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Electron Spin Resonance

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INTRODUCTION

1a). Plan of Lectures

In the last 10 years an increasing amount of research has been done related to the measurement of the slow tumbling of macromolecules, and an excellent review is given by J. S. Hyde and D. D. Thomas in Ann. Rev. Phys. Chem. 31, 293 (1980). This slow tumbling may be characterized quantitatively by a recently developed electron spin resonance (ESR) technique called saturation transfer (ST). The method consists in attaching a nitroxide paramagnetic molecule called a spin label to a particular site on a macro-molecule and using the instrumental technique of ESR to determine the extent of tumbling from an analysis of the spectra. Hyde and Thomas give a comprehensive list of applications and references

We believe that the subject is quite interesting with a great many things to be done in the area of biological applications. We selected the explanation of saturation transfer as the main purpose of these lectures.

There are two aspects of ESR which must be discussed in detail before we can explain the basic mechanisms involved in saturation transfer, and these are the static aspect which is anisotropy and the dynamic aspect which is saturation.

To understand anisotropy we must first understand what we mean by an anisotropic hamiltonian, how to treat it, and what we can expect its spectrum to look like. In turn to understand this we must have some knowledge of transition probabilities, perturbation theory, and matrix representations. To understand the dynamic aspect, that is to say saturation, we must have a knowledge of the Bloch equations.

1b). Basic Spectroscopy

EPR is a branch of spectroscopy, and like any other branch it requires a source of electromagnetic radiation, a sample and a detector. The different spectroscopic methods deal with the different energy gaps. It could be nuclear spectroscopy where the energies are high and the photons have a frequency in the range of 10^{18} to 10^{23} Hz or it could be infrared spectroscopy where the photons will have frequencies in the range 10^{12} to 10^{14} Hz.

1c). Instrumentation

Typical EPR spectroscopy, called X band uses photons of about 10^{10} Hz. The source of radiation, for this frequency is a device called a Klystron The E-M radiation travels through the wave-guide to the cavity and other devices. The reason for using waveguides is that at these frequencies a simple wire will have a large impedance due to what is called its skin deph.

The cavity and the so called Magic tee (slide 3) are equivalent to an AC bridge. Basically if the bridge is balanced the detector detects nothing, but when absorption is obtained in the sample the R part of the impedance of the cavity arm in the bridge, increases, the bridge becomes unbalanced and the detector detects a current.

People that use EPR know that actually you never adjust the bridge to zero detection and the reason is that the microwave crystal detector has more sensitivity when it is biased.

Very seldom is the absorption observed because if we want to cut noise we must reduce the number of high frequency components of the signal, if we do so the amplifiers and electronics in general will be the DC type which in turn are prone to instabilites.

To solve this a modulation of the magnetic field is superimposed on the external field. In this way the signal is modulated resulting in a signal proportional to the derivative of the absorption curve. A phase sensitive detector or lock-in-amplifier is used to detect and amplify the signal.

The same type of electronic modulation at another frequency is used to keep the klystron automatically locked to the frequency of the cavity of an EPR.

1d) Experimental Details

In a typical experiment the first step is to decide whether the sample will be liquid or solid. This difference is esential in the sense that many organic materials in solution use water or other polar solvents, and when placed inside the cavity they produce a strong absorption of the microwave radiation, reducing the Q of the cavity and consquently the signal to the point where it may disappear. On the other hand if it is solid then most of the time this problem does not arise. To solve the problem of liquids a special flat cell is used to reduce the losses.

For a solid a typical size is 2 or 3 mm x 4 or 5 mm x 4 or 5 mm and the volume of the liquid in a flat cell is about 1/2 mm x 5 mm x 20 mm. In either case there should be of the order of 10^{12} spins to be able to detect a signal.

EPR allows variable temperatures from below liquid helium, say 2 K obtained be pumping liquid helium to 473 K obtained with a small oven surrounding the cavity.

1e) Systems Studied

Typical chemical systems that have been studied by ESR are polymers, catalysts, rubber, long-lived free radicals, free radical intermediates, charred carbon, and chemical complexes, especially with transition metals.

A free radical is a compound which contains an unpaired spin, such as the methyl radical $\cdot CH_3$ produced through the breakup of methane

$$CH_4 \rightarrow \cdot CH_3 + \cdot H$$

where both the hydrogen atom and the methyl radical are electrically neutral. Free radicals have been observed in gaseous, liquid, and solid systems. They are sometimes stable, but usually they are short lived intermediates in chemical reactions.

