CHEM862 - *Magnetism & Paramagnetic Resonance*: Topics listing - Sept. 2011.

Prerequisite abilities: *d*-Configurations of transition metal ions; common crystal-field *d*-orbital splitting patterns.

Magnetism.

• Simple types of chemically relevant magnetism.
• Electronic configuration and magnetism: spin-orbit couplimg.
• Paramagnetism
• Relationships between multiplet splittings and *kT*.
• Quenching of OAM by CF splitting
• Effect of SOC on paramagnetic moment
• Temperature Independent Paramagnetism
• Doodling with data: Curie-Weiss law, Plots of $1/\chi$ *vs*. T, μ *vs*. T, χ *vs*. T, χT *vs*. T for paramagnets.
• Spin-crossover compounds
• Pascal's constants, Gouy method, Evans' method, the SQUID.
• Dinuclear compounds: exchange coupling between like & unlike halves - ferromagnetism and antiferromagnetism; *J*-values.
• Zero-field splitting - effects on paramagnetism & (anti)ferromagnetism - *D*-values.
• Coupling mechanisms - dipolar & superexchange, orbital topology.
• Other oligonuclear systems; magnetic chains - Baker, Ising & Heisenberg models.

ESR (EPR)

• Zeeman splitting and the origin of ESR.
• Electron/nucleus spin interactions.
• *g*-Values.
• Hyperfine & superhyperfine structure: stick spectra, spin polarisation.
• *g*-Anisotropy.
• Zero-field splitting.
• Crystal-field splitting: copper(II) examples.
• Cu(II) ESR: second-order field dependence.
• Quadrupole moments.
• Cu(II) ESR: (non)axial spectra.
• Spin relaxation.
• Iron ESR: low-spin iron(III).
• Rhombic & tetragonal distortions: Palmer, Gibson, Peisach/Blumberg models.
• Iron ESR: high-spin iron(III): rhombic distortions.
• Vanadium(IV).

Sources for CHEM.862 Topic: Molecular Magnetism & Paramagnetic Resonance
Fall 2011 (to be revised during Sept. 2011)

MagESR.Refs-22

Terms & States:

Standard inorganic texts, such as Cotton & Wilkinson; Housecroft & Sharpe's *Inorganic Chemistry*; Atkins *et al.*'s *Shriver & Atkins Inorganic Chemistry*; Gray's *Electrons & Chemical Bonding*; Drago's *Physical Methods for Chemists* (Saunders 1992); More specialized texts on atomic properties deal further with *J*-states and *jj* coupling.

Magnetism:

• R. L. Dutta & A. Syamal, *Elements of Magnetochemistry* (Affiliated East-West Press Pvt. Ltd., Delhi, 1993, ISBN 81-85336-92-X) [Reasonably current, comprehensive and cheap, but in and out out of print. Has chapters on ESR. Also look for 'Dutta Rabindra Lal' for apparent sole author version, *ca*. $35]

• A. Earnshaw, *Introduction to Magnetochemistry* (Academic Press 1968) [Out of print classic, with the essentials of transition metal paramagnets]

• A.F. Orchard, *Magnetochemistry*, Oxford U. Press, Oxford, 2003 (pb). [One of the few extant and available "textbooks" on magnetochemistry, but it's a bit quirky – *e.g.*, quirky symbolism, and the Index is pathetic.]

• F. E. Mabbs and D. J. Machin, *Magnetism and Transition Metal Complexes*, Dover, 2008. [$15 paperback reprint of the useful original; similar to Earnshaw.]

• S. Hatscher, H, Schilder, H. Lueken & W. Urland, *Practical guide to measurement and interpretation of magnetic properties*, *Pure Appl. Chem.* **77** (2005) 497-511. [This is the 'definitive' IUPAC guide & recommendations. Maybe this is all one needs ?]

• O. Kahn, *Molecular Magnetism* (VCH Publishers, New York, 1993). [Olivier's great '90's magnetochem. classic. You can pick up an unsigned copy for less than $2K]

• Eds. E. A. Boudreaux, L. N. Mulay, *Theory and Applications of Molecular Paramagnetism.* (Wiley, NY, 1976: QC763.T47) [A comprehensive source with useful example data tables]

• R. S. Drago's *Physical Methods for Chemists* (Saunders 1992). [Coverage much curtailed *vs*. 1st edition]

• P.W. Selwood, *Magnetochemistry*, Interscience, 1948 & 1956 [another classic with some useful descriptions & examples]

• L.N. Mulay & E.A. Boudreaux (Eds.) *Theory and applications of molecular diamagnetism*, Wiley, New York, 1976 (QD591 .T47 1976) [Just what it says, with some tabulated data. Like reading a murder mystery novel, but with no murder & no characters.]

