High Resolution Rotational Spectroscopy Study of the Zeeman Effect in the $^2\Pi_{1/2}$ Molecule PbF

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## Contents

Acknowledgements ................................................................................................................. 2

Abstract ................................................................................................................................... 3

1 Introduction .............................................................................................................................. 4
   1.1 Motivations ....................................................................................................................... 4
   1.2 Detecting the Electron EDM ............................................................................................ 7

2 Experimental Procedure ....................................................................................................... 11
   2.1 Supersonic-Jet Fourier Transform Microwave Spectroscopy ........................................... 11
   2.2 Mode Structure ................................................................................................................ 16
   2.3 Sample Preparation .......................................................................................................... 17
   2.4 External Fields .................................................................................................................. 17

3 Theory .................................................................................................................................... 20
   3.1 PbF and Electronic Angular Momentum ............................................................................ 20
   3.2 Hyperfine Structure ......................................................................................................... 22
   3.3 Ground Rotational Energy Level Structure of $^{208}$PbF .................................................. 25
   3.4 Zeeman Splitting in the $^{2}\Pi_{1/2}$ Molecule PbF ............................................................ 27
      3.4.1 Zeeman Interaction with Electronic Angular Momentum ........................................ 27
      3.4.2 Molecules with Orbital and Spin Angular Momentum ......................................... 31
      3.4.3 Body Fixed g-factors .............................................................................................. 32

4 Analysis .................................................................................................................................. 35
   4.1 Raw Data Analysis ............................................................................................................. 35
   4.2 Determining the ratio $G_\parallel/G_\perp$ ................................................................................. 42
   4.3 Global Fit in Terms of $G_\perp$ ......................................................................................... 44

5 Conclusion .............................................................................................................................. 47

Appendix: Matlab Code ............................................................................................................ 49
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Abstract

Motivated by the ongoing search for the CP-violating electron electric dipole moment (e-EDM), rotational spectra of the radicals $^{207}$Pb$^{19}$F and $^{208}$Pb$^{19}$F were measured using a supersonic jet Fourier transform microwave spectrometer. The e-EDM is one of a handful of readily measurable predictions of New Physics that could provide a severe constraint on various supersymmetric theories. Heavy diatomic molecules such as PbF are of particular interest in the e-EDM search as they contain very high internal electric fields, amplifying the effects of a possible e-EDM. In addition, PbF has a comparatively low sensitivity to external magnetic fields, reflected in its small molecular g-factor ($g \approx 0.05$). As the effects of background magnetic fields can closely mimic that of an e-EDM, PbF’s low g-factor provides a significant advantage over other candidate molecules in the design of a future e-EDM experiment.

Zeeman splitting was examined for $^{10}$PbF and $^{9}$PbF $J = 1/2$ and $J = 3/2$ transitions using three pairs of Helmholtz coils capable of generating magnetic fields up to $\sim 4$ Gauss. The observation of these field dependent spectra allowed for the determination of the two body-fixed g-factors, $G_\parallel$ and $G_\perp$, of the electronic wave function. The final values obtained were $G_\parallel = 0.1300 \pm 0.0025$ and $G_\perp = -0.3719 \pm 0.0051$. These values compare reasonably well with recently calculated values ranging from 0.082 to 0.122 and -0.319 to -0.382, respectively. The precise determination of the body fixed g-factors is an important step in a possible future e-EDM experiment using either the $^{207}$Pb$^{19}$F or $^{208}$Pb$^{19}$F molecule.
1 Introduction

1.1 Motivations

Albert Einstein was once asked why he wasn’t more excited by the discovery of new elementary particles. His response? “You know, it would be sufficient to really understand the electron.” Such a goal has occupied the minds of physicists since the turn of the last century, and yet, despite the many brilliant contributions that have thrust our knowledge forward, fundamental questions still remain.

The insight that pushed our collective understanding of the electron further than any other was perhaps Paul Dirac’s introduction of the relativistic wave equation for the electron in 1928 [24]. This equation marked the first appearance of the electron electric dipole moment (e-EDM). Today, one may write it as

\[ d_e = \eta \frac{q}{2mc} S, \]

where \( \eta \) is a dimensionless constant and \( q \) and \( m \) are the particle’s charge and mass, respectively. Dirac, however, focused his work on the magnetic dipole moment (MDM), dismissing the EDM as not holding any physical meaning. Not until 1950, when Purcell and Ramsey [22] proposed that a nonzero EDM would constitute the first evidence of parity violation, was the importance of the EDM understood and the search begun in earnest.

The three fundamental transformations through which symmetries can be classified in Quantum Field Theory (QFT) are charge conjugation, parity, and time reversal. These transformations refer to whether a given process would behave differently if all particles involved were given opposite charge, all spatial directions were reversed, or time was run backwards (Figure 1). A central tenet of QFT is that combining these three transformations (CPT) must always produce a symmetric result [10]. This idea appeared almost ironclad at the time of its inception as there had been no observational evidence of symmetry breaking under even a single transformation.\(^1\)

\(^1\)Richard Feynman used to explain parity conservation by describing a remote encounter with an alien civilization. In preparation for meeting and seeing each other for the first time, we are able to tell them how tall we are in terms of the H\(_2\) bond length and how long we live in terms of the nuclear decay rate of \(^{133}\)Cs. As we’re signing off, we remember one last important detail. “When we meet someone new it’s customary to extend our right hand as a greeting.” The aliens reply, “that’s great, but what is ‘right’?” Not until Wu et
In light of the proclamation of CPT invariance, finding a case of symmetry breaking became an obvious pathway to further the understanding of QFT. While MDMs are understood as an obvious consequence of charged particles with spin, EDMs are seemingly forbidden by both parity and time reversal invariance. To see why, we examine the Hamiltonian for a spin 1/2 particle in an electric and magnetic field:

\[ H = -\mu \cdot B - d_e \cdot E \]  

The transformation properties of \( B, E \) and \( \mu / d_e \) under each of the aforementioned symmetries are given in Table 1. These results quickly follow from the observation that \( B \) and \( \mu / d_e \) are axial vectors while \( E \) is a polar vector [31].

We see that \( \mu \cdot B \) is always even, and therefore, invariant under all transformations, while \( d_e \cdot E \) is odd under both P and T symmetry, suggesting that if an EDM were to exist P and T would not be valid symmetries for this Hamiltonian. This idea is displayed graphically in Figure 2.

Today, there are known processes that violate each of these symmetries individually and even some of them in tandem, e.g. CP violation. However, al.'s famous 1956 experiment demonstrating the first evidence of parity non-conservation was there a known physical process that could possibly allow one to answer this question.
Table 1: Transformation properties of $B$, $E$ and $\mu/d_e$. Adapted from Roberts [24].

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>$E$</th>
<th>$B$</th>
<th>$\mu/d_e$</th>
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<tbody>
<tr>
<td>C</td>
<td>$-$</td>
<td>$-$</td>
<td>$-$</td>
</tr>
<tr>
<td>P</td>
<td>$-$</td>
<td>$+$</td>
<td>$+$</td>
</tr>
<tr>
<td>T</td>
<td>$+$</td>
<td>$-$</td>
<td>$-$</td>
</tr>
</tbody>
</table>

there are a number of major unsolved questions in physics that suggest there are many more such processes waiting to be discovered. Of these remaining questions, perhaps the largest and most accessible is the Universe’s seeming preference for matter over antimatter, evident in our very existence. The physics community has been frantically searching for new sources of CP violation that differentiate the properties of particles and antiparticles to help explain this phenomena. Some of these searches require the most extravagant tools of modern physics and are currently being performed at the largest of particle accelerators such as the LHC. In contrast, searches for the e-EDM can be performed in so-called “table-top experiments” and have the potential to provide equally profound results.

Figure 2: A graphical representation of P and T violations for a generalized particle.

The expectation of the existence of additional sources of CP violation is fundamental for more practical reasons in the e-EDM search as well. If only
CP violation allowed by the Standard Model is considered, the predicted electron EDM is $|d_e^{SM}| < 10^{-38}\text{e}\cdot\text{cm}$ [33]. When one compares this to the current experimental upper limit of $|d_e| < 1.6 \times 10^{-27}\text{e}\cdot\text{cm}$ [23] one might be quite disheartened by the prospect of having to gain almost 11 orders of magnitude before having a chance of seeing the electron EDM. However, if there are additional sources of CP violation waiting to be found, the value of the electron EDM rapidly moves into a range potentially accessible by current experimental techniques.

This extreme sensitivity to physics beyond the standard model (New Physics) provides perhaps the greatest motivation for searching for the electron EDM. Even before the Standard Model was fully completed, physicists began to hypothesize about necessary extensions. Today, there are a staggering number of theories trying to characterize New Physics. Proposed theories vary widely, but virtually all include additional scalar fields providing new sources of CP violation. As Figure 3 shows, experimental results lowering the upper limit of the electron EDM have already forced a recasting of many theories. Moreover, if an experiment were to discover a precise value for the EDM it would drastically narrow the spectrum of viable New Physics theories.

1.2 Detecting the Electron EDM

As the motivations for finding the electron EDM have come into focus, experimental ingenuity has quickly followed. The simplest method of detecting an electric dipole moment would be to simply place the particle in an external electric field $E_{\text{ext}}$ and then proceed to measure the change in energy as one varies $E_{\text{ext}}$. Unfortunately, as it is the EDM of the electron that is of interest, one cannot simply place a free electron in an electric field with the expectation that it will remain there for very long. As an alternative, however, it is much more practical to keep an atom or molecule in an electric field long enough to take a measurement. This has led to the experimental design of using a paramagnetic atom or molecule in place of a free electron and interpreting any measured EDM as that of the unpaired electron belonging to the atom or molecule [6].