Free radicals and radical ions ordinarily have g-factors close to the free electron value of 2.0023 (e.g., for DPPH $g = 2.0036$). In low viscosity solutions, they exhibit hyperfine patterns with a typical overall spread of about 25 gauss. The scrupulous removal of oxygen often reveals hitherto unresolved structure. In high-concentration solids, a single exchange narrowed resonance appears ($\Delta H_{pp} \sim 2.7$) gauss for DPPH prepared form benzene solution. In irradiated single crystals the free radicals may have strongly anisotropic hyperfine interactions and slightly anisotropic g-factors.

Experimentally, the following have been detected by ESR: stable solid free radicals (a single exchange-narrowed resonance); stable free radicals in solution (hfs obtained); free radicals produced by irradiation (often at low temperature; sometimes single crystals); condensed discharges (free radicals produced in a gas condensed on a solid at low temperature); biological systems; biradicals; electrochemical generation of radical ions (polarography); triplet states; paramagnetic molecules (e.g., NO, NO_2, and ClO_2); and intermediates in chemical ractions.

Radical ions of many organic compounds can be produced in an electrolytic cell which is usually a flat quartz cell with a mercury pool cathode and a platinum anode. This electrolytic cell may be formed by placing the electrodes directly in a flat measuring cell located in the resonant cavity. When the applied voltage in the electrolytic system is increased, the current will first increase but soon it levels off to a plateau. Radical ions are formed in this plateau region. Radical formation can sometimes be observed visually because of color changes in the solution. To carry out the experiments the magnetic field is scanned for resonance over a 50 gauss region near the free electron value of $g = 2.0023$. Radical ions can also be formed in flow through cells.

Since oxygen is also paramagnetic, dissolved air must be scrupulously removed prior the the experiment. The best method is to use the freeze pump thaw technique where the sample is first frozen and then connected to a high vacuum source. After closing off the vacuum pump, the sample is melted and refrozen. The cycle is repeated until no air is released during the solid liquid transformation. The difference in spectra when dissolved oxygen is present and absent is dramatically shown in Figures 4 and 11 for a DPPH solution in benzene. For this type of experiment, very low power levels and low modulation amplitudes are necessary since line widths are typically in the 50-100 milligauss range.

A considerable amount of work has been done on free radicals and color centers which are produced by irradiation. Most irradiations are carried out with x-rays, γ-rays, or electrons whose energies far exceed chemical bond energies. Paramagnetic spins can also be produced photolytically by less energetic ultraviolet light, and also by neutrons.

Most ESR spectra are obtained after the sample is irradiated. Many paramagnetic centers are sufficiently long lived to warrant such a procedure. More sophisitcated experimental techniques entail simultaneous irradiation and ESR detection. This is particularly popular when the irradiation source is an ultraviolet lamp. Low temperature irradiation and detection can reveal the presence of new centers which can be studied at gradually increasing temperatures to elucidate the kinetics of their recomination. Routine spectrometers are satisfactory for most radiation-damage investigations.

Some typical systems that have been studied are ionic crystals (e.g., alkali halides, F centers, and other centers); solid organic compounds; liquid organic compounds; organic single crystals; polymers; semiconductors (e.g., Ge and Si); and photoconductors (e.g., dyes).

Most of the systems studied by ESR are synthetic or man made. Nevertheless, from the beginning of the field, various naturally occurring substances have been investigated, such as: minerals with transition elements [e.g., ruby (Cr/Al_2O_3), dolomite Mn/(Ca, Mg (CO_3))], minerals with defects (e.g., quartz); hemoglobin (Fe); petroleum; coal; rubber, and various biological systems.

ESR has been applied quite extensively to biological systems . One can follow the variations that occur under changing environmental

conditions by monitoring the intensity of a free radical signal. For example, the presence of free radicals has been studied in healthy and diseased tissue. If a transition metal ion is present, as in hemoglobin (Fe), then its valence state changes may be studied by ESR. Early concrete evidence that free radical activity is linked to photosynthesis was demonstrated by ESR. By irradiating cells containing chloroplasts with light in the same wavelength that produces photosynthesis, a sharp ESR resonance line was observed. When the incident light was turned off, the resonance soon weakened or disappeared completely.