• C. J. O'Connor, *Magnetochemistry - Advances in Theory & Experimentation, Progr.*

Inorg. Chem. **29** (1982) 203-283. [Quite a useful source - has heterobinuclear eqns.]

• S. Blundell, *Magnetism in Condensed Matter*, Oxford U. Press, 2001 (in Hagerty) QC173.458.M33 B58. [handy Physics book; the paperback has an odour like cat piss]

• Eds. R. D. Willett, D. Gatteschi, O. Kahn, *Magneto-Structural Correlations in Exchange-Coupled Systems* (Dordrecht/Reidel/Kluwer, Boston, 1983). [Specialized]

• B. N. Figgis & J. Lewis, *The Magnetic Properties of Transition Metal Complexes*, in *Prog. Inorg. Chem.* (1964) **6**, 37-239. [Similar to Earnshaw's approach, plus examples]

• M. M. Turnbull, T. Sugimoto, L.K. Thompson, *Molecule-Based Magnetic Materials* (ACS Symposium Series #644, 1996) [Specialized, but with O'Connor chapter on exptl. methods] QD940.M66.1996

• O. Kahn [Magnetism of Heteropolymetallic Systems] *Structure & Bonding (Berlin)* 1987, **68**, 89.

• http://www.auburn.edu/~youngd2/topics/magnet.html [general introduction]

• S. G. Vulfson, *Molecular Magnetochemistry*, Gordon & Breach 1998: QD591.V85.1998. [A Russian from St. Louis. Magnetique & electrical properties of small molecules. Not so hot for inorganic complexes, but has μ-tables and OK bit on expt'l. methods.]

• References on spin-crossover systems:
(a)Iron(II) tris(diimine) & bis(terimine) systems, H.A. Goodwin, *Topics Curr. Chem.* **233** (2004) 59-90.
(b) Iron(II) spin crossover compounds, P.J. van Koningsbruggen, Y. Maeda, H. Oshio, *Topics Curr. Chem.* **233** (2004) 259-324.
(c) Thermal spin crossover in Mn(II), Mn(III), Cr(II), Co(III) compounds, Y. Garcia, P. Gütlich, *Topics Curr. Chem.* **234** (2004) 49-62
(d) Spin crossover in cobalt(II) systems, H.A. Goodwin, *Topics Curr. Chem.* **234** (2004) 23-47.
(e) Light-induced spin crossover, A. Hauser, *Topics Curr. Chem.* **234** (2004) 155-198; Photomagnetism, P. Gütlich, Y. Garcia, T. Woike, *Coord. Chem. Rev*. 219/221 (2001) 839.
(f) Iron(II) spin crossover systems with multidentate ligands, H. Toftlund, J.J. McGarvey, *Topics Curr. Chem.* **233** (2004) 151-166.
(g) Cooperativity in spin crossover systems, K.S. Murray, C.J. Kepert, *Topics Curr. Chem.* **233** (2004) 195-228.
(h) E. König, *Prog. Inorg. Chem.* **35** (1987) 527; *Struct. Bonding (Berlin)* **76** (1991) 51.
(i) H. Toftlund, *Coord. Chem. Rev*. **94** (1989) 67-108 [iron(II)]
(j) König *et al., Chem. Rev.* **85** (1985) 219-234 [iron(II)]

Sources on ESR.

• *Electron Spin Resonance – Analysis and Interpretation*: P.H. Rieger, RSC Publishing, Cambridge, 2007. QC763.R54.2007.
At long last – a post-2000 ESR textbook that is maybe actually useful as a course text !

• *Biochemical Applications of Electron Spin Resonance (ESR) Spectroscopy*: D. Kosman & R.D. Bereman, in *Spectroscopy in Biochemistry*, Vol.II, Ed. J.E. Bell, CRC Press, 1981, pp57-108.
Written for the "layman" (*i.e.*, biochemists !) - a quite readable introduction to ESR, with bioinorganic & copper(II) examples and discussion of the "overshoot" Cu-line. Oxovanadium(IV) also discussed.

• *Electron Spin Resonance - Elementary Theory & Practical Applications*: J.E. Wertz & J.R. Bolton, McGraw-Hill, New York 1972 (1st.), 1986 (2nd.).
Fairly comprehensive and readable modern text.

• *Transition Ion Electron Paramagnetic Resonance*: J.R. Pilbrow, Clarendon Press, Oxford 1990.
An interestingly immodest modernization of the classical chemical physics approach of Griffith, Bleaney, Abragam *et al*. Quite comprehensive, and much of it is actually readable.

• Drago's *Physical Methods* has a survey section on 3d T.M. ESR (13-5).

