Electron Spin Resonance

1. Reference

Quantum Mechanics, by Eisberg and Resnick, p. 294

2. Introduction

In this experiment we will study one classical "particle" and one quantum mechanical particle. In particular, we will choose particles having the common properties of angular momentum and magnetic moment. The objective is to study how these particles behave in externally applied magnetic fields. The classical experiment should illuminate the concepts used later in the quantum mechanical system.

3. Classical System

For the classical particle, you will use a spinning billiard ball, containing a magnet embedded at its center. The objectives are to:

- a. place the ball in a magnetic field and determine the ball's magnetic moment
- b. add angular momentum to the ball and observe its motion
- c. determine the relationships among the motion of the ball and its angular momentum and magnetic moment.

4. Classical Theory

4.1 Magnetic Moment

Consider a loop of positive current *I* whose path encloses area *A*, as in Fig. 1.

 $\vec{\mu}$



Fig. 1 Magnetic Dipole woment of a current loop.

The area enclosed by the loop may be considered a vector: The magnitude of the vector is just the area. The direction of the vector area is given by the right-hand rule, with the fingers pointing in the direction of positive current flow. Then the thumb points in the direction of the resulting magnetic dipole moment. Then the magnetic dipole moment is given by:

$$\vec{\mu} = \vec{A}I \tag{1}$$

4.2 Torque

If we place a magnetic dipole moment in an external magnetic field, the dipole will experience a torque given by

$$\vec{\tau} = \vec{\mu} \times \vec{B} \tag{2}$$

where \vec{B} is the magnetic field.

Question 1:

If the object having the magnetic moment (but no angular momentum) is free to move, how will it move in the presence of the magnetic field?

4.3 Angular momentum

Question 2:

If the object is given angular momentum, parallel or anti-parallel to its magnetic moment,

and is placed it in a magnetic field, how will it move?

To help us answer question 2, carefully consider Figure 2.



Fig. 2 Torque acting on an object with angular momentum and oppositely directed magnetic moment in a magnetic field. (after Eisberg and Resnick, *Quantum Physics*)

The magnetic field acts on the magnetic dipole moment to produce a torque, given by eq.(2). This torque gives rise to a change in the angular momentum $d\vec{L}$ during the time dt such that

$$\vec{\tau} = \frac{d\vec{L}}{dt}.$$
(3)

The change dL causes \overline{L} to precess through an angle ωdt , where ω is the precession angular velocity. Note from Fig. 2 that

$$dL = L\sin\theta \ \omega dt$$

thus,

therefore,

$$\tau = \mu B \sin \theta = \frac{dL}{dt} = \omega L \sin \theta$$

$$\omega = \frac{\mu}{L}B.$$
 (4)

Eq.(4) is often re-stated as

$$\omega = \gamma B \tag{5}$$

where γ is called the *gyromagnetic ratio*.

5. Apparatus

We will use the TeachSpin Magnetic Torque apparatus for this "classical" part of the experiment. The apparatus consists of:

- a. a control box for supplying current to the magnetic field coils, setting the direction of the fields produced, turning on the air supply and controlling the strobe light.
- b. a pair of copper wire coils which can produce a magnetic field in the vertical direction. The relation between the current in the coils and the magnetic field produced is:

$$B = (1.36 \pm 0.03) \times 10^{-3} \text{ Tesla/amp.}$$
(6)

a cue ball with an embedded magnet, a small black handle for spinning the ball. The magnetic dipole is aligned parallel to the axis containing the black handle.

- d. an aluminum rod with a steel tip for holding a sliding plastic mass for changing gravitational torque on the ball.
- e. vernier calipers to measure the position of the sliding mass
- f. balance for weighing the sliding mass.
- g. Movable index to indicate a starting and stopping position of precession.
- h. Rotating saddle to provide a rotating magnetic field, perpendicular to the steady, vertical field.
- i. Stopwatch to measure the precession period.

6. Experimental Procedure

We will test eq.(4) using the following procedure.

6.1 Measure μ .

For this part of the experiment keep the angular momentum of the ball equal to zero.

Use gravitational torque balancing the magnetic torque to determine $\vec{\mu}$. To do so,

- a. Place the aluminum rod in the central hole of the cue ball's black handle, with the rod's magnetic end inserted into the ball.
- b. Place the sliding plastic mass on the aluminum rod.
- c. Set the magnetic field to point up, with the *field gradient* turned off.
- d. Adjust the current in the magnetic field coils so that the magnetic torque just balances the gravitational torque:

$$\vec{\mu} \times \vec{B} = -\vec{r} \times m\vec{g} \tag{7}$$

where r is the distance from the center of the ball to the center of the sliding mass, m, and g is the acceleration due to gravity. e. Draw a sketch of the ball showing the vectors in eq. (7) and demonstrate that eq.(7) reduces to:

$$\mu B = -rmg. \tag{8}$$

Eq.(8) suggests a technique for determining μ :

f. Move the sliding mass to about 10 positions along the aluminum rod and, at each position, determine the magnetic field needed to balance the ball.