1f) Parameters Measured

In general EPR is used to determine several parameters, typically:

g factor

A, hyperfine coupling constant

D, Zero field splitting

Q, quadrupole coupling constant

T_1, T_2, T_{12}, relaxation times

ΔH_{pp}, line width

τ tumbling or correlation time

In biological systems most of these factors give useful information as will be explained during these lectures.

For example, the g factor gives information about local symmetry. Hyperfine structure will give information about the type of coupling, ionic or covalent with nearby hydrogens, zero field splitting could provide information about the type of spin that Fe has.

Relaxation times could give information about the structure of proteins. Tumbling times give information about the motion of macromolecules. Line widths give information about interaction with the surroundings.

BASIC MATHEMATICS

2a) Matrix definitions

The general approach to be followed in those lectures is the setting up of secular equations by means of the direct product (inner product) matrix expansion technique. This may be regarded as a direct product counterpart to Condon and Shortley's formulation. The present chapter will outline the mathematical and quantum-mechanical properties of matrices and angular momentum operators, and thereby prepare the way for an understanding of the material in subsequent chapters.

Quantum-mechanical operators will be in the form of hermitian matrices, and the secular equations will constitute hermitian matrices. Before discussing unitary and hermitian matrices in detail it will be well to define several other types of square matrices. Some of these definitions will be in the form of an example of a 2 x 2 or 3 x 3 matrix.

For example the unitary matrix $\vec{U}$

$$U = \begin{pmatrix} a & b & c \\ d & e & f \\ g & h & i \end{pmatrix}$$

has the following adjoint matrix $\vec{M}^{+}$

$$\vec{M}^{+} = \tilde{\vec{M}}^{*} = \begin{pmatrix} a^{*} & d^{*} & g^{*} \\ b^{*} & e^{*} & h^{*} \\ c^{*} & f^{*} & i^{*} \end{pmatrix}$$

A symmetrical matrix is one which equals its transpose:

$$\vec{M} = \tilde{\vec{M}} = \begin{pmatrix} a & b & c \\ b & e & f \\ c & f & i \end{pmatrix}$$

An antisymmetrical matrix is the negative of its transpose:

$$\vec{A} = -\tilde{\vec{A}} = \begin{pmatrix} 0 & b & c \\ -b & 0 & f \\ -c & -f & 0 \end{pmatrix}$$

An orthogonal matrix is one with real matrix elements whose reciprocal is its transpose

$$\vec{A}^{-1} = \tilde{\vec{A}} = \begin{pmatrix} a & d & g \\ b & e & h \\ c & f & i \end{pmatrix}$$

It has the property that its determinant is ± 1

$$|A| = |A^{-1}| = \pm 1$$

A unimodular matrix has the determinant +1. A 3 x 3 proper rotation matrix is unimodular, while an improper rotation (i.e., rotation-inversion) matrix has a determinant of -1. An example of the former is

$$\vec{A} = \begin{pmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

For the following two by two unimodular matrix we have

$$\begin{pmatrix} \alpha & \beta \\ \gamma & \delta \end{pmatrix}$$

$$\alpha\alpha^{*} = +\delta\delta^{*}$$

$$\beta\beta^{*} = +\gamma\gamma^{*}$$

From the off-diagonal components one deduces

$$\frac{\alpha}{\beta} = -\frac{\delta}{\gamma}^{*}$$

$$\frac{\alpha}{\gamma} = -\frac{\delta}{\beta}^{*}$$

Let the determinant be +1:

$$\begin{pmatrix} \alpha & \beta \\ \gamma & \delta \end{pmatrix} = \alpha\delta - \beta\gamma = 1$$

$$\begin{pmatrix} \alpha^* & \gamma^* \\ \beta^* & \delta^* \end{pmatrix} = \alpha^*\delta^* - \beta^*\gamma^* = 1$$

From these expressions it follows that

$$\beta = -\gamma^*, \quad \alpha = \delta^*$$

to give, for the most general 2 x 2 unitary matrix with determinant +1,

$$\vec{U} = \begin{pmatrix} \alpha & -\gamma^* \\ \gamma & \alpha^* \end{pmatrix}$$

The corresponding matrix with determinant -1 is

$$\vec{U} = \begin{pmatrix} \alpha & \gamma^* \\ \gamma & -\alpha^* \end{pmatrix}$$

We shall have occasion to use the +1 case only for matrices which diagonalize a hermitian matrix. The Pauli spin matrices, on the other hand, are unitary matrices with a determinant -1.

