Electron Spin Resonance – A pedagogical analysis

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Abstract

When an electron is placed in a magnetic field, it gains or loses some energy by virtue of possessing a magnetic dipole moment. This happens both for free and bound electrons. For a bound electron the change of energy depends on the magnetic field, the total angular momentum quantum number (j) as well as the orbital angular momentum quantum number (l). To be precise, the change in the general case is determined by the magnetic quantum number (m_j) and a quantity called the Lande g-factor - which depends on j and l - together with the magnetic field H. When l =0, and the interactions of an electron with its environment are ignored, the theoretically expected value of g is 2. The measured value of g then bears an imprint of the environment. For paramagnetic solids, the most accurate measurement of g is achieved by employing a magnetic resonance technique pioneered by the Russian physicist Y. K. Zavoisky. In this experimental method, transitions between the two magnetic states corresponding to $m_j = m_s = \pm \frac{1}{2}$ are induced by an oscillating electromagnetic field, with a frequency ν ~ 10 MHz. The transition rate has a peak value when $h\nu = g\mu_B H$, where h is Planck's constant and μ_B, called the Bohr magneton, is a constant associated with atomic magnetic dipole moments. This phenomenon is referred to as electron spin resonance (ESR).Thus by finding out the value of H required to produce the resonance condition, corresponding to a pre-selected value of ν, the value of g can be determined. A similar method, namely the nuclear magnetic resonance (NMR) technique, is widely used to study magnetic properties of atomic nuclei. In this article we explain, in details, the Physics behind the electron spin resonance technique of Zavoisky.

Introduction

The aim of this article is to expound the principle of 'electron spin resonance' to M. Sc. students and laboratory instructors.

The theory presented here is semi-classical in nature and the diagrams are basically schematic. Throughout this article or note, c.g.s (e. m. u.) units have been used.

The angular momentum of an electron $\boldsymbol{j} = \boldsymbol{l} + \boldsymbol{s}$ (all in units of $\hbar$). Its magnetic dipole moment, on the other hand, is

$$\boldsymbol{\mu} = - \mu_B (\boldsymbol{l} + 2\boldsymbol{s})$$

where $\mu_B = e\hbar/2m_e$, is the Bohr magneton, *e* being the magnitude of the charge of an electron. See Fig.1. The 'effective value' of the magnetic moment (component along $\boldsymbol{j}$) is

$$\boldsymbol{\mu}_{\text{eff}} = - g\mu_B \boldsymbol{j}$$

where g, called the 'Lande g-factor' is given by

$$g = 1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)}$$

with $j = l \pm \frac{1}{2}$, since $s = \frac{1}{2}$. For an electron in the 's'-state, $l = 0$; hence $j = \frac{1}{2}$ and g =2. Such an electron can be found in the second nitrogen atom away from the di-phenyl end of the diphenyl picryl hydrazyl (DPPH) molecule.

Equation of motion: In the presence of a constant magnetic field H_c in the Z-direction (say), the direction of the angular momentum ($\boldsymbol{j}$) keeps turning around the Z-axis.

$$\hbar \frac{d\boldsymbol{j}}{dt} = \boldsymbol{\mu}_{\text{eff}} \times \boldsymbol{H}_c$$

or

$$\frac{d}{dt}(\boldsymbol{\mu}_{\text{eff}}) = \gamma\, (\boldsymbol{\mu}_{\text{eff}} \times \boldsymbol{H}_c)$$

where $\gamma = -g(e/2m_e)$. The turning or precession of $\boldsymbol{j}$ (or $\boldsymbol{\mu}_{\text{eff}}$) occurs with angular frequency $\omega_L = \gamma H_c$. Its magnitude, $|\omega_L|$, is referred to as the Larmor (precessional) frequency. See Fig.2.

Consider all the N electrons in the same quantum state (say the s-state) in a small volume ΔV of the sample and define the intensity of magnetization $\boldsymbol{M}$ by $\boldsymbol{M}\Delta V = \Sigma\, \boldsymbol{\mu}_{\text{eff,i}}$ (i =1,2...N). Then the evolution of $\boldsymbol{M}$ is governed by

$$\frac{d}{dt}(\boldsymbol{M}) = \gamma\, (\boldsymbol{M} \times \boldsymbol{H}_c)$$

For $\boldsymbol{H} = \boldsymbol{H}_c + \Delta\boldsymbol{H}(t)$, the equation of motion of $\boldsymbol{M}$ is

$$\frac{d}{dt}(\boldsymbol{M}) = \gamma\, (\boldsymbol{M} \times \boldsymbol{H})$$

