}{2} (A_{+1}^1 + A_{-1}^1) \\
a^{12} = -i \frac{1}{\sqrt{2}} A_0^1. \quad (B.12)
$$

Along with its antisymmetry, $a$ is completely described by these three equations. Likewise, for $s^{ij}$ we find

$$
s^{11} = \frac{1}{2} (S_{+2}^2 + S_{-2}^2) - \frac{1}{\sqrt{6}} S_0^2 \\
s^{22} = -\frac{1}{2} (S_{+2}^2 + S_{-2}^2) - \frac{1}{\sqrt{6}} S_0^2 \\
s^{33} = \frac{2}{\sqrt{6}} S_0^2 \\
s^{12} = \frac{1}{2} (S_{-2}^1 - S_{+2}^1), \quad (B.13)
$$

The traceless condition is seen to hold: $s^{11} + s^{22} + s^{33} = 0$. With the symmetry of $s$, we know all the components $s^{ij}$ in terms of the spherical components $S_2^q$.

The spherical tensor representation affords us an easy method of calculating expectation values. The Wigner-Eckart theorem states that the matrix elements of a spherical tensor are proportional to the Clebsch-Gordan coefficients, $\langle L M k q | L' M' \rangle$. If $L$ and $M$ are the total angular momentum and $z$-projection, respectively, and $\alpha$ represents all other quantum numbers, the Wigner-Eckart theorem states explicitly for spherical tensor $R_q^n$ \(^{29}\)

$$
\langle \alpha' L' M' | R_q^n | \alpha L M \rangle = \langle \alpha' L' | R^n | \alpha L \rangle \langle L M k q | L' M' \rangle. \quad (B.14)
$$

The theorem’s useful stems from the fact that the proportionality constant, denoted by the double-barred matrix element, is independent of $M, M'$, and $q$. The Clebsch-Gordan coefficients fully capture the dependence of the matrix elements on those quantum numbers. In this sense, $R_q^n$ is essentially being added, as an angular momentum, to $|LM\rangle$. Addition rules are inherited from the Clebsh-Gordan coefficients, such as $\langle \alpha' L' M' | R_q^n | \alpha L M \rangle = 0$ unless $q + M = M'$ and $L + k - L' = 0, 1, 2, \ldots, L + k$.

Finally, a corollary of the Wigner-Eckart theorem follows from the fact that the angular momentum operator $\tilde{L}$ itself satisfies Eq. (B.14). So any spherical tensor $R_q^n$ defined by the relations Eq. (B.5) also satisfies Eq. (B.14) and so

$$
\langle \alpha' L' M' | R_q^n | \alpha L M \rangle = f(\alpha, \alpha', L, L', k) \langle \alpha' L' M' | L_q | \alpha L M \rangle. \quad (B.15)
$$

The matrix elements of $R_q^n$ are proportional to those of $L_q$ through a proportionality constant independent of $q$, $M$, and $M'$. 
REFERENCES

5 Ralf Lehnert, Invited talk at Neutral Kaon Interferometry at a Phi-Factory: from Quantum Mechanics to Quantum Gravity, Frascati, Italy, 24 March 2006.