One should note that a real unitary matrix is equivalent to an orthogonal matrix. Also the matrix elements of a unitary matrix are related in such a way that every row is orthogonal to the complex conjugate of every other row, and each row is normalized to unity relative to the complex conjugate of itself. The same applies to the columns. For example, these rules applied to unitary matrix above give

$$ad^* + be^* + cf^* = 0$$

$$aa^* + bb^* + cc^* = 1$$

The same orthonormality properties apply to orthogonal matrices in which all matrix elements are real.

In these lectures we shall be interested in finding the eigenvalues of hermitian matrices. A hermitian matrix may be diagonalized by a unitary transformation, and the transformation matrix provides the coefficients for the engenfunctions of the system. This will become clear later when the $I_1 = I_2 = 1/2$ spin system is worked out in detail. At this time it will be helpful to illustrate the principles by an example.

The Pauli spin matrix, $\vec{\sigma}_y$:

$$\vec{\sigma}_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

is hermitian, and has the eigenvalues λ

$$\begin{pmatrix} 0 - \lambda & -i \\ i & 0 - \lambda \end{pmatrix} = 0$$

to give

$$\lambda^2 - 1 = 0$$

$$\lambda = \pm 1$$

The eigenvectors of the unitary matrix $\vec{U}$ which diagonalizes $\vec{\sigma}_y$ by $\vec{U}^{-1}\vec{\sigma}_y\vec{U} = \vec{\lambda}$:

$$\begin{pmatrix} \alpha^* & \gamma^* \\ -\gamma & \alpha \end{pmatrix}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}\begin{pmatrix} \alpha & -\gamma^* \\ \gamma & \alpha^* \end{pmatrix} = \begin{pmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{pmatrix}$$

are found from the relations ($\vec{\sigma}_y\vec{U} = \vec{U}\vec{\lambda}$)

$$\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}\begin{pmatrix} \alpha \\ \gamma \end{pmatrix} = \lambda_1 \begin{pmatrix} \alpha \\ \gamma \end{pmatrix}$$

Inserting the eigenvalue $\lambda_1 = +1$ and carrying out the mulitiplication gives

$$-i\gamma = \alpha$$

subject to the normalization condition

$$\alpha\alpha^* + \gamma\gamma^* = 1$$

with a possible result

$$\alpha = \frac{1}{\sqrt{2}}, \quad \gamma = \frac{-i}{\sqrt{2}}$$

since $\alpha\alpha^* = \gamma\gamma^*$ in this instance. The resulting unitary matrix has the explicit form

$$\vec{U} = \begin{pmatrix} \frac{1}{\sqrt{2}} & \frac{i}{\sqrt{2}} \\ \frac{-i}{\sqrt{2}} & \frac{1}{\sqrt{2}} \end{pmatrix}$$

The unitary transformation for a third-order hermitian matrix may be found by a similar procedure, but the manipulations become quite tedious. It is wise, therefore, to make use of a computer.

In these lectures we shall be concerned with the addition:

$$\begin{pmatrix} A & B \\ C & D \end{pmatrix} + \begin{pmatrix} a & b \\ c & d \end{pmatrix} = \begin{pmatrix} A + a & B + b \\ C + c & D + d \end{pmatrix}$$

multiplication:

$$\begin{pmatrix} A & B \\ C & D \end{pmatrix} \begin{pmatrix} a & b \\ c & d \end{pmatrix} = \begin{pmatrix} Aa + Bc & Ab + Bd \\ Ca + Dc & Cb + Dd \end{pmatrix}$$

and direct product expansion.

2b) Direct Product

The direct product is defined as

$$\begin{pmatrix} A & B \\ C & D \end{pmatrix} \times \begin{pmatrix} a & b \\ c & d \end{pmatrix} = \begin{pmatrix} Aa & Ab & Ba & Bb \\ Ac & Ad & Bc & Bd \\ Ca & Cb & Da & Db \\ Cc & Cd & Dc & Dd \end{pmatrix}$$

The first two operations are defined for matrices of the same order, n x n, and produce a matrix of that same order. The direct product expansion, on the other hand, forms an (mn) x (mn) matrix from an m x m and an n x n matrix.

