Principles and Application of Electron Paramagnetic Resonance - Video course

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Chemistry and Biochemistry

COURSE OUTLINE

In this course, it is proposed to give a good foundation to the underlying principles and simple applications of Electron Paramagnetic Resonance (EPR) Spectroscopy, along with a detailed exposition of the EPR spectrometer and how to record and analyze simple EPR spectra. First a short historical development will be given which encompasses the discovery the Zeeman effect, the existence of electron spin and Zavoisky's observation of electron spin resonance. The hurdles and hostilities that these pioneers faced will be mentioned. Then the phenomenon of magnetic resonance will be discussed in terms of classical mechanics and quantum mechanics. The necessary conditions for experimental observation of the resonance will be elucidated and the experimental techniques will be elaborated. Often the approach will be that of an experimentalist, so that the necessary theoretical concepts will be built from experimentally observed features, and not the other way round. A good part

Pre-requisites:

Introductory Quantum mechanics as can be found in the NPTEL site. In particular, treatment of angular momentum is fundamental to the study by EPR.Perturbation theory both time-independent and time-dependent will be needed.

Additional Reading:

- C. P. Poole, Jr., *Electron Spin Resonance: A Comprehensive Treatise on Experimental Techniques*, 2nd edition, New York, John Wiley and Sons, 1983.
- J. R. Pilbrow, *Transition Ion Electron Paramagnetic Resonance.* Oxford, England:Clarendon Press, 1991.
- A. Abragam A and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions.* Oxford, England: Oxford University Press, 1970.

Hyperlinks:

- **EPR resources from National Institute of Health, USA:** http://www.niehs.nih.gov/research/resources/epresr/index.cfm
- **Computer programs under MATLAB for simulating and fitting Electron Paramagnetic Resonance (EPR) spectra:** http://www.easyspin.org/

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will be devoted to a detailed description of EPR instrumentations, so that one clearly understands how the principles of EPR spectroscopy are implemented in the spectrometers, and also the methods to enhance their sensitivity. A detailed guided tour will be conducted explaining how to record the best quality EPR spectra, and how to analyze first-order EPR spectra. EPR study of free radicals, especially organic, has yielded much valuable information, and these will be highlighted. Some emphasis will be placed on EPR studies related to photochemical reactions. This will include the means of recording EPR spectra of transient radicals through steady-state and time-resolved techniques and the spin trapping technique. The phenomenon of Electron Spin Polarisation (ESP), the more modern term of Chemically Induced Dynamic Magnetic Polarization, will be explained, and special EPR instrumentation to detect it will be described. Then a general outline of the importance of electron spin relaxation on the magnetic resonance spectroscopy will be given, the Bloch equations will be introduced and their significance in the EPR lineshapes will be highlighted. Throughout this course, the emphasis will be on building a physical picture, with minimum use of the mathematical rigour.

COURSE DETAIL

Module No.	Topic/s
1	**Lecture 1: Remembering the**

	Masters: From Zeeman to Zavoisky Zeeman's observation of splitting of spectral lines; the difficulty of explaining the origin of Zeeman effect; Bohr model of hydrogen atom; Pauli's exclusion principle; Stern-Gerlach experiment; Uhlenbeck and Goudsmit's idea of 'spinning motion' of electron and its initial dismissal by Pauli and Lorentz; Intrinsic magnetic moment and angular momentum of electron; Zavoisky's observation of electron paramagnetic resonance.	
2	**Lecture 2: Introduction to EPR spectroscopy** The Zeeman effect; Magnetic moment of an electron due its spin and orbital angular momenta; Combination of angular momenta and explanation of fine structures in atomic spectra; Magnetic moment in a magnetic field; Zeeman splitting of energy levels; Electron Zeeman vs nuclear Zeeman effect; Magnetic resonance spectroscopy; Resonance	

