

# ELECTRON SPIN RESONANCE

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## INTRODUCTION

Electron paramagnetic resonance (EPR) or electron spin resonance (ESR) spectroscopy is a method for studying materials that have unpaired electrons. The basic concepts of EPR are analogous to those of nuclear magnetic resonance (NMR), but the spins excited are those of the electrons instead of the atomic nuclei. EPR spectroscopy is particularly useful for studying metal complexes and organic radicals. EPR was first observed in Kazan State University by Soviet physicist **Yevgeny Zavoisky** in 1944 and was developed independently at the same time by **Brebis Bleaney** at the **University of Oxford**.

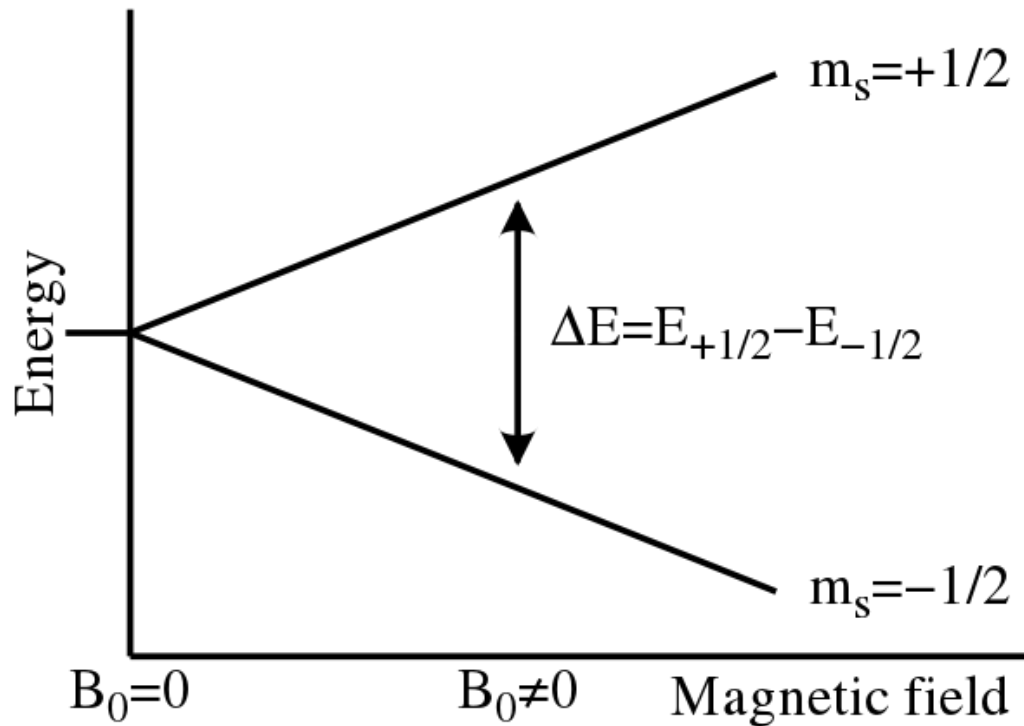
## Origin of an EPR signal

Every electron has a magnetic moment and spin quantum number  $s = \frac{1}{2}$ , with magnetic components  $m_s = +\frac{1}{2}$  and  $m_s = -\frac{1}{2}$ . In the presence of an external magnetic field with strength  $B_0$ , the electron's magnetic moment aligns itself either antiparallel or parallel to the field, each alignment having a specific energy due to the Zeeman effect :

$$E = m_s \cdot g_e \cdot \mu_B \cdot B_0$$

Where,

- $g_e$  is an electron's so-called g-factor( Landé g-factor) whose value is 2.0023 for the free electrons.
- $\mu_B$  is the Bohr magneton.