Question 3:

Do you really need to measure r directly to do this experiment?

Estimate uncertainties in your measurements and determine μ , with its uncertainty.

6.2 Adding angular momentum

You may provide angular momentum to the ball by spinning it using the black handle. Recall that, for a uniform, solid sphere, the angular momentum L is given by:

$$\vec{L} = \frac{2}{5} M R^2 \vec{\Omega}, \tag{9}$$

where M is the mass, R is the radius, and Ω is the spin angular velocity of the sphere. Note that for your sphere, the angular momentum and magnetic moment are parallel or anti-parallel.

- a. Measure the mass and radius of the ball.
- b. Turn on the magnetic field and set it to some intermediate value.
- c. Turn magnetic field *gradient on*. With this setting the currents in the upper and lower coils are in opposite directions, producing B = 0 at the center of the apparatus.

- d. Turn on the strobe light and set its frequency to about 5 Hz. Note that in order to measure this frequency accurately the frequency counter must count for several seconds. It updates every 10 seconds.
- e. Orient the ball so its black handle points toward the strobe light.
- f. Spin the ball using the black handle and reduce any wobble with your fingernail.
- g. As the ball's angular velocity slowly decreases, the white dot on the ball's black handle will begin to appear stationary in the strobe light. You now know the angular velocity of the ball. Quickly set the position marker as near as possible to the black handle, turn off the field gradient and start the stopwatch.
- h. Measure the time it takes for the ball to precess one complete cycle.
- i. Repeat steps 2 through 7 at 1/2 amp intervals. Estimate uncertainties in all measured quantities.
- j. Plot Ω vs. *B* with uncertainties.
- k. Check your experimental results for consistency with eq.(4). Take uncertainties into account.

7. Spin (Flip) Resonance

This part of the experiment provides a qualitative demonstration of how the ball, having both angular momentum and magnetic moment, behaves in a rotating magnetic field, perpendicular to the constant, vertical B field.

Remove the position indicator and install the magnetic field saddle. This saddle provides a field of constant magnitude, which may be rotated in the horizontal plane.

- a. With the vertical field set to a maximum, start the ball spinning with its black handle midway between the red dots on the saddle. As the ball precesses in one direction, manually rotate the saddle in the other direction. Try to move it smoothly and continuously. What effect does the rotating field have on the precessional motion?
- b. With the black handle midway between the red dots on the saddle, spin the ball again, but this time try to rotate the saddle in the same direction at an frequency *different* from the precession frequency. (This is tough!). How does the rotating magnet affect the precession?
- c. Repeat the experiment with the saddle rotating in the same direction at the same frequency as the precession. This requires some practice! How does the ball move now? Ask the lab staff for help if you have trouble here.

8. Quantum mechanical system

Electron Spin Resonance

8.1 ESR Theory

The electrons in atoms are bound in discrete energy states. Magnetic fields are generated within the atom by the

- orbital motion of the electrons around the atom
- spin of the electrons
- spin of the atomic nucleus.

If atoms are placed in an externally applied magnetic field, the interactions of the applied field with the internal fields listed above cause the energy levels of the atoms to shift.

Similarly, if the atoms are placed in a solid, the magnetic fields produced by neighboring atoms will also contribute to energy level shifts.

Electron Spin Resonance (ESR) is a technique for inducing and detecting transitions among energy levels. Energy level shifts are induced by application of a known magnetic field, while transitions among energy levels is induced by application of electromagnetic radiation of a known frequency. It is found that only for particular combinations of magnetic field and frequency are transitions induced.

Detection is accomplished by measuring the slight decrease in energy in the electromagnetic field which occurs when the energy is absorbed during the transition. A large ensemble of atoms is needed to absorb sufficient energy to be detectable.

It should be noted that the net energy shifts are due to the total field: applied and nearest neighbor. Since we know the value of the applied field, it follows that measuring the frequencies at which resonances occur is a probe into the details of the environment of the solid sample at the atomic scale.

The detailed study of solids using ESR is complex and beyond the scope of this course. Therefore, for simplicity we will study a much simpler system: "free" electrons, not bound to an atom. The sample we will use is the molecule DPPH (diphenyl-picri-hydrazyl), which has one, nearly free, electron per molecule.

9

8.2 States of a free electron in a magnetic field

The electron is a spin 1/2 particle. Thus, if an electron is placed in a steady magnetic field, the electron can be in only two possible energy states. In the semi-classical model we may think of the magnetic moment (or the angular momentum) of the electron precessing about the applied magnetic field with two possible orientations, one as shown in Fig. 2 and the other with the $\vec{\mu}$ and \vec{L} vectors reversed relative to \vec{B} .