	condition; Field-swept vs frequency-swept EPR spectra; Observation of hyperfine lines in several organic free radicals and transition metal complexes and the existence of electron-nuclear hyperfine interaction.	
3	**Lecture 3: Electron-Nuclear Hyperfine Interaction – I** Understanding the electron-nuclear hyperfine interaction; Hydrogen atom; Hydrogen molecule ion (H2+); Nuclear spin-degeneracy and relative intensity of hyperfine lines; EPR spectra of benzosemiquinone anion radical, methyl radical; Pascal triangle for several equivalent spin - ½ nuclei; Hyperfine lines due nuclear spin *I* = 1; EPR spectrum of TEMPOL free radical. **Lecture 4: Electron-Nuclear Hyperfine Interaction – II** Hyperfine lines due nuclear spin *I* > ½; EPR spectra of copper diethyl dithio-carbamate complex containing naturally abundant	

	and isotopically pure 63Cu nucleus; Linewidths and intensities of various hyperfine lines; EPR spectrum of di-vanadyl complex; Pascal-like triangle for several equivalent nuclei with *I* > ½; EPR vs ESR – EPR spectrum of singlet oxygen molecule; splittings due to coupling of orbital angular momentum with rotational angular momentum.	
4	**Lecture 5: Magnetic Moment in Magnetic Field – I** Review of vector algebra: Right-hand Cartesian coordinate system, scalars and vectors, vector addition and multiplication; Motion of a bar magnet in a magnetic field; Oscillation; Relation between the magnetic moment and orbital angular momentum of an electron; Bohr magneton; Lorentz force; Tesla vs Gauss. **Lecture 6: Magnetic Moment in Magnetic Field – II** Motion of a bar magnet in a magnetic field, contd.; Oscillation vs precession; Time-dependence	

	of the magnetic moment in a magnetic field; Gyromagnetic ratio; Larmor frequency; Effect of a small rotating magnetic field applied perpendicular to the Zeeman field; Condition for magnetic resonance.	
5	**Lecture 7: EPR Instrumentation – I** Recapitulation of the requirements of EPR transition; Comparison between a basic EPR spectrometer and an optical spectrometer; Microwave components – waveguides, bends, twist; Different microwave frequencies and EPR spectrometers; Source of microwave – klystron and Gunn oscillator; Klystron mode; Microwave cavity – transmission and reflection type; Modes in a microwave cavity; Microwave oven; Perturbation of modes due to a sample; TE102 modes in a rectangular cavity; TE011 modes in a cylindrical cavity; Fixed frequency EPR spectrometer; Quality factor (Q) of a cavity and its	

importance in sensitivity of the spectrometer.

Lecture 8: EPR Instrumentation – II

Magnetic field and electromagnet; Helmholtz coil; Requirements on the homogeneity; Measuring the magnetic field – Hall-effect Gaussmeter and NMR Gaussmeter; Microwave detector; Non-linearity and biasing of the detector; Coupling of microwave from waveguide to the cavity – role of an iris and a tuning screw; Describing microwave power in relative unit (dB) and absolute unit (dBm).

Lecture 9: EPR Instrumentation – III

A transmission-cavity EPR spectrometer; Microwave circulator; A reflection-cavity EPR spectrometer; Matching the microwave frequency to the resonance frequency of the cavity; Coupling the microwave from the waveguide to the cavity – role of an iris and a tuning screw; Undercoupling, overcoupling and

	critically coupling of the cavity; Biasing the detector using a directional coupler; Use of attenuators and phase shifters in the spectrometer; Balancing the microwave bridge analogous to a Wheatstone bridge; Appearance of the EPR spectra – positive or negative; Direct-detection EPR spectrometer; Q value and the response time of a direct-detection EPR spectrometer. **Lecture 10: EPR Instrumentation – IV** Improving the sensitivity of the E P R spectrometer; Signal-to-noise ratio; Signal averaging; Principle of lock-in or phase-sensitive detection; Magnetic field modulation and phase-sensitive detection; EPR spectrum in first-derivative form; Second-derivative form of EPR spectrum; Factors deciding the sense of the derivative spectrum; Magnetic f i e l d modulation and side bands; Effect on the response time of the spectrometer; Automatic frequency control of the microwave source.	
6	**Lecture 11: Quantum**	

