Electron Paramagnetic Resonance: Theory and Analysis

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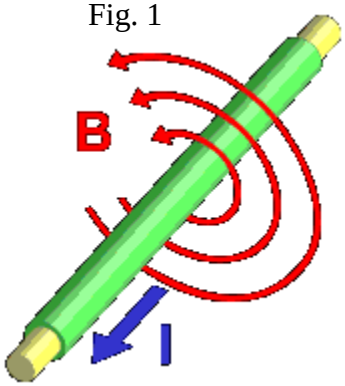
Electron paramagnetic resonance (EPR) is a powerful technique that allows researchers to probe fundamental physical properties of molecules. This paper explains the basic motivation and theory behind EPR. Data analysis and a particular example of probe design are briefly discussed.

Introduction

Since the dawn of the quantum era, physicists have ascribed more and more confounding properties to elementary particles. These peculiarities, however far removed from our daily experiences, still have a profound effect in our world. It is a result from quantum physics that electrons have an intrinsic angular momentum, called spin. In contrast to the classical concept of angular momentum, spin is a fundamental property of electrons and is not attributed to any mechanical motion. The magnitude of this spin is always ½ hbar. In addition to spin, electrons also have an inherent magnetic dipole moment; which means electrons act like minute bar magnets. This seemingly bizarre property is, in fact, responsible for the macroscopic phenomena of permanent magnets.

This magnetic moment property can be attributed to spin through a classical treatment. By modeling an electron as a ball of distributed charge with angular momentum equal to the quantum spin, a current flowing in a tiny loop arises[1]. This current produces a magnetic field, oriented

Fig. 1



by the right-hand rule, according to Ampere's Law:

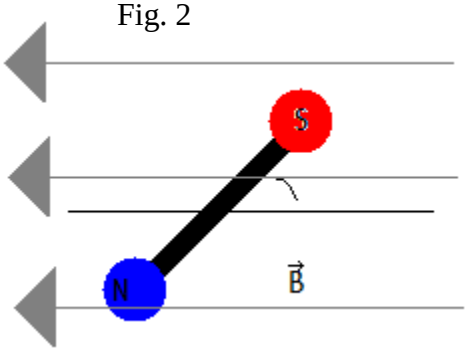
$$\nabla \times \mathbf{H} = \mathbf{J} \qquad (1)$$

Indeed, because of the idiosyncratic definition of current (i.e. the flow of positive charge) the magnetic moment points in the direction opposite of the electron's spin.

There are, however, problems with this model. Electrons have no size attributed to them, but are rather thought as point-like particles. This presents a problem, because points cannot rotate about. Moreover, the preceding explanation assumes some sort of distribution on a ball, but no mention is made as to what it is.

It was a while after the inception of Schrödinger's wave equation that this magnetic quantum number was discovered. In the absence of an external magnetic field, the different spin-magnetic moment states for electrons in an atom are nearly degenerate. That is, aside from hyperfine splitting of energy levels due to nucleus-electron interactions, electrons occupying the same shell and orbital have the same energy. Spectroscopy, historically, was not sufficiently precise to distinguish the energy differences[1]. A breakthrough was made by performing spectroscopic experiments in a magnetic field. The splitting of a single emission line into several lines corresponded to the splitting of these degenerate energy levels.

Fig. 2



This splitting, known as the Zeeman Effect, was due to the different magnetic moments obtaining different potentials in a magnetic field.

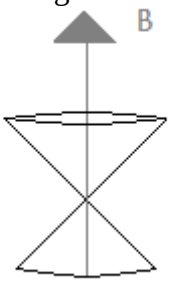
Classically this can be calculated by assuming electrons are magnetic dipoles with North and South Poles and dipole moment μ. The potential of the dipole in a magnetic field can be

defined by the work done by the torque exerted on the dipole in moving it from an aligned position to its current arrangement:

$$V = \int_0^{\alpha} \tau d\theta = \int_0^{\alpha} (\mu \hat{} B) d\theta = \mu B \int_0^{\alpha} \sin(\theta) d\theta \quad (2)$$

Which equals $2\mu B$ if we consider $\alpha = \pi$, corresponding to the potential energy associated with an anti-aligned electron. However, this picture isn't true to reality because an electron's magnetic moment is quantized (a direct consequence of the quantization of spin). Moreover, the magnetic moment obeys the Heisenberg uncertainty principle, therefore only one component can be known at a time (the knowledge of a second component vector would allow for the calculation of the third readily through a simple application of the Pythagorean Theorem).