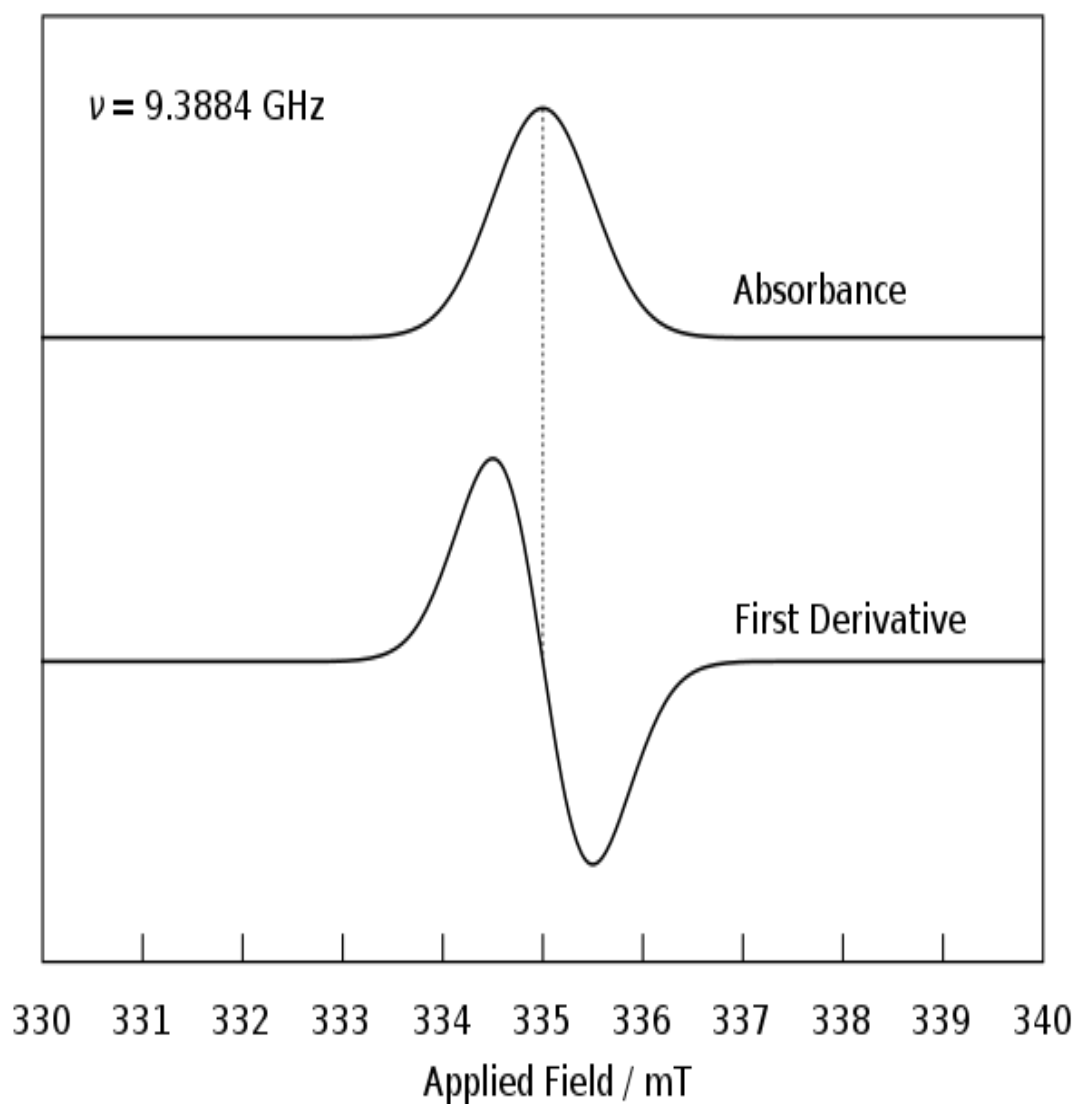
An unpaired electron can change its electron spin by either absorbing or emitting a photon of energy  $h\nu$  such that the resonance condition,  $h\nu = \Delta E$  is obeyed.

Hence, the fundamental equation of EPR spectroscopy is  $h\nu = g_e \mu_B B_0$ .

Experimentally, this equation permits a large combination of frequency and magnetic field values, but the great majority of EPR measurements are made with microwaves in the 9000–10000 MHz (9–10 GHz) region,

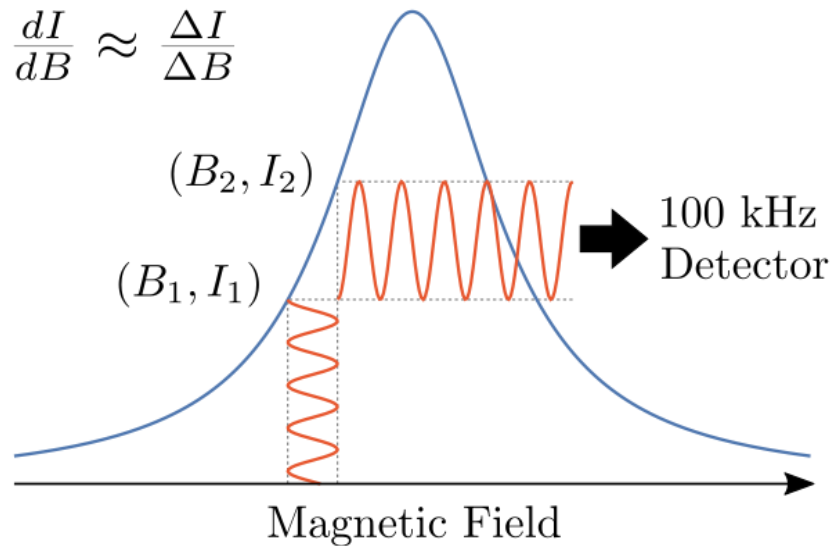
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with fields corresponding to about 3500 G (0.35 T). Furthermore, EPR spectra can be generated by either varying the photon frequency incident on a sample while holding the magnetic field constant or doing the reverse. In practice, it is usually the frequency that is kept fixed. A collection of paramagnetic centers, such as free radicals, is exposed to microwaves at a fixed frequency.