If the 'perturbation' is switched off at some time t, the x- and y-components (M_x , M_y) of $\boldsymbol{M}$ should disappear and M_z should approach a constant value (= M_c , say). The simplest 'phenomenological' way of capturing this change is to introduce the relaxation time approximation:

$$\frac{d}{dt}(M_z) = \gamma\, (\boldsymbol{M} \times \boldsymbol{H})_z + \frac{M_c - M_z}{\tau_1}$$

$$\frac{d}{dt}(M_x) = \gamma\, (\boldsymbol{M} \times \boldsymbol{H})_x - \frac{M_x}{\tau_2}$$

$$\frac{d}{dt}(M_y) = \gamma\, (\boldsymbol{M} \times \boldsymbol{H})_y - \frac{M_y}{\tau_2}$$

The relaxation times for the parallel component of $\boldsymbol{M}$ (i.e. M_z) and the perpendicular components of $\boldsymbol{M}$ (M_x , M_y) – τ_1, τ_2 respectively -are different, in general; τ_1 is determined by spin-lattice interaction while τ_2 is supposed to depend on spin-spin interaction.

Consider now a perturbation $\Delta\boldsymbol{H}(t) = 2H_0 cos\omega t\boldsymbol{i}$. It can be written as the sum of a clockwise and an anti-clockwise rotating vector, each of amplitude H_0:

$$2H_0 cos\omega t\boldsymbol{i} = (H_0 cos\omega t\boldsymbol{i} - H_0 sin\omega t\boldsymbol{j}) + (H_0 cos\omega t\boldsymbol{i} + H_0 sin\omega t\boldsymbol{j}) \equiv \boldsymbol{H}_{cw} + \boldsymbol{H}_{anti\text{-}cw}$$

The clockwise rotating component, $\boldsymbol{H}_{cw}$, follows the precessing $\boldsymbol{\mu}_{eff}$ vector (see Fig. 3); and, if $\omega = \omega_L$, tracks it perfectly. In the rest frame of the vector $\boldsymbol{H}_{cw}$, $\boldsymbol{\mu}_{eff}$ might now have appeared stationary; however precession around $\boldsymbol{H}_{cw}$ will pull it over to the other side signalling a transition from one energy state to another (- lower to higher magnetic energy state, implying absorption of energy from the oscillating radio-frequency field).See Fig. 4. No such transition can be induced by $\boldsymbol{H}_{anti\text{-}cw}$.
In considering the dynamics of the system, we may, therefore, ignore the effect of $\boldsymbol{H}_{anti\text{-}cw}$.

Bloch's equations

Replacing $\boldsymbol{H}$ by $\boldsymbol{H}_{eff} = \boldsymbol{H}_c + \boldsymbol{H}_{cw}$ we can rewrite the equations of evolution of $\boldsymbol{M}$. We thus arrive at Bloch's equations.

$$\frac{dM_z}{dt} = \gamma\left[-M_x H_0 sin\omega t - M_y H_0 cos\omega t\right] + \frac{(M_c - M_z)}{\tau_1}\ (M_c \equiv \chi_c H_c) \qquad (1)$$

$$\frac{dM_x}{dt} = \gamma\left[M_y H_c + M_z H_0 sin\omega t\right] - \frac{M_x}{\tau_2} \qquad (2)$$

$$\frac{dM_y}{dt} = \gamma[M_z H_0 cos\omega t - M_x H_c] - \frac{M_y}{\tau_2} \qquad (3)$$

Solution of the equations:

Assume that M_z becomes constant in the long run (steady state). This can happen if

$$M_x = Asin\omega t + Bcos\omega t \qquad (4)$$

$$M_y = Acos\omega t - Bsin\omega t \qquad (5)$$

so that

$$M_x H_0 sin\omega t + M_y H_0 cos\omega t = AH_0$$

Hence

$$\frac{dM_z}{dt} = -\gamma AH_0 + \frac{(M_c - M_z)}{\tau_1}$$

or

$$\frac{dM_z}{dt}+\frac{M_z}{\tau_1}=\frac{M_c}{\tau_1}-\gamma AH_0$$

Obviously, then, the value of M_z in the steady state ($M_{z,s}$) is

$$M_{z,s}=M_c-\tau_1\gamma AH_0 \tag{6}$$

Again, from eqs. (2), (4) and (5),

$$\omega Acos\omega t-\omega Bsin\omega t=\gamma\left[(Acos\omega t-Bsin\omega t)H_c+M_{z,s}H_0sin\omega t\right]-\frac{Asin\omega t+Bcos\omega t}{\tau_2} \tag{7}$$