Virtually all EDM experiments are designed to specifically measure a linear Stark shift $\Delta U$ that arises from the electric dipole term in the Hamiltonian (Equation 2) [9]. In the aforementioned case of using the unpaired valence electron in neutral atoms or molecules, the Stark shift is simply
\( \Delta U = d_e \cdot E_{\text{eff}} \), where \( E_{\text{eff}} \) is the internal electric field experienced by the free electron. Obviously, as the energy shift increases, the effects of an EDM become easier to observe. It follows that employing a highly polarized relativistic molecule such as PbF, PbO, ThO, or YbF that has an enormous internal electric field offers an immediate advantage.\(^2\) These molecules display internal electric fields on the order of \( 10^{11} \text{V/cm} \) [20], far in excess of static fields that can be created with power supplies and field plates in the lab. \(^{207}\)Pb\(^{19}\)F was selected for further study as it also has the advantages of a small g-factor (\( g \approx 0.04 \)), and displays sensitivity to the e-EDM in its ground electronic state. Other molecules, such as the aforementioned PbO [33], ThO [8] and YbF [17], do offer advantages in other areas, and are being studied by other groups.

As in any experiment designed to measure an extremely small quantity, being able to account for any systematic effects is an immediate priority. In

\(^2\)Classically, the average electric field experienced by an electron should be zero for a neutral molecule. The electric field experienced by the unpaired electron is entirely a result of the highly relativistic nature of its orbit in these heavy molecules. This effect is explained by Schiff’s Theorem [7].
the type of experiments described above, stray magnetic fields pose one of the greatest threats. These fields can couple with the magnetic moment $\mu$ to produce an effect that appears almost identical to the effect of an EDM. This particular systematic can be partly managed by the application of a precisely calibrated external electric field. As outlined by Shafer-Ray [29], applying an electric field of appropriate strength will decrease the effective magnetic moment of the molecule. As might be expected, the calculation of the optimum electric field rests on determining the expectation value of the Zeeman interaction energy

$$H_B = \mu_B \mathbf{B} \cdot \mathbf{\hat{G}} \cdot \mathbf{S} = G_\parallel B_0 S_0 - G_\perp (B_1 S_{-1} + B_{-1} S_1),$$  \hspace{1cm} (3)$$

where $\mu_B$ is the Bohr magneton, $G_\parallel = G_0$, $G_\perp = G_{\pm 1}$, $B_0 = B_z$, and $B_{\pm 1} = (B_x \pm iB_y)/\sqrt{2}$. $G_\parallel$ and $G_\perp$ are called body fixed g-factors, and describe the sensitivity of the molecule to external magnetic fields. The precision determination of these body fixed g-factors is vital in the design of an effective e-EDM experiment [28].

Moreover, precision measurements of the molecular parameters of $^{207}$Pb$^{19}$F enable one to make quantitative predictions of the exact response of the molecule to both an e-EDM and a possible nuclear anapole moment. The anapole moment is a P-odd, T-even interaction arising from a charge circulation–with handedness–in the nucleus, analogous to the current flow in a toroidal solenoid. It has been measured in atomic cesium by Weiman et al. [34]. Searches for anapole moments in other atoms and molecules have been conducted without success up to this point. While a measurement of an anapole moment in $^{207}$Pb$^{19}$F would not have nearly the impact of a successful e-EDM measurement, it would still provide a substantial leap in understanding of a parity-violating effect that remains somewhat mysterious. As Figure 4 indicates, a nuclear anapole moment is very nearly in range of current Fourier transform microwave spectroscopy techniques. The necessity of including the $\Omega$-doubled nuclear rotational coupling term in the current fit of the rotational spectroscopy data of $^{207}$Pb$^{19}$F is direct evidence of the approachability of a potential nuclear anapole measurement.
Figure 4: A depiction of the frequency scale required to make resolved measurements of the energy terms listed. $J$ is the total rotational angular momentum not including nuclear contributions, $S$ is the electronic spin angular momentum, $I$ is nuclear spin angular momentum, and $n$ is the internuclear axis. FT-Microwave spectroscopy techniques may approach the level of sensitivity required to detect a nuclear anapole moment. From Shafer-Ray [26].
2 Experimental Procedure

2.1 Supersonic-Jet Fourier Transform Microwave Spectroscopy

The microwave study of PbF was carried out with a Balle-Flygare-type Fourier transform microwave spectrometer located at the Gottfried-Wilhelm-Leibniz-Universität Hannover. This apparatus is described in great detail by Grabow, et al. [16, 15]. Only a brief overview of the system will be presented here.

The design represents an evolution of time domain molecular spectroscopy techniques introduced in the 1980s. In the first incarnations of microwave spectroscopy during the 1940s, a microwave source was simply directed through
a cell containing a molecule of interest in gaseous form and then into a detector monitoring intensity (figure 6). Varying the frequency of the microwave source allowed one to generate a spectrum of absorption frequencies. These early techniques directly probed rotational transitions in the frequency domain, but were not able to achieve sufficient sensitivity to investigate small populations of transient species.

Figure 6: A cartoon depiction of an early microwave spectrometer. [1]

The inability to properly investigate the spectra of short-lived species motivated the development of time domain spectroscopy, in which a microwave pulse is applied only briefly (∼1 microsecond) to a sample, inducing a radiative response which is monitored as a function of time. A large increase in sensitivity is noticed purely due to making measurements in the time domain since all frequencies in the spectrum are recorded simultaneously; This is an effect called the multiplex advantage [4, p. 710]. A Fourier transform is then employed to convert to the frequency domain. It should be noted that this process is quite similar to pulsed nuclear magnetic resonance (NMR) only with relaxation times on the order of $10^6 - 10^7$ faster.

The sample is studied in a supersonic jet as opposed to a static gas
cell, which introduces a number of additional enhancements to sensitivity. The rapid adiabatic expansion of the gas into the resonator chamber causes the internal energy of the molecules to be converted into directed kinetic energy. The result is a drastic drop in the rotational temperature of the molecules to approximately 2K, greatly simplifying the partition function of the system and populating the ground state rotational and vibrational energy levels. In addition, after these initial collisions, the particles continue on virtually collisionless trajectories greatly increasing the lifetimes of weakly bound species.

The geometry of the Hannover system provides further increases in resolution and sensitivity. By placing the pulsed nozzle on the resonator axis, the overlap of the molecules with the microwave fields is maximized. This is known as a “Coaxially Oriented Beam-Resonator Arrangement” (COBRA), and is depicted in figure 7.

Figure 7: COBRA Implementation: supersonic expansion source positioned in the center of the side of the Fabry-Perot resonator. The small L-shaped “hooks” above and below the source are the microwave antennae. The length of the antennae is $\lambda_{\text{min}}/2$, where $\lambda_{\text{min}}$ corresponds to the highest polarization frequency $\nu_{\text{max}}$ available. From Grabow et al. [14].
The supersonic jet interacts with the microwave radiation existing in the Fabry-Perot type resonator as a standing wave to generate a rotationally coherent and polarized molecular beam moving along the axis of the resonator. Even after the microwave pulse ends, the molecular beam remains rotationally coherent due to the collisionless nature of the supersonic expansion. The decay of this macroscopic oscillating dipole moment can now be tracked as a function of time and converted to the frequency domain with a Fourier transform. An example of this process is presented in figure 8. The frequencies of the desired rotational transitions can then be extracted by taking the mean value of the Doppler doublet which is generated as a result of the supersonic jet traveling along the propagation axis of the resonator which contains microwaves traveling both with and against the jet. The appearance of transitions as doublets, with predictable spacings dependent on the type of carrier gas employed in the expansion, is an invaluable tool in separating possible spectral lines from noise.

The complex interactions between the supersonic jet, the resonator cavity and antennae, the microwave radiation, and the high frequency electronic components result in a large number of variables available to optimize sensitivity. The relative timings of the laser, gas, and microwave pulses are particularly important. Most data was taken with a 250 µs delay between laser and gas pulses, a 250 µs gas pulse, and a 900 µs delay between laser and microwave pulses. Managing the delay between the end of the microwave pulse and beginning data reception is complicated by the large range in frequencies able to be probed by the apparatus. The goal is to begin receiving signal as soon as the pulsed radiation has completely dissipated from the cavity. However, as the frequency of the pulsed radiation decreases, the cavity tends to “ring” longer. A delay of 5 µs at high frequencies to a maximum of 18 µs at the lowest frequencies covered the demands of these experiments. Additionally, the power of the pulsed radiation should be neither too strong for the system, nor too weak to completely polarize the gas sample.

These optimizations were conducted by observing a particularly strong PbF rotational transition and attempting to maximize the observed signal. The large number of variables means that for most purposes one can adopt a “good enough” approach in managing this process. When properly optimized, spectra were consistently produced with signal to noise ratios sufficient to resolve transitions separated by more than 6 kHz and measure them to within 0.5 kHz accuracy over a range of 2 – 26.5 GHz.
Figure 8: An example observation of a ground state rotational transition of PbF.
2.2 Mode Structure

The centerpiece of the entire system is the Fabry-Perot resonator cavity. It is formed by two spherical concave mirrors. The cavity supports an infinite number of standing wave patterns called modes. Before making a measurement, a tuning procedure must occur in which a transmission curve of a selected “transverse electric magnetic” or \( \text{TEM}_{pq} \) mode is centered at the desired excitation frequency [14, p. 417]. The electric dipole interaction of the molecular sample is caused by exposure to microwave radiation propagating as a standing wave in a particular mode. The fundamental \( \text{TEM}_{00} \) modes are usually utilized as they provide the largest interaction volume with the molecular jet.