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### *Field modulation*



As previously mentioned an EPR spectrum is usually directly measured as the first derivative of the absorption. This is accomplished by using field modulation. A small additional oscillating magnetic field is applied to the external magnetic field at a typical frequency of 100 kHz.[4] By detecting the peak to peak amplitude the first derivative of the absorption is measured. By using phase sensitive detection only signals with the same modulation (100 kHz) are detected. This results in higher

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signal to noise ratios. Note field modulation is unique to continuous wave EPR measurements and spectra resulting from pulsed experiments are presented as absorption profiles.

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In real systems, electrons are normally not solitary, but are associated with one or more atoms. There are several important consequences of this:

- An unpaired electron can gain or lose angular momentum, which can change the value of its g-factor, causing it to differ from  $g_e$ . This is especially significant for chemical systems with transition-metal ions.
- Systems with multiple unpaired electrons experience electron–electron interactions that give rise to "fine" structure. This is realized as zero field splitting and exchange coupling, and can be large in magnitude.
- The magnetic moment of a nucleus with a non-zero nuclear spin will affect any unpaired electrons associated with that atom. This leads to the phenomenon of hyperfine coupling, analogous to J-coupling in NMR, splitting the EPR resonance signal into doublets, triplets and so forth. Additional smaller splittings from nearby nuclei is sometimes termed "superhyperfine" coupling.

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- Interactions of an unpaired electron with its environment influence the shape of an EPR spectral line. Line shapes can yield information about, for example, rates of chemical reactions.
  - These effects (g-factor, hyperfine coupling, zero field splitting, exchange coupling) in an atom or molecule may not be the same for all orientations of an unpaired electron in an external magnetic field. This anisotropy depends upon the electronic structure of the atom or molecule (e.g., free radical) in question, and so can provide information about the atomic or molecular orbital containing the unpaired electron.

### **Hyperfine coupling**

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Since the source of an EPR spectrum is a change in an electron's spin state, the EPR spectrum for a radical ( $S = 1/2$  system) would consist of one line. Greater complexity arises because the spin couples with nearby nuclear spins. The magnitude of the coupling is proportional to the magnetic moment of the coupled nuclei and depends on the mechanism of the coupling. Coupling is mediated by two processes, dipolar (through space) and isotropic (through bond).

This coupling introduces additional energy states and, in turn, multi-lined spectra. In such cases, the spacing between the EPR spectral lines indicates the degree of interaction between the unpaired electron and the perturbing nuclei. The hyperfine coupling constant of a nucleus is directly related to the spectral line spacing and, in the simplest cases, is essentially the spacing itself.

Two common mechanisms by which electrons and nuclei interact are the Fermi contact interaction and by dipolar interaction. The former applies largely to the case of isotropic interactions (independent of sample orientation in a magnetic field) and the latter to the case of anisotropic interactions (spectra dependent on sample orientation in a magnetic field). Spin polarization is a third mechanism for interactions between an unpaired electron and a nuclear spin, being especially important for  $\pi$  - electron organic radicals, such as the benzene radical anion. The symbols "a" or "A" are used for isotropic hyperfine coupling constants,

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while "B" is usually employed for anisotropic hyperfine coupling constants.

In many cases, the isotropic hyperfine splitting pattern for a radical freely tumbling in a solution (isotropic system) can be predicted.