		Mechanical Description of EPR – I Recapitulation of the classical view of EPR transition; Basics of quantum mechanics – wave function, time-dependent and time-independent Schrödinger equations; Angular momentum and its allowed values; Stationary states in quantum mechanics; Magnetic moment in a Zeeman magnetic field; Allowed states and energies; Rotating magnetic field in the *xy* plane; First-order time-dependent perturbation calculations. **Lecture 12: Quantum Mechanical Description of EPR – II** First-order time-dependent perturbation calculations, contd; Time-dependent evolution of states; Transition probability; Resonance condition.	
	7	**Lecture 13: Introduction to Spin Relaxation** Absorption, spontaneous emission and stimulated emission processes; Need	

	for relaxation processes in magnetic resonance spectroscopy; Phenomenological derivation of spin-lattice relaxation as an exponential process; Physical meaning of the spin-lattice and spin-spin relaxation processes; Role of the relaxation process in the appearance of EPR spectra.	
8	**Lecture 14: Theory of First-order EPR Spectra – I** Hamiltonian of hydrogen atom; Magnetic interactions and spin hamiltonian; Hamiltonian for Zeeman interaction; Hamiltonian for electron-nuclear dipolar interaction and its directional dependence; Hamiltonian for electron-nuclear isotropic hyperfine interaction; Importance of *s*-type of orbitals; Separating the total hamiltonian into a main unperturbed Hamiltonian and a perturbation hamiltonian. **Lecture 15: Theory of First-order EPR Spectra – II** Zeroth order wavefunctions and energies of	

	hydrogen atom; Splitting of energy levels due to electron Zeeman, nuclear Zeeman and electron-nuclear hyperfine interactions; Selection rules and allowed transitions; Frequency-swept and field-swept EPR spectra; First-order perturbation calculations and EPR spectra.	
9	**Lecture 16: How to Analyse First-order EPR Spectra** Recapitulation of the characteristics of first-order EPR spectra; Measuring isotropic hyperfine splitting constants of several free radicals using a ruler and a divider; Identifying the number of equivalent nuclei and their spins; What to do when the outer hyperfine lines are buried in the noise level; Use of computer programs for analysing and simulating first-order EPR spectra.	
10	**Lecture 17: How to Record EPR Spectra** Solid, liquid or gaseous sample; EPR sample tubes; Sample preparation;	

	Degassing and sealing of EPR samples; Choice of solvents; Polar solvents and use of capillary tubes and EPR flat cells; Sample placement inside the microwave cavity; Setting up the EPR spectrometer – tuning the microwave frequency, coupling, and AFC; Optimizing the magnetic field position, scan range, modulation amplitude, microwave power, scan time and output filter time-constant, the phase of the microwave bias power and the reference phase of magnetic field modulation frequency.	
11	**Lecture 18: Second-order Effects on EPR Spectra** Why second-order calculations; Spin hamiltonian of hydrogen atom; Separation of unperturbed and perturbation hamiltonians; First-order wavefunctions and energies; Second-order calculation of energies; Transition energies; Fixed-magnetic field and fixed-frequency EPR spectra; Distinction between	

		hyperfine splitting constant and hyperfine coupling constant; Second-order correction for calculating the *g*-values; EPR spectrum of CF·3 radical; Second-order calculations of R-CH·2 radical; Second-order effects on the EPR spectrum of a tri-nuclear Co complex.	
	12	**Lecture 19: Photochemistry and EPR Spectroscopy** Formation of paramagnetic species by photoexcitation; Means to record EPR spectra of transient radicals; Modifications for *in situ* photolysis; Need for flowing the reactants; Temperature control; Steady-state EPR spectra under continuous photolysis; Photolysis of *p*-benzoquinone in alcohol; Photolysis of acetone in 2-propanol;Spin-trapping technique; PBN and DMPO as the trapping agents; Spin-trapping experiment on photolysis of *p*-benzoquinone in alcohol; Problems with spin-trapping EPR studies; Time-resolved EPR spectroscopy; Recording EPR	

	spectra of transient species by time-resolved EPR technique; EPR spectrum at a given time; Time evolution of EPR signal at a given magnetic field; Photolysis of duroquinone in triethylamine; Photolysis of acetone in 2-propanol;Non-Boltzmann spin distribution and electron spin polarisation.	
13	**Lecture 20: Electron Spin Polarisation – I** Example of spin-polarised EPR spectra – photolysis of acetone in 2-propanol; Definition of polarisation; The first observation of spin-polarised EPR spectra of H and D atoms; Evidence of electron spin polarisation in steady-state EPR spectra; Comparison of steady-state and time-resolved EPR spectra during the photolysis of *p*-benzoquinone in 2-propanol; Spin-polarised NMR spectra; CIDEP, CIDNP, CIMP and Electron spin polarisation (ESP); Types of spin-polarised EPR spectra; Mechanism of single-phase hyperfine-independent	