Equating coefficients of $cos\omega t$ on the two sides

$$\omega A=\gamma H_cA-\frac{B}{\tau_2} \tag{8}$$

Similarly, equating coefficients of $sin\omega t$, we get

$$-\omega B=\gamma M_{z,s}H_0-\frac{A}{\tau_2}-\gamma BH_c \tag{9}$$

Identical equations can be obtained from eqs. (3), (4) and (5). From eq.(9),

$$B=\frac{\gamma M_{z,s}H_0-\frac{A}{\tau_2}}{\gamma H_c-\omega}=\frac{\gamma(M_c-\tau_1\gamma AH_0)H_0-\frac{A}{\tau_2}}{\gamma H_c-\omega} \tag{10}$$

Using eq. (10) in eq. (8) we get

$$A=\frac{\gamma M_cH_0\tau_2}{\tau_2^2(\gamma H_c-\omega)^2+\tau_1\tau_2\gamma^2H_0^2+1} \tag{11}$$

From eq. (10),

$$B=\frac{\gamma M_cH_0-(\tau_1\gamma^2H_0^2+\frac{1}{\tau_2})A}{\gamma H_c-\omega}$$

or

$$B=\frac{\gamma M_cH_0\left[\tau_2^2(\gamma H_c-\omega)^2+\tau_1\tau_2\gamma^2H_0^2+1-(\tau_1\gamma^2H_0^2+\frac{1}{\tau_2})\tau_2\right]}{(\gamma H_c-\omega)(\tau_2^2(\gamma H_c-\omega)^2+\tau_1\tau_2\gamma^2H_0^2+1)}$$

i.e.

$$B=\frac{\gamma\tau_2^2M_cH_0(\gamma H_c-\omega)}{(\tau_2^2(\gamma H_c-\omega)^2+\tau_1\tau_2\gamma^2H_0^2+1)} \tag{12}$$

Using the definition of γ, viz. $\gamma=g(e/2m_e)\approx\omega_L/H_c$ (as $H_0\ll H_c$), ω_L being the Larmor frequency, we have

$$A = \frac{\gamma M_c H_0 \tau_2}{\tau_2^2(\gamma H_c - \omega)^2 + \tau_1\tau_2\gamma^2 H_0^2 + 1}$$

$$\approx \chi_c \omega_L \tau_2 \times \frac{H_0}{\tau_2^2(\omega_L - \omega)^2 + \tau_1\tau_2\gamma^2 H_0^2 + 1} \qquad (13)$$

Similarly

$$B \approx \chi_c \omega_L \tau_2 \times \frac{(\omega_L - \omega)\tau_2 H_0}{\tau_2^2(\omega_L - \omega)^2 + \tau_1\tau_2\gamma^2 H_0^2 + 1} \qquad (14)$$

Finally

$$M_x \approx \frac{1}{2}\chi_c \omega_L \tau_2 \times \frac{2(\omega_L - \omega)\tau_2 H_0 cos\omega t + 2H_0 sin\omega t}{\tau_2^2(\omega_L - \omega)^2 + \tau_1\tau_2\gamma^2 H_0^2 + 1}$$

$$\equiv \chi'(2H_0 cos\omega t) + \chi''(2H_0 sin\omega t)$$

where $\chi'(\chi'')$ is the real (imaginary) part of the magnetic susceptibility. Both χ' and χ'' are functions of the frequency ω. Note that when

$$\boldsymbol{H} = H_c\boldsymbol{k} + (2H_0 cos\omega t)\boldsymbol{i}$$

the value of the intensity of magnetization $\boldsymbol{M}$ (in complex-number form) is

$$\boldsymbol{M} = \boldsymbol{\chi_c} H_{\boldsymbol{c}}\boldsymbol{k} + 2\chi^* H_0 e^{i\omega t}\boldsymbol{i}$$

where

$$\chi^* = \chi' - i\chi''$$

and χ_c is the static susceptibility(independent of ω).Thus the magnetic energy dissipated per unit volume per second is*

$$Q = \frac{\omega}{2\pi}\oint \boldsymbol{H} \cdot d\boldsymbol{M} = 2\omega\,\chi'' H_0^2$$

The value of $M_{z,s}$:

$$M_{z,s} = M_c - \tau_1\gamma A H_0$$

$$= \chi_c H_c \times \frac{1 + \tau_2^2(\omega_L - \omega)^2}{\tau_2^2(\omega_L - \omega)^2 + \tau_1\tau_2\gamma^2 H_0^2 + 1}$$

Graphs of variations of χ' and χ'' as functions of ω are given in Dekker's book. From the graphs (or the formulas) for these quantities it is clear that χ' behaves 'anomalously' near ω_L, and χ'' has a peak at ω_L as expected in a *resonance* phenomenon.