Fig. 3



Because of the quantized nature of the magnetic moment, the dipole pictured in Fig. 2 could not vary in orientation through continuous angles. Instead it could only assume a few discrete orientations. For an electron those are either "up" or "down", referring to the direction of the known component of the vector in relation to the external magnetic field.

This restriction defines a half cone, where the magnetic moment is known to inhabit. The calculation above can be confirmed experimentally by measuring the energy difference between electron states for various field strengths and then plotting V versus B. The slope of the line is roughly $2\mu_B$ where μ_B is the Bohr magneton. Nevertheless, this simple-minded picture doesn't quite work. The 2 in the equation is known as the Landé g Factor, and because the way quantum mechanics works, it is actually slight greater than 2. Quantum mechanically the energy difference is more appropriately described by $\mu_B g B$[1].

Electron Paramagnetic Resonance

Electron Paramagnetic Resonance, or EPR, exploits the concepts above to probe the inner electronic properties of materials. Imagine a sample of tiny magnetic dipoles; at first any orientation of the dipoles will be equally likely, but if the sample is exposed to an external magnetic field, a preferred direction is chosen. Associated with each dipole is a potential, determined strictly by its orientation with respect to the magnetic field. It turns out that the Maxwell-Bolztmann distribution models the allocation of energies in the previous scenario reasonably well[3]. In thermal equilibrium, the majority of dipoles will be aligned with the magnetic field, but some will be unaligned. The probability density in energy is given by

$$f_E\,dE = f_p\left(\frac{dp}{dE}\right)\,dE = 2\sqrt{\frac{E}{\pi(kT)^3}}\,\exp\left[\frac{-E}{kT}\right]\,dE. \qquad (3)$$

The energy in this equation is a direct consequence of potential, and is therefore a function of θ.

The simplest sample to consider would be a free electron gas. Because of the quantum nature of electrons, there would only be two available energy levels, rather than a spectrum. The Maxwell-Bolztmann distribution can still yield a histogram, but it needs to be renormalized before being treated as a probability density function. In thermal equilibrium there will be many electrons in the lowest energy state (aligned with the field) and a few electrons in the highest. The EPR procedure involves shining electromagnetic radiation of fixed microwave frequency through a sample and measuring the absorbance. Meanwhile, the external magnetic field applied to the sample is varied. When $V = \mu_B gB$ matches the energy carried by the microwaves, a peak in absorbance

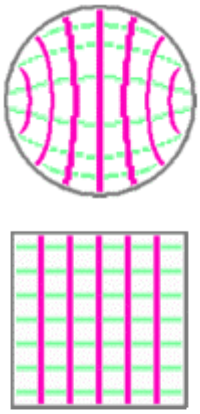
appears. This is because there will be many electrons absorbing the waves and jumping from the lower energy state into the excited, anti-aligned state.

Samples under scrutiny at the Hill lab are much more varied and exotic than free-electron gases. Chemistry has allowed the adept manipulation of a compound's net magnetic moment. This molecular magnetic moment arises from unpaired electrons in the constituent atoms. These compounds are called single molecular magnets, frequently referred to as SMMs. SMMs can be studied through EPR because of the magnetization response they afford. Although single molecular magnets can exhibit more than two spin energy levels, they can still be studied through similar methods, yielding a variety of peaks in the EPR spectrum. From the absorbance data their magnetic moments and quantum numbers can be reconstructed using a phenomenological Hamiltonian, which takes into account the Zeeman splitting and other finer interactions between the parts of the compound. SMMs display a variety of phenomena, such as anisotropy. Anisotropy occurs when there is a preferred direction for the magnetic moment of the electrons in the molecule, caused by the very structure of the compound. The preferred direction is often called the easy axis, and the directions perpendicular to it are collectively called the hard plane. Another interesting phenomenon displayed by SMMs is the tunneling of magnetic moment. This event is characterized by the magnetic moment of the molecule going from one state to another without passing through any intermediary states, which would be otherwise forbidden due to prohibitive energy costs. SMMs have sparked a great deal of interest because of their remarkable tunneling properties and their behavior as quantum systems[2]. These features make single molecular magnets attractive components for quantum computers, whether it be for storage media, or switching in logical components.