Mode selection is particularly important in investigating the Zeeman effect. Described in detail in Section 3, the selection rules of the Zeeman effect depend on the relative orientation of the microwave radiation and the external magnetic field responsible for the effect. As depicted in Figure 9, the non-fundamental modes can have complex configurations often making it impossible to select for a purely parallel or perpendicular orientation with the magnetic field. The end result is that producing readily interpretable Zeeman spectra is dependent on careful mode selection.

Figure 9: Linearly polarized resonator mode configurations for circular mirrors. A 2-dimensional analog of the spherical mirrors of the Fabry-Perot resonator. From Kogelnik & Li [18]
2.3 Sample Preparation

The PbF compound is created in situ through the use of laser ablation. A Nd:YAG laser (1064nm, 500mJ) is directed onto a rotating lead rod and emits pulses at a rate of 20Hz. When the laser pulse contacts the rod, a highly localized, superheated metal plasma is produced consisting of fully ionized lead ions and free electrons with temperatures exceeding 10000K [30]. This is conducted in the presence of a neon carrier gas containing trace amounts of SF₆ (∼ 1%). The high density of the neon carrier gas surrounding the plasma is sufficient to recombine and cool the electrons and lead ions, but not before some of the highly energetic lead ions are able to tear fluorine atoms from the SF₆ molecules. This produces a number of weakly bound compounds including the diatomic PbF. Sufficient formation of PbF was found to occur with carrier gas pressures ranging from 3.5-6 bar, with a steep decline in generation at pressures below 3.5 bar. Optimal laser power was determined pragmatically by maximizing the output signal of a known transition, and was usually slightly below the maximum output power available. An illustration of the sample preparation and insertion mechanism is presented in Figure 10.

Figure 10: An illustration of the laser ablation optics and supersonic jet interface. From Grabow [13]

2.4 External Fields

As previously noted, due to having an unpaired electron, PbF will display detectable Zeeman splittings from the Earth’s magnetic field alone. To com-
pensate for the Earth’s field, 3 pairs of Helmholtz coils are installed in a three axis arrangement around the resonator cavity as depicted in Figure 11.

![Figure 11: Arrangement of Helmholtz coils around the resonator cavity. From Grabow et al.[14].](image)

While the magnitude of Zeeman splittings are proportional to the total strength of the external magnetic field, the selection rule applied depends on the relative orientation of the magnetic field and the microwave electric field \(\Delta M_F = 0\) if parallel and \(\Delta M_F = \pm 1\) if perpendicular). We utilized this fact to effectively zero the horizontal and vertical components of the Earth’s magnetic field within the resonance chamber through the following process: A transition was chosen that exhibits no splitting under the \(\Delta M_F = 0\) selection rule (such as an \(F = 1/2 \rightarrow 1/2\)). The antenna that generates microwave fields above 10 GHz is oriented vertically within the resonator chamber. Therefore, any Zeeman splittings observed for such a transition are purely a result of a horizontal magnetic field. We tracked the magnitude of the splittings as we increased the current in each of the two horizontally oriented Helmholtz coils and then used a simple linear fit to determine the current at which the horizontal field was minimized. Having effectively zeroed
the horizontal components of the Earth’s field, we repeated this procedure with a transition that exhibited $\Delta M_F = 0$ splitting. Now any splittings observed would be purely the result of a vertical magnetic field allowing us to make a determination of the vertical field required for compensation.

When we wanted to investigate the Zeeman effect itself after this calibration was completed, a purely vertical field could be applied by simply turning off the vertically oriented Helmholtz coils. This produced a parallel field orientation for transitions above 10 GHz and a perpendicular orientation for transitions below 10 GHz due to the low frequency microwave antenna being aligned horizontally. A similar procedure could produce a purely horizontal magnetic field.\(^3\) Varying the current in the Helmholtz coils from purely compensatory levels allowed us to investigate Zeeman splittings under a wide range of field strengths up to a maximum of $\sim 4$ Gauss.

Of paramount concern when investigating the Zeeman effect is the homogeneity of the magnetic field over the entire resonance cavity. The magnetic field $B$ produced along the coil axis $y$ is given by

$$B = \mu_0 \left( \frac{IR^2}{2} \right) \left( \frac{1}{(R^2 + (d/2 - y)^2)^{3/2}} + \frac{1}{(R^2 + (d/2 + y)^2)^{3/2}} \right),$$

where $I$ is the applied current, $d$ is the distance between the coils, and $R$ is their radius. A similar equation can be written for the radial dependence. One finds that a sufficiently homogenous field is produced when $d$ is greater than the separation of the resonance reflectors [14, p. 430]. The at least approximate homogeneity of the field is apparent during the zeroing process as Zeeman splittings disappear over a reasonably broad range of currents. This would not be possible if the magnetic field generated by the Helmholtz coil arrangement was not sufficiently uniform over the volume of the expanding molecules.

\(^3\)N.B. The horizontal coil oriented perpendicular to the molecular beam will always be perpendicular to the microwave radiation. Only the horizontal coil oriented along the axis of the molecular beam is able to produce a field parallel to the electric field at low frequencies.
3 Theory

3.1 PbF and Electronic Angular Momentum

Lead monofluoride (PbF) is a relatively unusual diatomic molecule in that it has electronic angular momentum even in its ground energy state. As neutral PbF has an odd number of electrons (91, precisely) it is obviously not possible for the sum of the orbital angular momenta of its electrons and the sum of the electron spins to be zero. The result is that PbF is a $^2\Pi_{1/2}$ molecule, meaning that in its ground state, the total electronic spin $S = 1/2$ (the left superscript is equal to the multiplicity $2S + 1$), the electronic orbital angular momentum along the internuclear axis $\Lambda = \pm 1$ (thus a $\Pi$ state), and the component of its total angular momentum along the molecular axis $\Omega = 1/2$. Molecules with an odd number of electrons are colloquially referred to as free radicals.

While fluorine only has a single stable isotope ($^{19}\text{F}$) with a nuclear spin of $1/2$, lead has four stable isotopes, each with considerable natural abundance. Lead isotopes can be split into two categories, the even isotopes ($^{204}\text{Pb}$, $^{206}\text{Pb}$, and $^{208}\text{Pb}$) which have a net zero nuclear spin, and the odd isotope ($^{207}\text{Pb}$) which has a net nuclear spin of $1/2$. The additional nuclear spin of $^{207}\text{Pb}$ substantially complicates the resulting energy level structure of PbF formed from this isotope.

These four sources of angular momentum (electronic orbital and spin, and both nuclear spins) all couple with each other and with molecular rotation to produce a complex molecular system that does not lend itself easily to direct analysis. To address the contribution of electronic angular momenta, a framework of approximations known as “Hund’s Coupling Cases” is often employed to bring the analysis to a more manageable level. There are five standard Hund’s cases describing five ideal linear molecules which differ depending on the relative strength of the various couplings [12].

The coupling present in PbF most closely resembles Hund’s coupling case (a) in which $L$ and $S$ are strongly coupled to the internuclear axis (Figure 12). In this case, the components of $L$ and $S$ along the internuclear axis are

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$^4$N.B. In an atom, orbital angular momentum is usually described by the quantum number $L$, but in a diatomic molecule the coupling of this angular momentum to the internuclear axis causes the vector $L$ to precess around the axis and is therefore no longer a constant. Instead, we tend to refer to the component of orbital angular momentum along the internuclear axis $M_L$, or its magnitude $|M_L| = \Lambda$, which are well defined.
constant, and are denoted as $\Lambda$ and $\Sigma$, respectively. Note that in general, the possible values for these quantum numbers are $\Lambda = 0, 1, 2, \ldots, L$ and $\Sigma = S, S-1, \ldots, -S$. It will be useful to define the total angular momentum along the internuclear axis $\Omega = \Lambda + \Sigma$, and the total angular momentum excluding nuclear spin $J = \Omega, \Omega + 1, \Omega + 2, \ldots$, which is simply the sum of $\Omega$ and the end-over-end rotation of the molecule $O$. Figure 12 details the precession of $\Omega$ and $O$ around $J$, which is fixed in space.

As mentioned above, Hund’s cases are only approximations, making them great starting points, but are ultimately in need of a number of corrections to fully reflect physical reality. What Hund’s cases do not take into account is the ability of a third angular momentum vector to cause at least a partial uncoupling of 2 other vectors. For PbF, the relevant effect is the uncoupling of electronic angular momenta (both spin and orbital) from the internuclear axis due to end-over-end rotation of the molecule.