	electron spin polarisation – the triplet mechanism (TM); Conditions for TM to operate; Characteristics of EPR spectra arising from TM. **Lecture 21: Electron Spin Polarisation – II** Mechanism o f mix-phase hyperfine dependent electron spin polarisation; Importance of a pair of radicals and their evolution; Radical pair mechanism (RPM); Overall spin states of the radical pair and interconversion of singlet and triplet radical pairs; Importance of the difference in the frequencies of precession; Conditions for RPM to operate; Characteristics of EPR spectra due to RPM; Dominance of TM or RPM in observed time-resolved EPR spectra; Insight into the detailed dynamics of photophysical and photochemical pathways from spin-polarised time-resolved EPR spectra.	
14	**Lecture 22: Anisotropic Interactions in EPR Spectroscopy** Common	

	examples of anisotropic properties; Averaging of anisotropic properties due to rapid tumbling motions; Need for restricted motion; Origin of *g*-anisotropy; *g*-matrix; *g*2-matrix; Principal axes and principal values of the *g*-matrix; Effective *g*-values; Symmetry of crystals; Examples of anisotropic EPR spectra of vacancies in single crystals; EPR lineshapes from powder samples or frozen solutions; Examples of powder EPR spectra; Electron-nuclear dipolar interaction; Anisotropic hyperfine coupling constants; Principal values of the hyperfine coupling constants; Powder patterns due to anisotropic hyperfine coupling; Lineshapes due to combined effects of *g*-anisotropy and hyperfine anisotropy.	
15	**Lecture 23: Theoretical Basis of isotropic Hyperfine Coupling** Hamiltonian of the isotropic hyperfine interaction; Role of the wavefunction in	

	determining the isotropic hyperfine coupling constant; Concepts of electron density, spin density and spin population; Meaning of negative spin density; Determinantal wavefunction; Atomic spin population; Relation between spin population of C-atom and the hyperfine splitting due to the H-atom in >C·H radical; Configuration mixing.	
16	**Lecture 24: Spin Relaxation and Bloch Equations – I** Magnetisation; Boltzmann distribution of spins at thermal equilibrium; Magnetic susceptibility and Curie law; Non-equilibrium magnetisation and electron spin relaxation process; Bloch's proposal of longitudinal (spin-lattice) and transverse (spin-spin) relaxation processes; Time dependence of magnetization in the presence of relaxation – Bloch equations. **Lecture 25: Spin Relaxation and Bloch Equations – II**	

	Time dependence of magnetization in the presence of relaxation – Bloch equations in the laboratory coordinate system. Rotating coordinates; Time dependence of a vector in a rotating coordinate system; Bloch equations in a rotating coordinate system; Physical meaning; Steady-state solutions of Bloch equations in the rotating coordinate system; EPR lineshapes – absorption and dispersion EPR signals; Measuring the relaxation times from the EPR lineshapes, and problems associated with that; Bloch equations as a function of magnetic field.

References:

The list here is merely suggestive and possibly representative. There are many other good books and course materials as well.

1. Principles of Electron Spin Resonance (Ellis Horwood Series in Physical Chemistry)
N. M. Atherton
Hardcover: 500 pages
Publisher: Ellis Horwood Ltd; Revised edition (October 1993)
Language: English
ISBN-10: 0137217625

ISBN-13: 978-0137217625

2. Electron Paramagnetic Resonance: Elementary Theory and Practical Applications, 2nd Edition
John A. Weil, James R. Bolton
ISBN: 978-0-471-75496-1
Hardcover
664 pages
Publisher: Wiley (March 2007)
3. Electron Spin Resonance Spectroscopy of Organic Radicals
Fabian Gerson and Walter Huber
Edition - July 2003
XV, 464 Pages, Softcover
ISBN-10: 3-527-30275-1
ISBN-13: 978-3-527-30275-8
Wiley-VCH, Weinheim
4. Electron Spin Resonance:Analysis and Interpretation
Philip Rieger
ISBN: 978-0-85404-355-2
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