Procedure and Operation

Envisioning and designing an EPR experiment is far from easy. The first hurdle to clear is finding a source for a strong and uniform magnetic field. However, with the advent of superconducting magnets, very strong magnetic fields can be created and maintained with minimal energy input. The only problem posed by superconducting magnets is their requirement for low temperatures to behave in the superconducting regime. The actual superconducting coil is kept refrigerated in a bath of liquid helium at temperatures as low as 4K. This liquid helium is shielded from the outside environment by several layers of vacuum insulation and a bath of liquid nitrogen. The second challenge faced by EPR experimentalists is finding a way to guide the electromagnetic waves down into the magnet's chamber, where the experiment is taking place. To this end a variety of wave guides are employed, depending on the energy range being studied. Wave guides restrict and control the way electromagnetic waves propagate and evolve. The physics can be understood by solving Maxwell's wave equations for specific boundary conditions (e.g. electric field equal to 0 at boundaries). Rectangular waveguides have been the most commonly used apparatus. Waves propagating in a rectangular waveguide have the added advantage of maintaining their polarization, which is oriented in one of the two dimension of a cross-section of the guide[3]. However, for the study undertaken at the National High Magnetic Field Laboratory, NHMFL, in Tallahassee, Florida, a special probe with cylindrical waveguides was constructed. Because of the unique geometry, the guide supports a different mode of propagating waves. In addition to geometry, the dimensions of the

Fig. 4



waveguide have to be taken into account. To support the propagation of electromagnetic waves, a waveguide has to be at least the size of the wavelength. Also, it is beneficial to keep the dimensions close to a multiple of the wavelength.

The probe was designed to be used in the 32mm bore magnets available in the Tallahassee facility. The schematics of the magnets are shown in Figures 4 and 5:

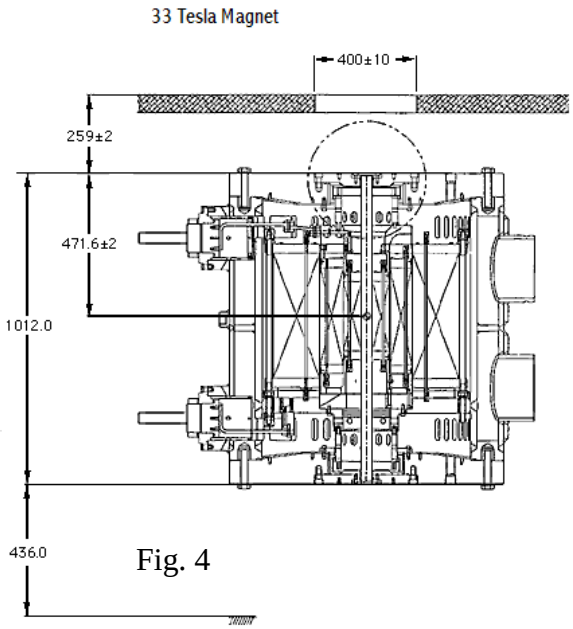


Fig. 4

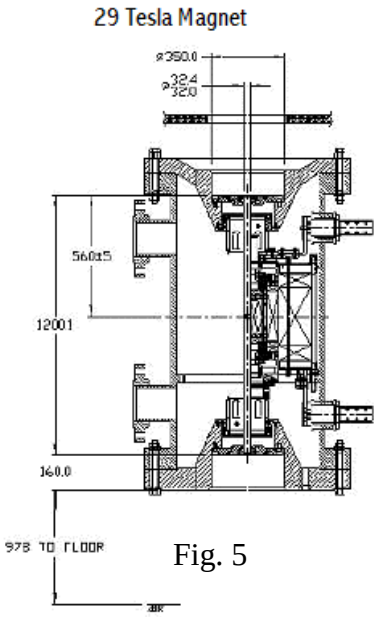


Fig. 5

The probe was made compatible with multiple bore lengths by having an adjustable Ultra-Tor™ constriction fitting. Moreover, because of the imperative need of avoiding ferromagnetic materials in the chamber, the entire probe was made of stainless steel and brass, which are nonmagnetic.

At the Hill lab, the microwaves used to excite the system are produced by a Millimeter Vector Network Analyzer, or MVNA. But before an experiment can begin, the first step is to perform a frequency sweep to identify favorable absorption peaks. The MVNA can then be tuned to a chosen frequency and the signal adjusted for maximal

amplitude. The phase of the signal is tracked and locked by a computer controlling the MVNA. Explicit knowledge of the phase is needed because the nonlinear diodes used to boost the MVNA's low frequency signal into higher frequencies. To make sense of the absorbance one needs to pay careful attention to the phase, as it may freely mix with the amplitude and skew the results.

Data Analysis

A typical EPR spectrum may have many peaks. The physics of the situation are not quite as simple as Zeeman splitting. There are often many energy levels, and therefore many possible transitions. If there are n distinct energy levels there is a maximum of ${}^{n}C_{2}$ transitions possible, or n(n-1)/2. However, transitions are subject to conservation laws, and so not all are allowed. Furthermore, not all transitions are necessarily within the energy range being explored, and the energy transitions may occasionally become degenerate at specific fields.

Phase and amplitude mixing frequently occurs, which pollutes the data and may altogether cloud the absorption spectrum, as shown in figures 8 and 9. Figure 8 is a plot of the *absorption* spectrum. It is therefore interesting to note it has a positive peak, which is wholly unexpected. This can be explained by examining the phase in figure 9. The amplitude and phase are mixing and presenting spurious results.

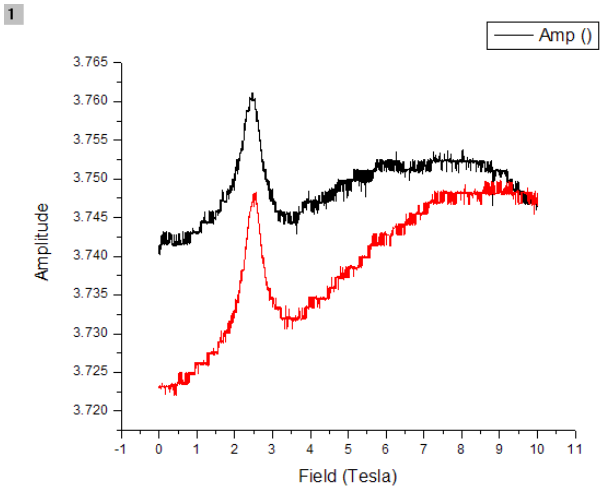


Fig. 8

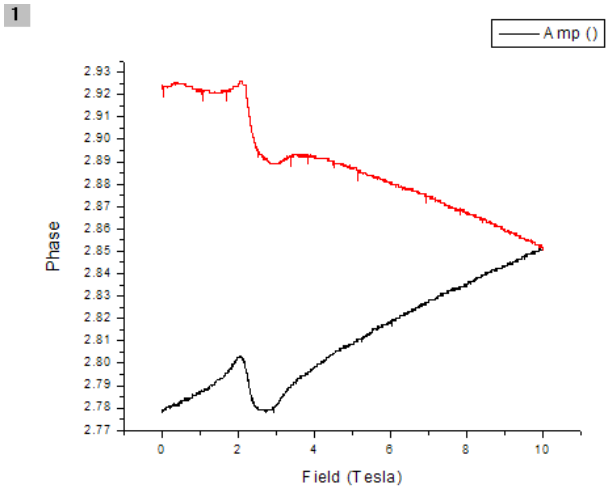


Fig. 9

Red trace corresponds to down sweep; black corresponds to up sweep of field.