As Gordy & Cook [11] describe, spin uncoupling causes a change in the effective rotational constant of the molecule, and accordingly a shift in rotational energy levels. The effect of L-uncoupling is even more dramatic. Ordinarily, the positive and negative $M_L$ states are degenerate, as there is no difference in energy levels corresponding to the parallel or antiparallel orien-
tation of $M_L$ along the internuclear axis. Overall molecular rotation allows one to differentiate between these two orientations, therefore breaking the vector symmetry and degeneracy of the energy levels. The net result is a splitting of each $J$ level into two sublevels. This is referred to as $\Lambda$-type doubling. One might naively assume that each sublevel corresponds to either the projection of $+\Lambda$ or $-\Lambda$ on the internuclear axis. Instead, the energy levels of the split states correspond to linear combinations of the wave functions of both states,

$$\psi_+ = \frac{1}{\sqrt{2}} [\psi(\Lambda) + \psi(-\Lambda)]$$

$$\psi_- = \frac{1}{\sqrt{2}} [\psi(\Lambda) - \psi(-\Lambda)]$$

3.2 Hyperfine Structure

At this point, the spin rotational Hamiltonian for our molecule would be simply

$$H_{SR} = H_{\text{rot}},$$

where the Hamiltonian $H_{\text{rot}}$ incorporates all of the effects of electronic orbital and spin angular momentum discussed above, as well as the rotation of the molecule itself. There are a number of other terms we must add to $H_{SR}$ before it fully describes PbF. A more complete equation would look like

$$H_{SR} = H_{\text{rot}} + H_0 + H_1 + H_{\text{ext}},$$

where $H_0$ describes hyperfine splitting as a result of the interaction between the nuclear spins and orbiting electrons, $H_1$ describes small corrections to hyperfine structure as a result of additional couplings between three or more vector quantities, and $H_{\text{ext}}$ describes the response of the molecule to external electric and magnetic fields (the Stark and Zeeman effect, respectively). A brief summary of the physics of $H_0$ as explained by Townes & Schawlow [32] follows here. A discussion of $H_1$ is outside the scope of this thesis and can be

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5 More technically, the molecular rotation produces a magnetic field which induces an admixing of adjacent $\Lambda$ states.

6 The positive and negative subscripts used here should not be confused with electronic parity, which will be introduced subsequently.
found in the literature [5, 3], while $H_{\text{ext}}$ will be explored in depth in a later section. The orders of magnitude of these effects for PbF in low rotational states are presented in Table 2.

<table>
<thead>
<tr>
<th>Interaction</th>
<th>Magnitude</th>
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<td>$H_{\text{rot}}$</td>
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</tr>
<tr>
<td>$H_0$</td>
<td>0.2 – 10 GHz</td>
</tr>
<tr>
<td>$H_1$</td>
<td>10 kHz</td>
</tr>
<tr>
<td>$H_{\text{ext}}$</td>
<td>10 kHz</td>
</tr>
</tbody>
</table>

Table 2: Orders of magnitude for each interaction of $H_{\text{SR}}$. A magnetic field on the order of 1 Gauss is used to determine $H_{\text{ext}}$.

As noted above, the most significant source of hyperfine structure for PbF is due to nuclear magnetic dipole moments arising from a nonzero nuclear spin $I$. For $(\text{even})\text{Pb}^{19}\text{F}$ only the fluorine nucleus has a magnetic dipole moment. With $^{207}\text{Pb}^{19}\text{F}$ the dipole moments of both nuclei must be considered. The nuclear magnetic dipole moments can either interact with the electronic orbital angular momentum $L$ or spin angular momentum $S$. The dominant effect in PbF is an $I \cdot S$ interaction. This interaction will be described below.

An explanation of $I \cdot L$ interactions can be found elsewhere [32, p. 195], but the important result is the interaction Hamiltonian

$$H_{IL} = \frac{2\mu_B\mu_I}{I} \left( \frac{1}{r^3} \right)_{\text{avg}} I \cdot k,$$

(9)

where $k$ is a unit vector pointing along the internuclear axis, $\mu_B = \frac{e\hbar}{2m_e}$ (the Bohr magneton), $\mu_I$ is the nuclear magnetic moment, and $I = \hbar \sqrt{I(I+1)}$.

In classical electricity & magnetism, the interaction energy between two dipoles $\mu_1$ and $\mu_2$ is given by

$$W_{\mu_1\mu_2} = \frac{\mu_1 \cdot \mu_2}{r^3} - \frac{3(\mu_1 \cdot r)(\mu_2 \cdot r)}{r^5},$$

(10)

where $r$ is the vector that runs between the centers of each dipole. Now, simply substituting the actual nuclear and electron spin dipoles

$$\mu_1 = \frac{\mu_I}{I} \mathbf{I}$$

(11)

$$\mu_2 = -2\mu_B \mathbf{S},$$

(12)
respectively, into Equation 10 we find
\[
W_{\mu_1\mu_2} = (H_{IS})_1 = \frac{2\mu_B\mu_I}{I} \left[ \mathbf{I} \cdot \mathbf{S} \frac{3(\mathbf{I} \cdot \mathbf{r})(\mathbf{S} \cdot \mathbf{r})}{r^5} \right].
\] (13)

In addition to this classical dipole interaction there is another interaction between the electron and nucleus that arises due to relativistic corrections to the molecular wave function. As lead has a particularly heavy nucleus, this interaction is substantial in our case. The Hamiltonian for this interaction is given by
\[
(H_{IS})_2 = \frac{16\pi}{3} \frac{\mu_B\mu_I}{I} \psi^2(0) \mathbf{I} \cdot \mathbf{S}.
\] (14)

Combining these effects, a full description of nucleon-electron interactions can be given in terms of three of the Frosch and Foley parameters, \(a, b\) and \(c\), which essentially describe the relative strength of the interactions described above for a particular molecule. The full Hamiltonian simply becomes the linear combination
\[
H_0 = a\Lambda \mathbf{I} \cdot \mathbf{k} + b\mathbf{I} \cdot \mathbf{S} + c(\mathbf{I} \cdot \mathbf{k})(\mathbf{S} \cdot \mathbf{k}).
\] (15)

Here,
\[
a = \frac{2\mu_B\mu_I}{I},
\] (16)
\[
b = \frac{2\mu_B\mu_I}{I} \left[ \frac{8\pi}{3} \psi^2(0) - \frac{3\cos^2 \theta - 1}{2r^3} \right]_{\text{avg}} \quad \text{and,}
\] (17)
\[
c = \frac{3\mu_B\mu_I}{I} \left( \frac{3\cos^2 \theta - 1}{r^3} \right)_{\text{avg}},
\] (18)

where \(\theta\) arises through the transformation of \(\mathbf{r}\) to \(\mathbf{k}\), and physically describes the angle between the internuclear axis and the vector pointing from the nucleus to the electron. Equation 15 theoretically applies to all electrons in the molecule, but in practice only matters for unpaired electrons as the contribution from a paired electron will be exactly canceled by that of its opposite spin pair. It is also important to note that Equation 15 is only valid when \(\Lambda\) and \(S\) are constant, or so called “good” quantum numbers. This will be the case as long as they remain tightly coupled to the internuclear axis. Second order terms that involve changes in \(\Lambda\) and \(S\) give extremely small
contributions to the overall energy relative to the terms in Equation 15 [32, p. 196].

There are multiple coupling possibilities for nuclear spin angular momenta that are closely related to Hund’s cases for electron spin-orbit coupling. For a Hund’s case (a) molecule one finds that the total nuclear spin is coupled either to the internuclear axis (called case (\(a_\alpha\))), or, as in the case of PbF, coupled to \(J\) (case \((a_\beta)\)). With coupling of this type, it is useful to introduce the total angular momentum quantum number \(F = J + I\).

3.3 Ground Rotational Energy Level Structure of \(^{208}\)PbF

In addition to the angular momentum quantum numbers already introduced, rotational energy states can be further distinguished by a property known as parity. Parity describes how a quantum state behaves under the symmetry operation of space-fixed inversion. This operation involves inverting the coordinates of all the particles of a quantum system (i.e. a reflection across the origin) to produce an equivalent equilibrium configuration with either an identical wave function or a wave function changed in sign only. If the wave function does not change sign the system is said to have a positive parity, and if it does change sign, a negative parity.

More precisely, as outlined by Brown & Carrington [4], define an operator \(P^*\) to be the operator that transforms a function \(f(X_i, Y_i, Z_i)\) into a new function \(g(X_i, Y_i, Z_i) = f(-X_i, -Y_i, -Z_i)\), where \((X_i, Y_i, Z_i)\) are the coordinates of a point measured in an arbitrary space-fixed coordinate system. A quantum system that transforms as

\[
P^*\psi(X_i, Y_i, Z_i) = \psi(X_i, Y_i, Z_i)
\]

has a positive parity. While a system that transforms as

\[
P^*\psi(X_i, Y_i, Z_i) = -\psi(X_i, Y_i, Z_i)
\]

has a negative parity. Parity governs a number of quantum selection rules. For the dipole induced transitions that we are interested in, the parity selection rules are

\[
+ \Leftrightarrow - + \Leftrightarrow + - \Leftrightarrow -
\]

The collection of total angular momentum \(F\) and \(M_F\), spin-rotational angular momentum \(J\), total nuclear angular momentum \(I\), and electronic
parity $p_s$ constitute a full basis set for $H_{SR}$. While this basis set proves useful for our purposes there are many other possible bases with which one can write $H_{SR}$. For example, an omega ($\Omega = \pm 1/2$) basis set is related to our parity basis set by

$$|F, I, J, M_F, p_s\rangle = \frac{1}{\sqrt{2}}\left( |F, I, J, M_F, \Omega = \frac{1}{2}\rangle + p_s(-1)^{J-I/2}|F, I, J, M_F, \Omega = -\frac{1}{2}\rangle \right).$$

The parity basis set introduced here is used by Rupasinghe et al. [27] in a fully rigorous calculation of the first two rotational states of both $^{207}$PbF and $^{208}$PbF. The results of their calculation for $^{208}$PbF are presented here in Figure 13.

Figure 13: Predicted electric dipole transitions of the first two rotational states of $^{208}$PbF. Transition frequencies accurate to $\pm 1$kHz. Numbers in brackets are arbitrary energy level labels. From Rupasinghe et al. [25]
3.4 Zeeman Splitting in the $^{2}\Pi_{1/2}$ Molecule PbF

In general, most molecular spectra do not display a strong dependence on weak magnetic fields. This is another byproduct of most molecules not having electronic angular momentum in the ground state. For these molecules, their tiny magnetic moments arise solely due to molecular rotation or nuclear spin. It typically requires fields of many kilogauss to observe energy level splittings arising due to the interaction of an external magnetic field with these magnetic moments.

