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Introductory Chapter: Electron Paramagnetic Resonance

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1. Introduction

Electron paramagnetic resonance (EPR) is similar to the nuclear magnetic resonance (NMR) where both of them describe the case of resonance of an atomic particle as a result of high-frequency electromagnetic radiation absorption in the presence of external magnetic field. The main difference is that NMR is related to nucleus, while EPR is related to the unpaired electron.

1.1. Basic concepts

The electron, as a charged rotating particle, possesses a magnetic field which makes the electron appears as a minute magnet [1]. In normal cases, for the unpaired electron (single electron), the spin energy levels are degenerate, and electrons spin randomly.

After applying an external magnetic field, spin energy levels split, and electrons spin either aligned to or opposite to the direction of the magnetic field. Splitting of the spin energy levels results in the emergence of some energy difference (ΔE); hence, electrons aligned parallel to the external magnetic field and occupying the lower energy level are more than those aligned antiparallel to the external magnetic field and occupying the upper energy level.

When incident photon energy ($h\nu$) matches the energy difference between the two energy levels, some electrons are excited in the upper energy level and flip their spin direction. After a time (t_1), the relaxation time, excited electrons return to their original state emitting photons whose energy is equal to ΔE .

Such process is expressed by the following formula:

$$h\nu = \Delta E = gBHM \quad (1)$$

where h is Planck's constant, ν is the microwaves frequency, and g is the spectroscopic splitting factor: $g_e = 2.002319304386(20)$, where g_e is the spectroscopic splitting factor for a free electron [2, 3].

μ_B is Bohr magneton, B is the basic unit of a small magnet for an electron spin, H is the magnetic flux density of the external magnetic field, and M is the magnetic quantum number, $M: M = \pm 1/2$. **Figure 1** represents the process of electron spin resonance (ESR).

1.2. Spectrometer structure

A conventional continuous wave (cw) spectrometer is represented in **Figure 2**. The figure is composed of four groups: the source components, the magnet system, the detection system, and the modulation system. The function of the first group, the source, is to produce the electromagnetic radiation and holds the sample to be subjected to the incident waves. The source region also controls and directs the incident microwaves. The magnet system helps to provide the required magnetic field necessary for splitting the energy level; the field must be homogeneous and stable over the desired range. Both of the modulation system and the detection system act to amplify the received signal and to record it [3].

1.3. High-field high-frequency measurements

Usually, EPR measurements are carried out at X-band and Q-band due to the instrumental availability, where conventional electromagnets can provide up to 1 Tesla. However, higher spectral resolution needs led to the use of more advanced EPR measurements with higher microwave bands and more intensive magnets. Currently, there are many bands for EPR measurements according to the practical requirements. **Table 1** represents different microwave frequencies and the corresponding values for magnetic field [4, 5].

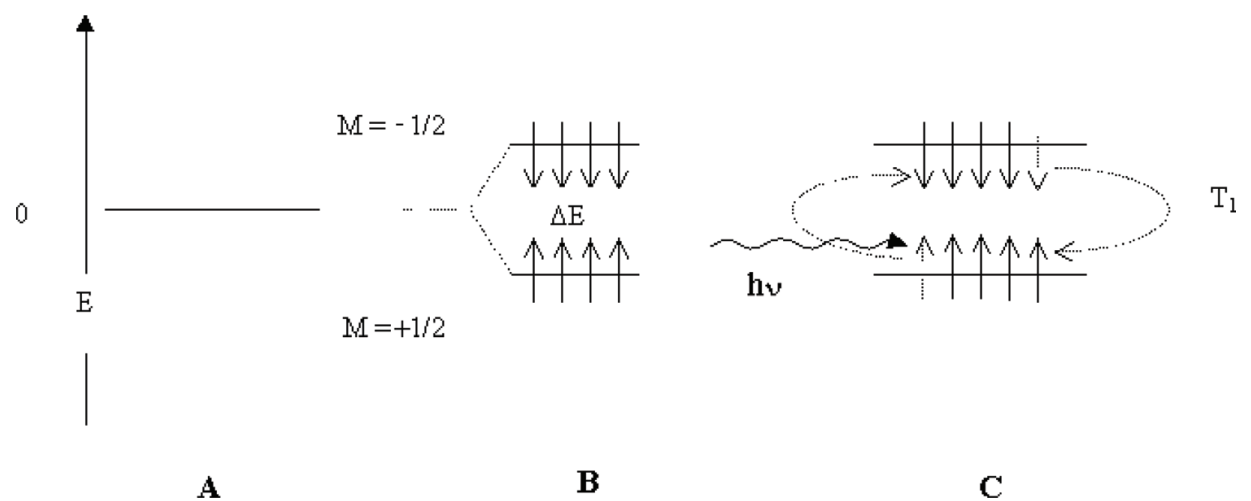


Figure 1. (A) No applied magnetic field and no spin levels splitting. (B) Energy separation of an unpaired electron spin under a magnetic field (Zeeman effect). (C) Flipping of spins by microwave absorption and flopping of spins within the spin-lattice relaxation time, T_1 .