The real and imaginary parts of χ are actually related via the Kramers-Kroenig dispersion relations (See Jackson's Classical Electrodynamics or Dekker's book). Notice that $M_{z,s}$ is smaller than M_c. This is due to the pumping action of the oscillating magnetic field, which puts more electrons in the higher energy state ($\boldsymbol{\mu}_{\text{eff}}$ opposite to $\boldsymbol{H}$), through absorption of energy, than the case when there is no such oscillating field.

The actual experimental arrangement is shown in Fig. 5. See reference no. 3 for details of the experimental procedure.

Conclusion

Determination of the Lande *g*-factor for an unpaired electron in the $l = 0$ state by Zavoisky's technique is now a standard prescribed experiment in the post-graduate Physics syllabi of Indian universities. In the course of explaining to the I-Ph. D. students of the Bose Institute the principles involved in the measurement of *g*, we have felt the acute need for an article that collects together the relevant study materials. We have attempted to do just that. It is meant to complement the material presented in manuals furnished by the manufacturers of the instrument. Hope the students and teachers (laboratory instructors) would find the article useful.

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* See the Appendix for an alternative derivation.

References

1. The theory, given here, is an elaboration of the treatment developed in: Solid State Physics – A. J. Dekker.

2. The quantum mechanical theory, without the relaxation mechanisms, is given in: Modern Quantum Mechanics – J. J. Sakurai

3. The experimental arrangement depicted in Fig. 5 is described in:

www.iitr.ac.in/uploads/CMP (4. Electron spin resonance (ESR).pdf – IIT Roorkee)