Molecules with electronic angular momentum, however, exhibit substantial Zeeman splitting in response to magnetic fields of less than one gauss. Because the magnetic moment due to a given amount of angular momentum is inversely proportional to mass, the magnetic moments arising from the unpaired electron are on the order of 1800 times larger than those arising from nuclear spin. We are therefore able to ignore the direct interaction of the magnetic field with the nuclear magnetic moment to a very good approximation in our analysis of a $^{2}\Pi_{1/2}$ molecule. This does not imply that nuclear spin can be ignored in its entirety though, as the coupling between nuclear spin $I$ and molecular angular momentum $J$ described in the previous section will appreciably modify any observed Zeeman splitting.

With these considerations in place, an examination of the spin and orbital magnetic moments emerges as the logical place to start a discussion of the Zeeman effect in PbF as these moments are responsible for approximately 95% of the observed Zeeman splitting [4, p.351]. If greater precision is required the theory developed here is easily adaptable to additional considerations such as the interactions described above.

3.4.1 Zeeman Interaction with Electronic Angular Momentum

Each $\hbar$ of orbital angular momentum $L$ produces a magnetic moment of one Bohr magneton, defined as $\mu_B = \frac{e\hbar}{2m_e}$. Accordingly, the generated magnetic moment is $\mu_L = -\mu_B L$, where its convenient to express $L$ in units of $\hbar$. Each $\hbar$ of spin angular momentum $S$ creates a little more than 2 Bohr magnetons, resulting in the magnetic moment $\mu_S = -g_s\mu_B S$, where $g_s = 2.00232$ is the spin g-factor for the electron.\(^7\) The minus signs in these equations simply

\(^7\)In a semi-classical description of spin, a unit of spin angular momentum would produce the same magnetic moment as a unit of orbital angular momentum, such that $g_s = 1$. The correction arises when the full framework of relativistic quantum mechanics is applied,
indicate that the angular momentum vectors point in the opposite direction of the generated magnetic moments. In general, the g-factor is an expression of the amount of magnetic moment arising from a particular amount of angular momentum.

As before, it is useful to combine the spin and orbital angular momenta into an overall angular momentum \( \mathbf{J} \). Since at this point we are ignoring any contributions from the nucleus, \( \mathbf{J} \) represents the entirety of the angular momentum possessed by the molecule. The resulting magnetic moment is

\[
\mathbf{\mu}_J = -g_J \mu_B \mathbf{J} \quad \text{and} \quad |\mathbf{\mu}_J| = -g_J \mu_B \sqrt{J(J+1)},
\]

(23)
as \( |\mathbf{J}| = \sqrt{J(J+1)} \) when expressed in units of \( \hbar \).

Now, classical electromagnetic theory predicts the Hamiltonian for the interaction between a magnetic dipole moment \( \mathbf{\mu} \) and an applied magnetic field \( \mathbf{B} \) to be

\[
H_B = -\mathbf{\mu} \cdot \mathbf{B}.
\]

(24)

As explained by Gordy & Cook [11], in the molecular fixed frame, the interaction of the component of the magnetic moment along \( \mathbf{J} \) with the applied magnetic field, causes \( \mathbf{J} \) to precess around \( \mathbf{B} \) as detailed in Figure 14. The component of the magnetic moment along \( \mathbf{J} \) is not necessarily constant, but replacing it with its average value \( \langle \mathbf{\mu}_J \rangle \) is a reasonable approximation for our purposes. The Hamiltonian then becomes,

\[
H_B = -\langle \mathbf{\mu}_J \rangle \frac{\mathbf{J} \cdot \mathbf{B}}{|\mathbf{J}|} = -\langle \mathbf{\mu}_J \rangle B \cos(\mathbf{J}, \mathbf{B}),
\]

(25)

utilizing the definition of the dot product. By inspection of Figure 14, \( \cos(\mathbf{J}, \mathbf{B}) = J_z/|\mathbf{J}| = M_J/\sqrt{J(J+1)} \). Substituting this result into Equation 25 gives

\[
H_B = -\langle \mathbf{\mu}_J \rangle \frac{M_J B}{\sqrt{J(J+1)}}.
\]

(26)

And finally, replacing \( \langle \mathbf{\mu}_J \rangle \) with \( \mu_J \) from Equation 23 we find

\[
H_B = E_B = g_J \mu_B M_J B,
\]

(27)
resulting in \( g_s = 2(1 + \alpha/2\pi + \ldots) \), where \( \alpha \approx 1/137 \) is the fine structure constant.
We see now that the magnitude of the interaction depends on the value of $M_J$. Recall that $M_J = -J, \ldots, 0, \ldots, J$ and we can conclude that an applied magnetic field will cause a rotational energy level to split symmetrically into $2J+1$ evenly spaced energy levels.\(^8\) The selection rules for the Zeeman effect are

$$M_J \rightarrow M_J \quad \text{and} \quad M_J \rightarrow M_J \pm 1.$$ \hspace{1cm} (28)

To observe the $\Delta M_J = 0$ transitions the applied magnetic field must be parallel to the electric field vector of the microwave radiation. These transitions are known as $\pi$ components. To observe the $\Delta M_J = \pm 1$ transitions, which are referred to as $\sigma$ components, the magnetic field must be perpendicular to the microwave radiation. When the magnetic field is neither directly parallel or perpendicular to the microwave radiation, both $\pi$ and $\sigma$ components will be present.

Continuing with our generalized perspective, we can also compute the frequency shifts caused by the Zeeman effect using Equation 27 and the simple quantum mechanical relation $E = h\nu$. For $\Delta M_J = 0$, we find for a transition between energy levels $J$ and $J'$ which has frequency $\nu_0$ in zero

\(^8\)Even though we’ve entirely ignored any nuclear contribution to Zeeman splitting up to this point, this result continues to hold when the nucleus is considered by simply replacing $J$ with $F = J + I$. 

Figure 14: A diagram depicting the precession of the angular momentum vector $\mathbf{J}$ around an external magnetic field $\mathbf{B}$. 

29
Figure 15: A depiction of the Zeeman effect for a $J = 3/2 \rightarrow J = 5/2$ transition. The $\Delta M_J = \pm 1$ components ($\sigma$ components) are selected when the magnetic field is applied perpendicular to the electric vector. The $\Delta M_J = 0$ components ($\pi$ components) are visible when the magnetic and electric field vectors are parallel.

In the presence of a magnetic field, the Zeeman effect causes the transition to be split into components with frequencies

$$\nu_{\pi} = \nu_0 + (g_J' - g_J)\frac{\mu_B BM_J}{h},$$

(29)

and for $\Delta M_J = \pm 1$, split into components with frequencies

$$\nu_{\sigma} = \nu_0 + (g_J' - g_J)\frac{BM_J}{h} \pm g_J\frac{\mu_B B}{h}.$$

(30)

A number of useful observations can be made from these two equations. If the g-factor $g_J$ is constant between the two states, Equation 29 predicts there will be no visible Zeeman effect when viewing the $\pi$ components, while Equation 30 predicts all $\sigma$ components will be superimposed on the two frequencies $\nu_0 \pm g_J\mu_B B/h$. If $g_J$ is different for the two states, the spectrum will be significantly more complex, with $2J + 1$ visible $\pi$ components and $2(2J + 1)$ visible $\sigma$ components.
3.4.2 Molecules with Orbital and Spin Angular Momentum

The framework developed above applies to a very generalized $J$. To apply this analysis to a specific molecule one must consider the form of the coupling between the various angular momentum vectors. This is the question of which Hund’s case applies, which is dealt with in Section 1.1. Working under the assumption that PbF is characterized by Hund’s case (a), the electronic spin and orbital magnetic moments are tightly coupled to the molecular axis. The moment due to the combined components of spin and orbital electronic angular momentum along the internuclear axis is

$$\mu_{\Omega} = -\mu_B(\Lambda + g_s\Sigma),$$

(31)

where $\Lambda$ and $\Sigma$ are the previously described orbital and spin quantum numbers. One should note that with regards to Zeeman splitting, the off-axis components of these angular momentum vectors are entirely ignorable as a coupling with the molecular axis is required to affect the rotational energy levels of the molecule. Using our framework developed above, and through a close examination of Figure 12, we can write

$$\langle \mu_J \rangle = \mu_{\Omega} \cos(\Omega, J) = -\mu_B \frac{(\Lambda + g_s\Sigma)|\Lambda + \Sigma|}{\sqrt{J(J+1)}}.$$  

(32)

Then to determine $g_J$ we return to Equation 23 to find

$$g_J = \frac{(\Lambda + g_s\Sigma)|\Lambda + \Sigma|}{J(J+1)}.$$  

(33)

There are two important observations that can be made from this result. First, $g_J$ is inversely proportional to $J$, meaning at higher values of $J$ the magnitude of Zeeman splitting will decrease. Second, and particularly relevant for our purposes, for a $^2\Pi_{1/2}$ molecule either $\Lambda = 1$ and $\Sigma = -1/2$ or $\Lambda = -1$ and $\Sigma = 1/2$. In either case, evaluating Equation 33 reveals that the contribution from the spin angular momentum will roughly cancel the contribution from the orbital angular momentum (recall $g_s = 2.00232$). The net result is that a $^2\Pi_{1/2}$ molecule such as PbF is far less sensitive to external magnetic fields than other molecules with electronic angular momentum. As a precise cancellation of external fields is of vital importance to electron EDM experiments, PbF’s very low $g_J$ value gives it a significant advantage over other candidate molecules with different EDM-sensitive ground states.
3.4.3 Body Fixed g-factors

As the value of $g$ is state dependent, it is useful to define parameters that still describe the magnitude of the response to an external magnetic field, but are fixed for a particular molecule. These parameters are the body fixed g-factors $G_\parallel$ and $G_\perp$. To conceptualize these parameters it is necessary to introduce a slightly more robust framework than we have needed so far.