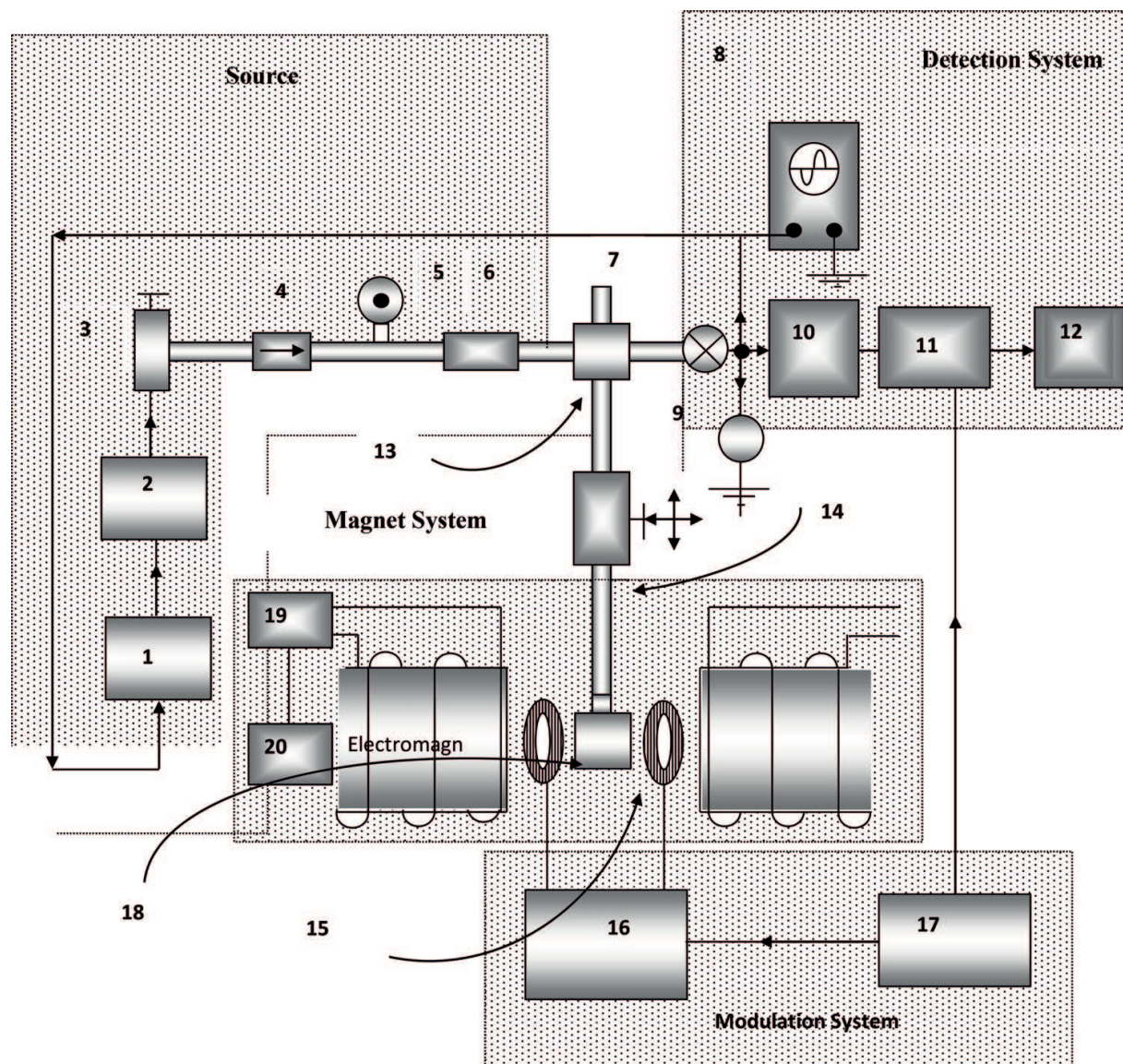


Figure 2. Block diagram of a typical X-band EPR spectrometer employing 100 kHz phase-sensitive detection. (1) Automatic frequency control. (2) Microwave source power supply. (3) Microwave source (klystron or Gunn diode). (4) Isolator. (5) Frequency counter. (6) Attenuator. (7) Terminating load. (8) Oscilloscope. (9) Detector crystal. (10) 100 kHz signal amplifier. (11) 100 kHz signal detector. (12) Pen recorder and data bank (or computer). (13) Circular or hybrid tee. (14) Cavity system. (15) 100 kHz modulation coils. (16) 100 kHz power amplifier. (17) 100 kHz oscillator. (18) Resonant cavity. (19) Magnet power supply. (20) Field scan drive [3].

Waveband	L	S	C	X	P	K	Q	U	V	E	W	F	D
λ/mm	300	100	75	30	20	12.5	8.5	6	4.6	4	3.2	2.7	2.1
ν/GHz	1	3	4	10	15	24	35	50	65	75	95	111	140
H/T	0.03	0.11	0.14	0.33	0.54	0.86	1.25	1.8	2.3	2.7	3.5	3.9	4.9

Table 1. Different microwave bands and the corresponding magnetic field.

The higher the frequency is used, the more intensive magnetic field is needed to reach the resonance. High-field high-frequency measurements can provide more detailed spectra and hence more molecular information.

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