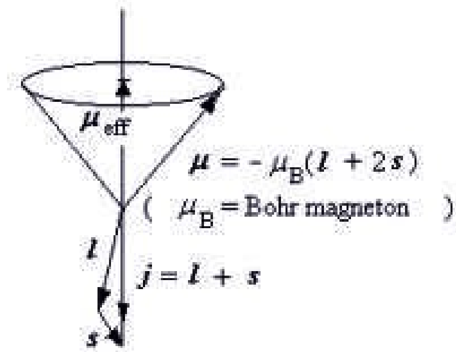

Fig. 1

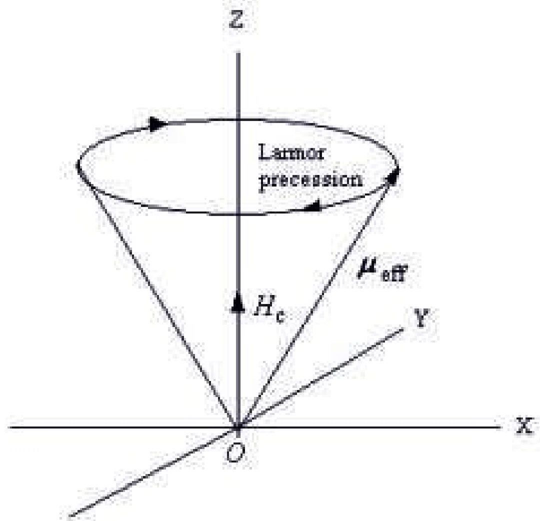

Fig. 2

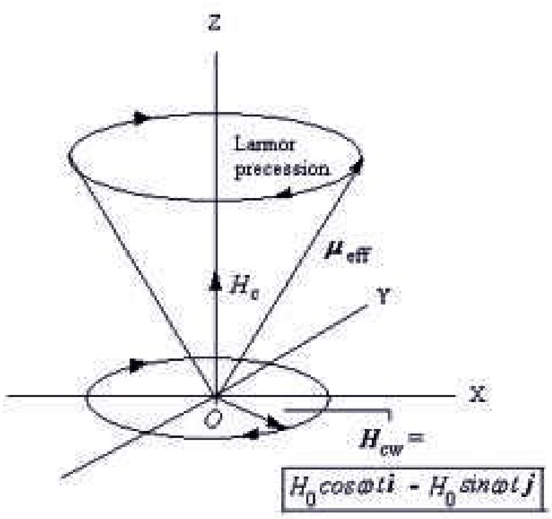

Fig. 3

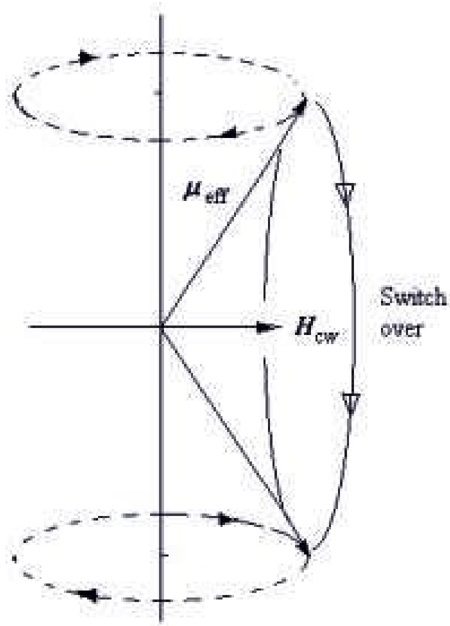

Fig. 4

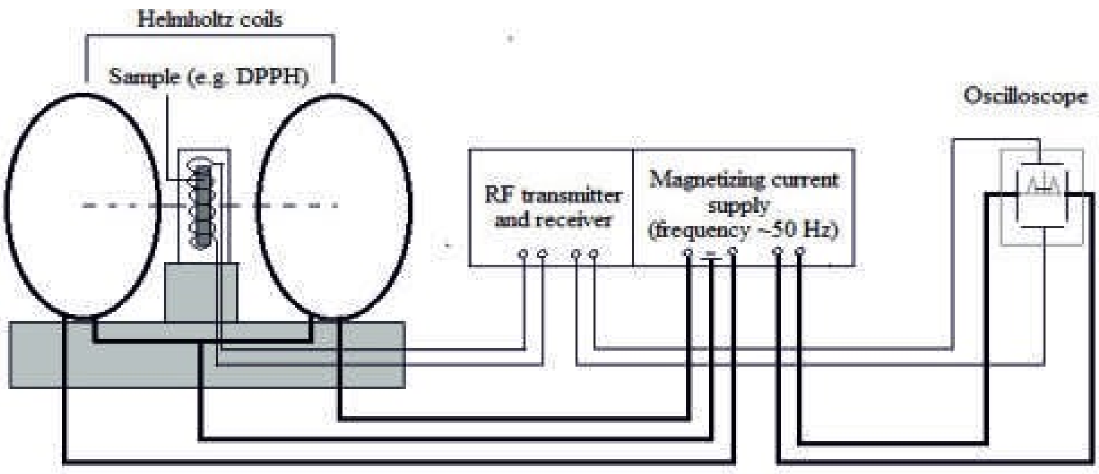

Fig. 5

Appendix

Alternative calculation of hysteresis loss:

Considering only the co-rotating component of the radiofrequency magnetic field (that induces the transitions) together with the constant magnetic field

$$\boldsymbol{H} = H_c\boldsymbol{k} + H_0 cos\omega t\boldsymbol{i} - H_0 sin\omega t\boldsymbol{j}$$

As before, magnetization ($\boldsymbol{M}$) is given by

$$\boldsymbol{M} = \chi_c H_c\boldsymbol{k} + [\chi'(2H_0 cos\omega t) + \chi''(2H_0 sin\omega t)]\boldsymbol{i} + [\chi''(2H_0 cos\omega t) - \chi'(2H_0 sin\omega t)]\boldsymbol{j}$$

Thus the hysteresis loss/ cycle is

$$Q = \frac{\omega}{2\pi}\oint \boldsymbol{H}\cdot d\boldsymbol{M}$$

or

$$Q = \frac{\omega}{2\pi}\int_0^T [H_0 cos\omega t\boldsymbol{i} - H_0 sin\omega t\boldsymbol{j}] \cdot \{[\chi'(-2H_0\omega sin\omega t) + \chi''(2H_0\omega cos\omega t)]\boldsymbol{i} + [\chi''(-2H_0\omega sin\omega t) - \chi'(2H_0\omega cos\omega t)]\boldsymbol{j}\}dt$$

$$= \frac{\omega}{2\pi}\cdot 2H_0^2\omega \cdot \int_0^T \{cos\omega t(\chi'' cos\omega t - \chi' sin\omega t) + sin\omega t(\chi'' sin\omega t + \chi' cos\omega t)\}dt$$

$$= \frac{\omega}{2\pi}\cdot 2H_0^2\omega \cdot \frac{2\pi}{\omega}\cdot\left[\frac{1}{2}\chi'' + \frac{1}{2}\chi''\right] = 2\omega\chi'' H_0^2$$

This is identical to what we have derived earlier.

(Thanks are due to Dr. Swapan Kumar Saha for suggesting this alternative approach.)