Operating in the molecular-fixed frame, and following Shafer-Ray [26], we return to Equation 27, and write the Hamiltonian for the Zeeman interaction as

$$H_B = \mu_B (g_s S + L) \cdot B.$$  \hspace{1cm} (34)

Now, to parameterize the components of $B$ and $S$, let $B_0 = B_z$ and $B_{\pm 1} = \mp (B_x + i B_y)/(\sqrt{2})$ while $S_0 = S_z$ and $S_{\pm 1} = \mp S_{\pm 1}/\sqrt{2}$. Then,

$$B \cdot S = \sum_{t=-1}^{1} (-1)^t B_{t}^1 S_{-t}^1.$$  \hspace{1cm} (35)

Likewise,

$$B \cdot L = \sum_{t=-1}^{1} (-1)^t B_{t}^1 L_{-t}^1,$$  \hspace{1cm} (36)

where $B^1, S^1$ and $L^1$ are rank-1 tensors. Combining the prior three results, the interaction of the molecule in quantum state $|JM\Omega\rangle$ with an external magnetic field is given by

$$\langle J'M'\Omega'|H_B|JM\Omega\rangle = \langle J'M'\Omega'|\mu_B \sum_{t=-1}^{1} (-1)^t (g_s B_{t}^1 S_{-t}^1 + B_{t}^1 L_{-t}^1)|JM\Omega\rangle$$

$$= \langle J'M'\Omega'|\mu_B \sum_{t=-1}^{1} (-1)^t G_{t}^1 B_{-t}^1|JM\Omega\rangle,$$  \hspace{1cm} (37)

where $G_{t}^1 = (g_s S_{t}^1 + L_{t}^1)$. Now, to define the constant parameters $G_\parallel$ and $G_\perp$
we need to isolate the contribution of the tensor $G^1$. We are able to write

$$\langle J'M_j'\Omega'\mid \mu_B \sum_{t=1}^{1} (-1)^t G^1_{-t} B^1_{-t} \mid JM_j \Omega \rangle = \langle J'M_j'\Omega'\mid \mu_B \sum_{s,t} (-1)^t G^1_{-t} D^1_{st} B^1_s \mid JM_j \Omega \rangle,$$

$$= \mu_B \sum_{s,t} (-1)^t \langle J'M_j'\Omega'\mid D^1_{st} \mid JM_j \Omega \rangle \langle \Omega'\mid G^1_{-t} \mid B^1_s \rangle.$$

Here $D^1_{st}$ is a rank-1 tensor. The details of the derivation of $D^1_{st}$ are beyond the scope of this thesis and are not particularly relevant to the current argument. For a full explanation see Shafer-Ray et al. [27]. Continuing, for a $^2\Pi_{1/2}$ molecule $\Omega = \pm 1/2$, therefore $\langle \Omega'\mid G^1_{-t} \mid \Omega \rangle$ is the 2x2 matrix

$$\langle \Omega'\mid G^1_{-t} \mid \Omega \rangle = \begin{pmatrix}
\frac{1}{2} G^1_0 \mid \frac{1}{2} \\
\frac{1}{2} G^1_{-1} \mid \frac{1}{2}
\end{pmatrix}$$

We relate the tensor $G^1$ to the constants $G_\perp$ and $G_\parallel$ with the relations $G^1_{\pm 1} = G_\perp S^1_{\pm 1}$ and $G^1_0 = G_\parallel S^1_0$, where $S^1_t$ is the body-fixed spherical tensor operator for the electronic pseudo-spin angular momentum, such that

$$S^1_0 \mid \Omega = \pm \frac{1}{2} \rangle = \pm \frac{1}{2} \mid \Omega = \pm \frac{1}{2} \rangle$$

$$S^1_{\pm 1} \mid \Omega = \pm \frac{1}{2} \rangle = \pm \frac{1}{\sqrt{2}} \mid \Omega = \pm \frac{1}{2} \rangle.$$

Finally, substituting into Equation 39 we find

$$G_\parallel = 2 \frac{1}{2} G^1_0 \mid \frac{1}{2} \rangle = -2 \langle - \frac{1}{2} \mid G^1_0 \rangle - \frac{1}{2} \rangle$$

$$G_\perp = \sqrt{2} \langle - \frac{1}{2} \mid G^1_{-1} \rangle \frac{1}{2} \rangle = -\sqrt{2} \langle \frac{1}{2} \mid G^1_{-1} \rangle - \frac{1}{2} \rangle.$$

The spherical tensor framework very briefly introduced throughout this section provides the full machinery for a rigorous determination of $g$ that includes the comparatively small effects of hyperfine mixing of adjacent rotational states and the nuclear magnetic moment. Using the parity basis set introduced in Section 3.3, Shafer-Ray et al. [27] find $g$ for $^{208}$PbF in terms of the body fixed g-factors $G_\parallel$ and $G_\perp$ to be

33
\[ g(F, J, p_s) = \frac{1}{2F + 1} \left( \frac{1}{2J + 1} + \frac{J - F}{\sqrt{F(F + 1)}} \sin 2\theta + \frac{J - F}{F(F + 1)} \sin^2 \theta \right) G_\parallel \\
+ (-1)^{J-1/2} p_s \left( \frac{1}{2F + 1} \cos 2\theta + \frac{\sin 2\theta}{2\sqrt{F(F + 1)}} \right) G_\perp \\
- \frac{\mu_N}{\mu_B} \left( \frac{2F - J}{2J + 1} \cos 2\theta + \frac{1}{2F(F + 1)} \sin^2 \theta \right) g_F, \]

(44)

where

\[ \theta = \frac{1}{2} \arctan \left[ \frac{2\sqrt{F(F + 1)}(A_\parallel + (-1)^F p_s A_\perp)}{2B(2F + 1)^2 - A_\parallel - (-1)^F p_s (A_\perp + (2F + 1)^2 p_s)} \right]. \]

(45)

Here \( \theta \) is an angle that describes the hyperfine mixing between the \( J = F - 1/2 \) and \( J = F + 1/2 \) states and \( A_\parallel \) and \( A_\perp \) are the parameters that describe the fluorine hyperfine interaction. Interpreting this equation in terms of our 95% approximation we can set \( \theta = 0 \) and approximate \( \mu_N/\mu_B \propto m_e/m_p \approx 1/1800 \approx 0 \). Equation 44 then becomes

\[ g(F, J, p_s) = \left( \frac{1}{2F + 1} \right) \left( \frac{G_\parallel}{2J + 1} + p_s (-1)^{J-1/2} G_\perp \right). \]

(46)
4 Analysis

We observed Zeeman splitting for $^9\text{PbF}$ and $^{10}\text{PbF}$ rotational transitions. While our sensitivity allowed us to observe all of the pure transitions in both of these molecules associated with the first two $J$ levels, not all of these lines were suitable for a full Zeeman analysis. The Zeeman effect causes the total intensity of a given transition to be distributed amongst all Zeeman components. Therefore, for lines with unsplit intensities near the limit of our apparatus' sensitivity, attempting to look for Zeeman components would be a futile endeavor. As a result, we generally chose to focus our observations on the most intense lines while still attempting to examine a sample that represented all possible combinations of quantum numbers.

One of our ultimate goals for this research is to precisely determine the values of the molecular constants $G_\parallel$ and $G_\perp$ to aid in the design of a future e-EDM experiment. As detailed in Section 3, these constants are closely related to the magnetic moments, and more directly, the g-factors of each quantum state. The g-factors describe the magnitude of Zeeman splitting for a given magnetic field. Observing Zeeman splitting under magnetic fields of known strength therefore provides all the information necessary for an experimental determination of $G_\parallel$ and $G_\perp$. The details of making this determination are found within this section.

4.1 Raw Data Analysis

The calculations in this section will continue to make use of the approximation established in most of Section 3.4 of ignoring the contributions to the total molecular g-factor from hyperfine rotational mixing and nuclear g-factors. It is relatively straightforward to incorporate these additional terms in the following process, but conceptual clarity is lost due to a large increase in the amount of required algebraic manipulation. The full treatment is described by Shafer-Ray et al. [27], and the results from applying this full treatment will be presented along with the values generated by the approximate process described herein.

As was glimpsed at the end of Section 3.4.3, when hyperfine mixing and nuclear g-factors are ignored

$$g(F,J,p_s) = \left(\frac{1}{2F+1}\right)\left(\frac{G_\parallel}{2J+1} + p_s(-1)^{J-1/2}G_\perp\right).$$

(46)
Figure 16: Zeeman splitting of a $^{207}\text{PbF}$ $F = 3/2 \rightarrow F = 5/2$ transition. Case (a) shows the four $\pi$ components, while case (b) shows eight $\sigma$ components.

In addition, from Equation 27, the change in energy of a quantum state $i$ due to the application of an external magnetic field $B$ is

$$U_i = \mu_B g_i M_{F_i} B.$$  \hspace{1cm} (47)

It follows trivially that

$$\frac{U_i}{\mu_B B} = M_{F_i} \left( \frac{1}{2F_i + 1} \right) \left( \frac{G_{\parallel}}{2J_i + 1} + p_{s_i}(-1)^{J_i - 1/2}G_{\perp} \right).$$  \hspace{1cm} (48)

Since spectroscopic techniques measure a transition between energy levels rather than a single level in isolation, the actual measurable quantity of
interest is $\Delta U/B = U_2/B - U_1/B$, where the subscripts 1 and 2 refer to two different quantum states. Assuming that we are able to assign the appropriate quantum numbers to all observed transitions, extracting the ratio $\Delta U/B$ from each Zeeman line allows the fitting of our data to a modified Equation 48, and the values of $G_\parallel$ and $G_\perp$ to be determined.