• *Electron Paramagnetic Resonance of d Transition Metal Compounds*. F. E. Mabbs & D. Collison, Elsevier 1992 (Studies in Inorganic Chemistry #16).
A thick, costly book with lots of equations, simulations of energy levels and spectral properties. Covers Fe(II). Hardly a choice for reading on the beach, but if you find a copy for only $350, maybe you should buy it for profit.

• *Theory & Applications of Electron Spin Resonance*: W. Gordy, Vol. XV of *Techniques of Chemistry* Series, Eds. W. West/ A. Weissberger, Wiley-Interscience, New York, 1980.
Readably written in less mathematical language for the chemist rather than physicist - a good place to find lots of useful tidbits. Not much on transition metals.

• *Electron Paramagnetic Resonance of Hemoproteins*: G. Palmer, in *The Porphyrins*, Vol. IV - Physical Chemistry Part-B, Ed. D.H. Dolphin, Academic Press, New York 1979, pp 313-353.
Oft-cited source of theory and some examples for heme iron ESR.

• N. D. Chasteen, *Vanadyl(IV) EPR Spin Probes: Inorganic & Biochemical Aspects*, in *Biological Magnetic Resonance*, Eds. L.J. Berliner & J. Reuben, Vol. 3, Plenum, NY 1981, pp 53-114. [Lucid vanadyl ESR, from the doyen thereof.]

• B.J. Hathaway & D.E. Billing, *Coord. Chem. Revs*. (1970) **5**, 143-.
The classic source of fundamentals in ESR of copper(II) in various structural situations, and how to interpret the spectra. It had its detractors, principally Dom McKenzie: *J. Chem. Soc. (A)* (1970) 3095-3099, though he tackles only the UV-Vis interpretations.

• A. Bencini & D. Gatteschi, *ESR Spectra of Metal Complexes of the First Transition Series in Low-Symmetry Environments*, in *Transition Metal Chemistry: a Series of Advances*, Vol. 8, Eds. G.A. Melson & B. N. Figgis, M. Dekker, New York, 1982 (QD172.T6.T7.V8.1982)

• T.F. Yen, Ed.: *Electron Spin Resonance of Metal Complexes*, Plenum NY, 1969 (QD475.S9.1968)

• ESR of particular biometallic systems: various volumes in the *Methods in Enzymology* series: *e.g.*, #226, #227, #232(?), earlier ones Ed. by Hirs/Timasheff ?

• Reviews:*Electron Spin Resonance*: Specialist Periodical Reports of the Royal Society of Chemistry (Annually).

• *Plots of $A_{||}$ vs. $g_{||}$ for Cu(II) systems:*
1) J. Peisach & W.E. Blumberg, *Arch. Biochem. Biophys*. (1974) **165**, 691-.
2) A.W. Addison, *Spectroscopic & Redox Trends from Model Copper Complexes*, in *Copper Coordination Chemistry: Biochemical & Inorganic Perspectives*, Eds. K.D. Karlin & J. Zubieta, Adenine Press, NY, 1983, pp 109-128.

• *EPR of iron in biological systems*: Gibson, J. F., in *ESR and NMR of Paramagnetic Species in Biological and Related Systems* (Proc. NATO Adv. Study Inst., Acquafredda di Maratea, Italy, June 1979) Eds. Bertini, I; Drago, R. S., 1979, D. Reidel Publishing Co., Dordrecht, pp225-248
References, and one of the popular varieties of theoretical models for iron(III) EPR:

• Rhombicity maps for low-spin Fe(III) hemes:
1) Peisach, Blumberg & Adler: *Electron Paramagnetic Resonance Studies of Iron Porphin & Chlorin Systems*, *Ann. NY Acad. Sci.* (1973) **206**, 311-327.

2) Blumberg & Peisach, *Low-Spin Compounds of Heme Proteins*, in *Bioinorganic Chemistry: ACS Advan. Chem. Ser.* (1971) **100**, 271-291

3) Blumberg & Peisach, *Low-Spin Compounds of Heme Proteins*, in *Probes of Structure & Function of Macromolecules & Membranes*, Eds. B. Chance, C.P. Lee & T. Yonetani, Academic Press, NY, (1970) Vol.-2, pp 215-227.

4) Anisotropy scale for high-spin Fe(III) hemes:
(a) *Departures from axial symmetry as measured by EPR for high spin ferric heme proteins*: Peisach, J.; Blumberg, W. E., in *Probes Struct. Funct. Macromol. Membranes, Proc. Colloq. Johnson Res. Found., 5th* Ed: Chance, B., 1971, Academic Press, NY, Vol- 2, pp 231-9
(b) *Effects of protein conformation on the heme symmetry in high spin ferric heme proteins as studied by electron paramagnetic resonance*: Peisach, J.; Blumberg, W. E.; Ogawa, S.; Rachmilewitz, E. A.; Oltzik, R., *J. Biol. Chem.* **1971**, *246* , 3342-55.