Note: This model is useful, but has some limitations: The presence of a welldefined vector implies knowledge of the x and y components of the vector, but quantum mechanics tells us that these components are really indeterminate.

In these two states, the magnitudes of the components of spin angular momentum parallel to the field (in the *z*-direction) are $\pm \hbar/2$.

The magnetic moments associated with these states are

$$\mu_z = \pm g \mu_B / 2 \,, \tag{10}$$

where $\mu_B = e\hbar/2m$ is called the "Bohr magneton." For the free electron, for which all the angular momentum is spin (rather than orbital) angular momentum, g = 2.0023. The energy of a magnetic dipole moment in a magnetic field is given by

$$E = -\vec{\mu} \cdot \vec{B}. \tag{11}$$

Thus, the energy difference between the two states is

$$\Delta E = 2\mu_{\rm s}B = g\mu_{\rm B}B. \tag{12}$$

8.3 ESR for the free electron

8.3.1 Energy perspective

If we apply electromagnetic radiation with frequency *f*, such that

$$hf = \Delta E \,, \tag{13}$$

where ΔE is given by eq.(12), we should induce transitions between the two energy states.

8.3.2 Angular momentum perspective

Eq.(13) can also be written

$$\hbar\omega = \Delta E \,. \tag{14}$$

At resonance it turns out that ω of eq.(14) is the same as that of Fig.2, i.e., the precession angular velocity of the electron around the magnetic field. Thus, photons of angular

frequency ω carrying angular momentum \hbar , cause the electron's spin to change state.

Question 4:

Is angular momentum conserved in this process? Explain.

8.4 Gyromagnetic ratio of the electron

Combining eqs.(12) and (14) gives

$$\omega = \frac{g\mu_B}{\hbar}B.$$
 (15)

It should be noted that, for a free electron in a magnetic field, the magnitude of the spin magnetic moment is

$$\left|\vec{\mu}\right| = g\mu_B \sqrt{s(s+1)} \quad , \tag{16}$$

and the magnitude of the spin angular momentum is

$$\left|\vec{S}\right| = \sqrt{s(s+1)} \quad \hbar. \tag{17}$$

Thus, the ratio of magnetic moment to angular momentum is

$$\frac{\left|\vec{\mu}\right|}{\left|\vec{S}\right|} = \frac{g\mu_B}{\hbar} , \qquad (18)$$

which appears also in eq.(15).

Eq.(15) is often re-written as

$$\omega = \gamma B, \tag{19}$$

where γ is called the *gyromagnetic ratio*. Eq.(19) is analogous to eq.(5) for the classical case. In both cases γ is the ratio: magnetic moment/angular momentum. The factor *g* is required by quantum mechanics.

9. ESR Apparatus

We use the Daedalon ESR apparatus, consisting of

- 60 Hz AC power supply for Helmholtz coils
- tunable radio frequency oscillator with frequency and feedback controls
- Helmholtz coils, connected in parallel such that B=0.48xI, where B is in milli-Tsesla and I is the sum of the currents, in Amps, flowing in each coil.
- Sample probe, containing DPPH, surrounded by a coil

10. ESR Experimental Procedure

Make the electrical connections as shown in Fig.3:

- a. Adjust the height of the probe to be the same as the center of the Helmholtz coils.
- b. Slide the probe through the side slot in the Helmholtz coil support, so that the axes of the probe's RF coil and Helmholtz coils are perpendicular.
- c. Set the Helmholtz coil current to about 2/3 of its maximum value.

d. Set the scope to display in voltage vs. time mode. Ground both channels 1 and 2 and move their traces to the center (zero volt) line. Then DC couple both channels.



Fig. 3 ESR electrical connections.

- e. Set the tuning frequency to its minimum.
- f. Set the oscillator to be marginal by adjusting the feedback to give a maximum signal. Note that if the RF oscillator stops oscillating, the frequency display will read zero. If that happens, readjust the frequency and/or feedback controls.
- g. Measure V on channel 1 at which resonance occurs on channel 2. Since the modulating (60 Hz) field is periodic, you should see several resonances across the scope screen. Measure several of these resonances for each *B* field, frequency combination. Note that channel 1 is measuring the "sense" signal, for which 1 volt is produced by 1 Amp flowing from the power supply (1/2 amp flowing through

each coil). This current should be used to calculate the magnetic field from the relation given above. Repeat this measurement for a few of the resonance points on the scope display. Estimate uncertainties in your measurements.

- h. Increase the frequency and re-adjust the *B* field to find new resonances. Repeat steps 7 and 8 through the full range of frequencies available.
- i. Plot the resonant frequency vs. magnetic field.
- j. From your data, obtain a value for γ , the gyromagnetic ratio. Is this value consistent with eq.(15)?

Question 5:

What would you expect to happen to the ESR signal if the RF *B* field were applied parallel to the direction of the Helmholtz field? Try it and report your findings.

Question 6:

What does the experiment of Question 5 have to do with angular momentum?