Precisely evaluating $\Delta U/B$ for each of the observed transitions is accomplished by plotting the position of each spectral line as a function of the applied external magnetic field and performing a linear regression to determine the corresponding slope (Figure 17). While nominally the apparatus is able to measure lines to within 0.5 kHz, due to the nature of Zeeman spectra, which often contain many spectral lines in a very small region, additional error can be introduced. If lines are very close together (within 3 line widths, or about 8 kHz) the Fourier transform process can cause weaker lines to be “pushed” slightly by more intense lines. In these cases, a slightly larger error needs to be assigned to the weaker lines. The $1\sigma$ uncertainty becomes $\pm 1/2 \times \text{FWHM} = \text{HWHM}$. In the least ideal cases, the $2\sigma$ uncertainty can reach $\sim 4$ kHz.

The component of the magnetic field along each of the three axes($k = 1, 2, 3$) defined by the placement of the Helmholtz coils was determined from the value of the current $I$ running through each of the coils and the usual relation

$$B_k = \frac{\mu_0 n I R_k^2}{(R_k^2 + (d_k/2)^2)^{3/2}} - B_0,$$

where here $\mu_0$ is the permittivity of freespace, $n$ is the number of turns in the coils, and $d_k$ and $R_k$ are the coil separation and radius for each Helmholtz pair, respectively. $B_0$ describes the contribution from the Earth’s magnetic field and any other static local background fields. The value of $B_0$ is determined through a procedure described in Section 2.4.
Figure 17: Linear regression performed for the $\sigma$ components of the 22691.934 MHz $^{208}\text{PbF} \ F = 0 \rightarrow F = 1$ transition. The upper points correspond to the $M = 0 \rightarrow M = 1$ transition, while the lower points are from the $M = 0 \rightarrow M = -1$ transition. Error bars are too small to fully resolve at this scale.
Ordinarily, magnetic fields were applied either directly parallel or perpendicular to the microwave electric field vector, to select for either $\pi$ or $\sigma$ components, respectively. As a check on the calibration of the coils, a field could also be applied at some other angle causing both types of components to appear in the spectra simultaneously. As the magnitude of Zeeman splitting depends only on the total strength of the magnetic field, the splittings caused by this off-axis field could be compared to splitting caused by a single axis field of the same magnitude, revealing whether the pair of coils generating this field was calibrated correctly. This was checked in detail for three cases (22574.9 MHz (Figure 18), 22541.9 MHz, 22658.9 MHz) and agreement was found to be between 0.5 – 1.5% for all three coil pairs.

Figure 18: Analysis of a $^{208}$PbF $F = 1 \rightarrow F = 2$ transition in the presence of an off-axis magnetic field. The three blue interior lines correspond to $M = 0$ ($\pi$) components, while the four red exterior lines are $M = \pm 1$ ($\sigma$) components. Error bars are too small to see at this scale.
Also tested was any dependence on the sign of the three axial magnetic fields. At current levels of precision, a difference in the value of $\Delta U/B$ for a negative versus positive axial magnetic field would likely indicate the presence of a residual field due to the magnetization of one or more components of the apparatus. This was investigated for four cases (22658.9 MHz (Figure 19), 22541.9 MHz, 18333.5 MHz, 18497.136 MHz) and no difference in magnitude of $\Delta U/B$ was detected within the bounds of a two sigma error.

Figure 19: $\sigma$ components of the $^{207}{\text{Pb}}F$ $F = 1/2 \rightarrow F = 3/2$ transition. There was no difference found in the value of $\Delta U/B$ within a two sigma error for the positive and negative field cases.

A summary of the observed splittings for $^{208}{\text{Pb}}F$ and $^{207}{\text{Pb}}F$ are presented in Tables 3 and 4, respectively.
Table 3: Predicted and observed Zeeman shifts of the $J = 1/2$ and $J = 3/2$ transitions for $^{208}\text{Pb}^{19}\text{F}$. $\Delta U/B$ is given in MHz/Gauss, while the number in parenthesis gives the two standard deviation error of the final digits of precision. The subscripts $L$ and $U$ refer to the upper and lower energy level of the transition, respectively.

<table>
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<tr>
<th>Unsplit Line (MHz)</th>
<th>$F_L$</th>
<th>$F_U$</th>
<th>$M_{F_L}$</th>
<th>$M_{F_U}$</th>
<th>$\Delta U/B$ Predicted [25]</th>
<th>$\Delta U/B$ Observed</th>
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<td>0.1125(76)</td>
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<td>0</td>
<td>-1</td>
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<tr>
<td>8390.066</td>
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<td>-0.07267(52)</td>
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<td>-0.10323(79)</td>
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<td>0</td>
<td>-0.11666</td>
<td>-0.11133(41)</td>
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4.2 Determining the ratio \( G_\parallel / G_\perp \)

After determining \( \Delta U/B \) for each observed Zeeman line, one might assume that \( G_\parallel \) and \( G_\perp \) could be precisely determined through a global fit of one’s data to Equation 48. Proceeding directly to a global fit at this point, however, would sacrifice some of the extreme precision of our spectroscopic measurements due to not knowing the strength of the magnetic field to the same level of precision. \( G_\parallel \) is most likely to be affected by this imprecision, as it is smaller than \( G_\perp \) in both weight and value. Fitting directly to Equation 48 could result in finding an incorrect value for \( G_\parallel \) due to the fit attempting to compensate for an unaccounted difference in the value of \( B_\perp \) and \( B_\parallel \).

To avoid a determination of \( G_\parallel \) that is biased by our lack of precise knowledge of the magnetic field, we instead first determine the field independent ratio \( G_\parallel / G_\perp \) rather than attempting to find \( G_\parallel \) and \( G_\perp \) individually. Examining Equation 48 reveals that the weight of \( G_\parallel \) decreases as \( J \) increases. As we are most concerned with losing sensitivity to \( G_\parallel \), we want to look at transitions with the lowest \( J \) values in our determination of \( G_\parallel / G_\perp \). We will also find momentarily that choosing two transitions with opposing parity changes is necessary to isolate the desired ratio. With these considerations in mind, the following two \(^{208}\text{PbF} \ F = 0 \rightarrow F = 1 \) transitions are obvious candidates:

\[
(J = \frac{1}{2}, F = 0, p_s = -1) \rightarrow (J = \frac{3}{2}, F = 1, p_s = +1), 18462.193 \text{ MHz} \quad \text{(A)}
\]

\[
(J = \frac{1}{2}, F = 0, p_s = +1) \rightarrow (J = \frac{3}{2}, F = 1, p_s = -1), 22691.931 \text{ MHz}. \quad \text{(B)}
\]

These transitions will display no Zeeman splitting when subjected to a parallel magnetic field (\( \Delta M_F = 0 \)), so we examine them under a perpendicular field (\( \Delta M_F = \pm 1 \)). Again from Equation 48, notice that an \( F = 0 \) state will exhibit no Zeeman splitting as \( M_F \) can only be 0 in this case. It follows that

\[
\Delta U_A = \frac{1}{3} \left( \frac{G_\parallel}{4} - G_\perp \right) \tag{50}
\]

\[
\Delta U_B = \frac{1}{3} \left( \frac{G_\parallel}{4} + G_\perp \right) \tag{51}
\]

for the \( M_F = 0 \rightarrow M_F = 1 \) transition. The combination of splittings

\[
\Gamma_{BA} = \frac{\Delta U_B + \Delta U_A}{\Delta U_B - \Delta U_A} = \frac{G_\parallel}{4G_\perp} \tag{52}
\]

42
Table 4: Observed Zeeman shifts of the $J = 1/2 \rightarrow J = 3/2$ transitions for $^{207}$Pb$^{19}$F. $\Delta U/B$ is given in MHz/Gauss, while the number in parenthesis gives the two standard deviation error of the final digits of precision. The subscripts $L$ and $U$ refer to the upper and lower energy level of the transition, respectively.

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<th>Unsplit Line (MHz)</th>
<th>$F_L$</th>
<th>$F_U$</th>
<th>$M_{F_L}$</th>
<th>$M_{F_U}$</th>
<th>$\Delta U/B$</th>
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<td>5/2</td>
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<td>1/2</td>
<td>0.09819(81)</td>
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reveals the desired ratio. Now, applying our data we derive the relation

\[ \Gamma_{BA} = \frac{G_{\parallel}}{4G_{\perp}} = -0.0928 \pm 0.0013 \]  
\[ G_{\parallel} = (-0.371 \pm 0.005)G_{\perp}. \]  

Finally, this relation can be substituted for \( G_{\parallel} \) in Equation 48 with the result

\[ \frac{U_i}{\mu_0 B} = M_{F_i} \left( \frac{G_{\perp}}{2F_i + 1} \right) \left( \frac{-0.371 \pm 0.005}{2J_i + 1} + p_s_i (-1)^{J_i-1/2} \right) \]  

From this point a global fit of the data can be performed while adjusting the single parameter, \( G_{\perp} \). Once \( G_{\perp} \) is determined, Equation 54 can be used to obtain the value of \( G_{\parallel} \).