There are some analysis techniques employed to help extract the physics from the data. Trial and error can be used to subtract the phase from the amplitude. A heuristics approach is attempting to make both sides of a peak of equal height. The code below attempts to fit the absorbance by subtracting a multiple of the corrected phase (phase centered about 0) from the amplitude and solving system (1) for **c**.

(1) A’ = A - cP, where A and P are functions of x, the field strength.

A’(x1) = A’(x2)

Both x1 and x2 are chosen arbitrarily close to the peak. This process is subject to guessing, but despite its nondeterministic nature, it still yields good results.

The code presented in snippet 1 is written in the Origin scripting language. It formats the raw data file and performs a bit of data analysis. The code centers the phase data and corrects the background for a peak at roughly 3 Tesla.

Snippet 1

```
delete col(1);
wks.col1.type = 4;
worksheet -a 2;

Col(8) = data(1,3000,1);
Col(8) = null;
Col(9) = data(1,3000,1);
Col(9) = null;

max = -300;
min = 300;
for(i=i;i<2600;i++){
      if(max < Col(3)(i)){
            max = Col(3)(i);
      }
      if(min > Col(3)(i)){
            min = Col(3)(i);
      }
}
mean = (max+min)/2;
col(8)=col(3) - mean;


x1 = Col(2)(2);
x2 = Col(2)(4.5);
y1 = Col(8)(2);
y2 = Col(8)(4.5);
c = (x2 - x1)/(y2 - y1);
col(9) = Col(2)-c*Col(A);
```

After correcting for phase, a background can be fitted to the data to normalize the amplitude. Solving a 3x3 system of equations will approximate the background to an order two polynomial. Ultimately the amplitude A is divided by the polynomial P_2 to flatten the spectrum and bring out a well defined peak. Alternatively, the amplitude A can be divided by its maximum, often giving good results for relatively flat backgrounds.

Snippet 2 is an example of fitting the background approximated by an order two polynomial.

Snippet 2

```
#include <stdio.h>

int main() {
	double x1, x2, x3, y1, y2, y3;
	double a, b, c;
	int flag = 1;

	printf("Input x1 and y1 with a space in between(x1 y1):  ");
   while(flag==1){
		printf("\n\n\n");
		printf("(x1 y1):  ");
		scanf("%lf %lf", &x1,&y1);
		printf("(x2 y2):  ");
			scanf("%lf %lf", &x2,&y2);
			printf("(x3 y3):  ");
			scanf("%lf %lf", &x3,&y3);

			b = ((y1 - y3)/(x1*x1 - x3*x3) - (y1 - y2)/(x1*x1 - x2*x2))*((x1 +
x3)*(x1+x2)/(x2 - x3));
			a = (y1 - y3 + b*(x3 - x1))/(x1*x1 - x3*x3);
			c = y1 - a*x1*x1 - b*x1;
			printf("a = %.3lf\n", a);
			printf("b = %.3lf\n", b);
			printf("c = %.3lf\n", c);

			printf("Continue? (press 1)  ");
		scanf("%d", &flag);
		}
		system("pause");

	return 0;
}
```

Other values, such as peak area, can be correlated with the temperature or angle of the system. Such analysis is instrumental in the study of anisotropy of single molecular magnets.

Conclusion

Since the advent of Electron Paramagnetic Resonance studies, many different systems have been studied and different techniques for probing of the quantum world devised. With a better understanding, great leaps in computing and other technologies can be made. To further these goals, new hardware and procedures are being developed. By further delving into the quantum world we can validate our models and improve our understanding of how the very small works.

Acknowledgements

The author acknowledges Professor Hill, S. Kim, C. Koo, J. Lawrence, and NSF.

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