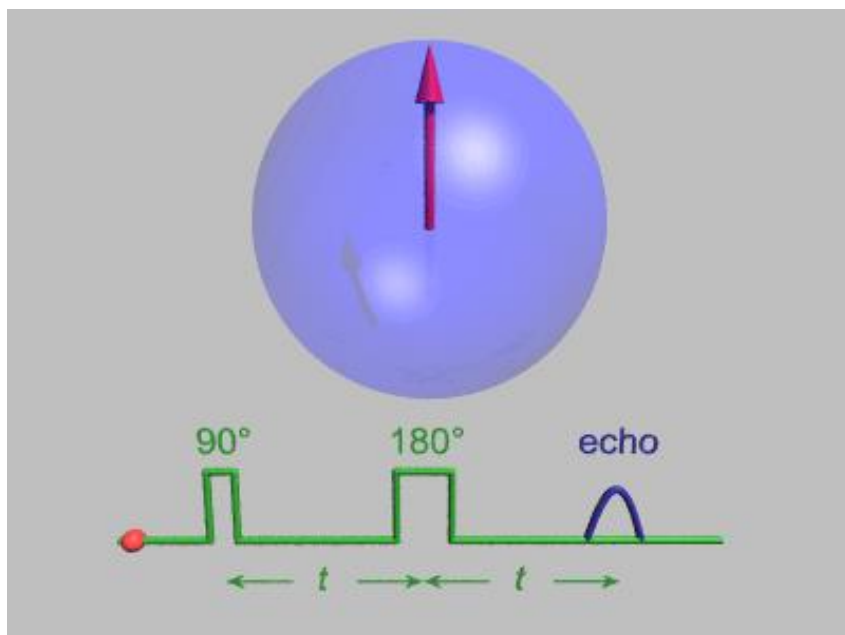
In the field of quantum computing, pulsed EPR is used to control the state of electron spin qubits in materials such as diamond, silicon and gallium arsenide.

Pulsed electron paramagnetic resonance (EPR) is an electron paramagnetic resonance technique that involves the alignment of the net magnetization vector of the electron spins in a constant magnetic field. This alignment is perturbed by applying a short oscillating field, usually a microwave pulse. One can then measure the emitted microwave signal which is created by the sample magnetization. Fourier transformation of the microwave signal yields an EPR spectrum in the frequency domain. With a vast variety of pulse sequences it is possible to gain extensive knowledge on structural and dynamical properties of paramagnetic compounds. Pulsed EPR techniques such as electron spin echo envelope modulation (ESEEM) or pulsed electron nuclear double resonance



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(ENDOR) can reveal the interactions of the electron spin with its surrounding nuclear spins.



Electron paramagnetic resonance (EPR) or electron spin resonance (ESR) is a spectroscopic technique widely used in biology, chemistry, medicine and physics to study systems with one or more unpaired electrons. Because of the specific relation between the magnetic parameters, electronic wavefunction and the configuration of the surrounding non-zero spin nuclei, EPR and ENDOR provide information on the structure, dynamics and the spatial distribution of the paramagnetic species. However, these techniques are limited in spectral and time resolution when used with traditional continuous wave methods. This resolution can be improved in pulsed EPR by

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investigating interactions separately from each other via pulse sequences.

### **Material characterization**

EPR/ESR spectroscopy is used in geology and archaeology as a dating tool. It can be applied to a wide range of materials such as organic shales, carbonates, sulfates, phosphates, silica or other silicates.] When applied to shales, the EPR data correlates to the maturity of the kerogen in the shale.

EPR spectroscopy has been used to measure properties of crude oil, such as determination of asphaltene and vanadium content.[18] The free-radical component of the EPR signal is proportional to the amount of asphaltene in the oil regardless of any solvents, or precipitants that may be present in that oil.[19] When the oil is subject to a precipitant such as hexane, heptane, pyridine however, then much of the asphaltene can be

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subsequently extracted from the oil by gravimetric techniques. The EPR measurement of that extract will then be function of the polarity of the precipitant that was used.[20] Consequently, it is preferable to apply the EPR measurement directly to the crude. In the case that the measurement is made upstream of a separator (oil production), then it may also be necessary determine the oil fraction within the crude (e.g., if a certain crude contains 80% oil and 20% water, then the EPR signature will be 80% of the signature of downstream of the separator).

EPR has been used by archaeologists for the dating of teeth. Radiation damage over long periods of time creates free radicals in tooth enamel, which can then be examined by EPR and, after proper calibration, dated. Similarly, material extracted from the teeth of people during dental procedures can be used to quantify their cumulative exposure to ionizing radiation. People (and other mammals) exposed to radiation from the atomic bombs, from the Chernobyl disaster] and from the Fukushima accident have been examined by this method.

Radiation-sterilized foods have been examined with EPR spectroscopy, aiming to develop methods to determine whether a food sample has been irradiated and to what dose.

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