### 4.3 Global Fit in Terms of \( G_{\perp} \)

The data from 29 observed Zeeman splittings of \(^{208}\text{Pb}^{19}\text{F}\) were fit in an ordinary least squares manner to the single parameter \( G_{\perp} \). This fit was performed twice. Once with Equation 55 (Figure 20), consistent with the approximations made throughout this section, and once with the more rigorous Equation 44. Final results are presented and compared with published theory in Table 5. The full model using Equation 44 finds

\[ G_{\perp} = -0.3719 \pm 0.0051 \]
\[ G_{\parallel} = 0.1300 \pm 0.0025. \]

Note that the approximate result deviates from that of the full model by \( \sim 0.3\% \) for \( G_{\perp} \) and \( \sim 5\% \) for \( G_{\parallel} \), consistent with our estimations of the quality of our approximations. The analysis has also assumed that \( G_{\perp} < 0 \) as predicted by theory. Performing the fit under this assumption gives a variance in \( \Delta U/B \) of 0.0011, while performing the fit with \( G_{\perp} > 0 \) gives a variance of 0.0046. As we’re not directly sensitive to the sign of \( G_{\perp} \) due to our fit depending on the ratio \( G_{\parallel}/G_{\perp} \), we can’t make any definitive conclusions, but the data are consistent with the theoretical predictions of Kozlov et al. [19]. Finally, although the values for both \( G_{\parallel} \) and \( G_{\perp} \) are in reasonable agreement with available theoretical results, this measurement provides a significant leap in the precision of our knowledge of these parameters.
Table 5: Zeeman parameters of $^{208}\text{PbF}$

<table>
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</tr>
</thead>
<tbody>
<tr>
<td>$G_\perp$</td>
<td>$-0.3710 \pm 0.0051$</td>
<td>$-0.3719 \pm 0.0051$</td>
<td>$-0.382$</td>
<td>$-0.438 &lt; G_\perp &lt; -0.269$</td>
<td>$-0.319$</td>
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<tr>
<td>$G_\parallel$</td>
<td>$0.1376 \pm 0.0025$</td>
<td>$0.1300 \pm 0.0025$</td>
<td>$0.122$</td>
<td>$0.034 &lt; G_\parallel &lt; 0.114$</td>
<td>$0.082$</td>
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</table>
Figure 20: Ordinary least squares fit of $^{29}$Pb$^{19}$F Zeeman splittings to the single parameter $G_\perp$. Also plotted are the predicted values for each splitting and the resulting fit.
5 Conclusion

Rotational microwave spectroscopy of the PbF radical was conducted with controlled magnetic fields at Gottfried-Wilhelm-Leibniz-Universität Hannover. The data collected allowed for a determination of the Zeeman interaction parameters $G_{\parallel}$ and $G_{\perp}$ presented in Table 5. As expected, the values of these parameters, and therefore the value of the molecular g-factor, are quite small in comparison to those of molecules in other ground states. As being able to account for the effects of stray magnetic fields is vital in any e-EDM experiment, PbF’s small g-factor provides a considerable advantage. Furthermore, the precision determination of these parameters is a vital step in the design and implementation of a possible future e-EDM experiment using PbF. Working at the level of precision described herein represents an increase in precision for the PbF e-EDM project of $\sim$ 4 orders of magnitude (Figure 21).

Figure 21: Evolution of precision of the PbF e-EDM project. The work described in this thesis is marked by the red point. From Shafer-Ray [26].

Further Zeeman analysis of the molecule at the current precision may
allow for a conclusive determination of the sign of $G_1$. Making this measurement would require resolving the specific contribution of the nuclear magnetic moment to the observed Zeeman splitting. The percent contribution of the nuclear moment is largest for a particular $J = 5/2 \rightarrow J = 7/2$ transition. However, sensitivity of the Hannover system decreases as the $J$ level increases due to the supersonic expansion forcing most molecules into the lowest energy levels complicating the measurement.

The features resolved during this work indicate a level of precision tantalizingly close to that required to detect a predicted P-odd, T-even nuclear anapole moment [28]. Detection of such an anapole moment would be the first evidence of an anapole moment in a molecular system, nicely complementing the 1997 discovery of an anapole moment in atomic Cesium by Weiman et al. [34]. Further investigation of the techniques required for making such a measurement is certainly warranted.

The ultimate goal, of course, remains the detection of the electron EDM. Possible tests of New Physics that are realistic with current technology remain sparse. There is an almost overwhelming variety of theories of New Physics and few concrete reasons to prefer one over the other. A tangible experimental result that tests these theories’ predictions, such as the discovery of the e-EDM, would provide a giant leap toward clarity amongst the chaos.
Appendix: Matlab Code

function [fitted, quality] = lastfit(dataset)
%This function computes Gperp by employing a global weighted least squares
%fit to inputted data of Zeeman splitting of 208PbF using equation (44). In
%addition displays various factors describing the quality of the fit.

dataS = importfile(dataset);
%data can be imported from a properly formatted excel or csv file.

data = dataS.data;

%The inputted data set must include Zeeman splitting in the format of U/B
%properly labeled with the F,J,M,p quantum numbers of both states. Weights
%should be given in the format 1/\sigma^2.

FL = data(:,4);
FU = data(:,5);
JL = data(:,2);
JU = data(:,3);
pL = data(:,6);
pU = data(:,7);
ML = data(:,8);
MU = data(:,9);
splits = data(:,10);
Error = data(:,11);
Weights = data(:,12);

%defining needed constants
GF = 5.25773;
muN = 7.622593e6;
muB = 13.9962457e9;
%empirically determined constants and ratios as outlined in the text
rat = (-0.371-0.0046)/1.009;
rat2 = -2.991/1.009*GF*(muN/muB);
Apar = 255.99097;
Aperp = 409.9061;

%compute mixing angle for upper and lower states
thetaU = 0.5*atan((2*sqrt(FU.*(FU+1)).*(Apar + (-1).^(FU).*pU*Aperp))./(2*(2*FU+1).^2 - Apar - (-1).^(FU).*pU.*(Aperp + (2*FU +1).*2*pU)));
thetaL = 0.5*atan((2*sqrt(FL.*(FL+1)).*(Apar + (-1).^(FL).*pL*Aperp))./(2*(2*FL+1).^2 - Apar - (-1).^(FL).*pL.*(Aperp + (2*FL +1).*2*pL)));

49
%Equation (44) in terms of the single parameter Gperp

\[
\begin{align*}
\text{xdat} &= \frac{\mu_u}{2 fu+1} \cdot \left( \frac{J_u\cdot 1}{2 J_u+1} \cdot \sin(2\theta_u) \right) \\
&\quad + \left( J_u-fu \right) \cdot \left( \frac{1}{\sqrt{fu \cdot (fu+1)}} \right) \cdot \sin(2\theta_u)^2 \\
&\quad + \frac{p_u \cdot (-1)^{J_u-0.5} \cdot \left( \frac{\mu_u}{2 fu+1} \cdot \cos(2\theta_u) \right)}{2} \\
&\quad - \frac{\mu_l}{2 fl+1} \cdot \left( \frac{J_l\cdot 1}{2 J_l+1} \cdot \sin(2\theta_l) \right) \\
&\quad + \left( J_l-fl \right) \cdot \left( \frac{1}{\sqrt{fl \cdot (fl+1)}} \right) \cdot \sin(2\theta_l)^2 \\
&\quad + \frac{p_l \cdot (-1)^{J_l-0.5} \cdot \left( \frac{\mu_l}{2 fl+1} \cdot \cos(2\theta_l) \right)}{2}; \\
\end{align*}
\]

\[
\begin{align*}
\text{int} &= \frac{\mu_u}{2 fu+1} \cdot \left( \frac{1}{2 J_u+1} \cdot \frac{\mu_u}{2 fu+1} \cdot \cos(2\theta_u) \right) \\
&\quad - g_F \cdot \left( \frac{\mu_n}{\mu_B} \right) \cdot \left( \frac{(2 fu\cdot J_u \cdot \cos(2\theta_u))}{2 J_u+1} \right) \\
&\quad + \frac{(2 fu \cdot (fu+1)) \cdot (-1) \cdot \sin(2\theta_u)^2}{2}; \\
&\quad - \frac{\mu_l}{2 fl+1} \cdot \left( \frac{1}{2 J_l+1} \cdot \frac{\mu_l}{2 fl+1} \cdot \cos(2\theta_l) \right) \\
&\quad + g_F \cdot \left( \frac{\mu_n}{\mu_B} \right) \cdot \left( \frac{(2 fl\cdot J_l \cdot \cos(2\theta_l))}{2 J_l+1} \right) \\
&\quad + \frac{(2 fl \cdot (fl+1)) \cdot (-1) \cdot \sin(2\theta_l)^2}{2}; \\
\end{align*}
\]

\[Y = \text{splits} - \text{int};\]

%produces the desired weighted least squares fit
options = fitoptions;
options.Weights = Weights;
[fitted,quality] = fit(xdat,Y,poly1,options);

%generate plot of the fit
hold on
errorbar(xdat,Y,Error,'.k')
plot(fitted,'r')
holdoff
end

%subfunction manages the import of data.
function newdata = importfile(fileToRead)

DELIMITER = ',';
HEADERLINES = 1;
newdata = importdata(fileToRead, DELIMITER, HEADERLINES);
vars = fieldnames(newdata);
for i = 1:length(vars)
    assignin('base', vars{i}, newdata.(vars{i}));
end
References


[27] N. E. Shafer-Ray, T.Zh. Yang, P.M. Rupasinghe, C.P. McRaven, Benjamin Murphy, Alexander Baum, Trevor J. Sears, Lukas D. Alphei, and Jens-Uwe Grabow. Precise characterization of the ground X1 state of $^{206}$PbF, $^{207}$PbF, and $^{208}$PbF. To be Published.