Column vectors may be added:

$$\begin{pmatrix} A \\ B \end{pmatrix} + \begin{pmatrix} a \\ b \end{pmatrix} = \begin{pmatrix} A + a \\ B + b \end{pmatrix}$$

and expanded as direct products

$$\begin{pmatrix} A \\ B \end{pmatrix} \times \begin{pmatrix} a \\ b \end{pmatrix} = \begin{pmatrix} Aa \\ Ab \\ Ba \\ Bb \end{pmatrix}$$

A square matrix times a column vector gives another column vector, and similarly for the reciprocal operator:

$$\begin{pmatrix} A & B \\ C & D \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} = \begin{pmatrix} Aa + Bb \\ Ca + Db \end{pmatrix}$$

$$(a^* b^*) \begin{pmatrix} A & B \\ C & D \end{pmatrix} = (Aa^* + Cb^* \quad Ba^* + Db^*)$$

and the simple scalar product is

$$(a^* \; b^*) \begin{pmatrix} A \\ B \end{pmatrix} = Aa^* + Bb^*$$

These operations are easily generalized to higher dimensions.

BASIC QUANTUM MECHANICS

3a) Angular Momentum Operators

Before proceeding to the matrix formulation of angular momentum operators, it will be appropriate to summarize their principal operator properties.

An angular momentum $\vec{J}$ has a degeneracy of $2J + 1$, with its magnetic quantum number m assuming the integral or half-integral values within the range $-J \leq m \leq J$. The z component of the angular momentum operates on the ket vector $|m\rangle$ in accordance with the relation

$$J_z |m\rangle = m|m\rangle$$

raising and lowering operators are defined as

$$J^{+} = J_x + iJ_y$$
$$J^{-} = J_x - iJ_y$$

with

$$J^{+}|m\rangle = \sqrt{(J - m)(J + m + 1)}\ |m + 1\rangle$$

$$J^{-}|m\rangle = \sqrt{(J + m)(J - m + 1)}\ |m - 1\rangle$$

and

$$J^2|m\rangle = J(J + 1)|m\rangle$$

3b). Matrix Representation

In order to employ the direct product method for spins with magnitudes greater than 2, it is necessary to know the corresponding spin matrices. These are easily generated from the Pauli matrices, the former giving the diagonal matrix elements for J_z and the latter the matrix elements adjacent to the diagonal for J_x and J_y. All other matrix elements vanish. We shall be content to write down the matrices for low magnitudes of J, and then to point out a convenient mnemonic method for constructing them.

The various matrices for J = ½, 1, and 3/2 have the following explicit forms, where J may be any orbital, spin, or total angular momentum:

$$\text{unit matrix} \rightarrow \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \rightarrow \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \rightarrow \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

$$\vec{J}_x \rightarrow \tfrac{1}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \rightarrow \tfrac{1}{2}\begin{pmatrix} 0 & \sqrt{2} & 0 \\ \sqrt{2} & 0 & \sqrt{2} \\ 0 & \sqrt{2} & 0 \end{pmatrix} \rightarrow \tfrac{1}{2}\begin{pmatrix} 0 & \sqrt{3} & 0 & 0 \\ \sqrt{3} & 0 & 2 & 0 \\ 0 & 2 & 0 & \sqrt{3} \\ 0 & 0 & \sqrt{3} & 0 \end{pmatrix}$$

$$\vec{J}_y \rightarrow \tfrac{1}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \rightarrow \tfrac{1}{2}\begin{pmatrix} 0 & -i\sqrt{2} & 0 \\ i\sqrt{2} & 0 & -i\sqrt{2} \\ 0 & i\sqrt{2} & 0 \end{pmatrix} \rightarrow \tfrac{1}{2}\begin{pmatrix} 0 & -\sqrt{3}i & 0 & 0 \\ \sqrt{3}i & 0 & -2i & 0 \\ 0 & 2i & 0 & -\sqrt{3}i \\ 0 & 0 & \sqrt{3}i & 0 \end{pmatrix}$$

$$\vec{J}_z \rightarrow \tfrac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \rightarrow \tfrac{1}{2}\begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix} \rightarrow \tfrac{1}{2}\begin{pmatrix} 3 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -3 \end{pmatrix}$$

$$\vec{J}^2 \rightarrow \tfrac{3}{4}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \rightarrow 2\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \rightarrow \tfrac{15}{4}\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

$$\vec{J}^{+} \rightarrow \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \rightarrow \begin{pmatrix} 0 & \sqrt{2} & 0 \\ 0 & 0 & \sqrt{2} \\ 0 & 0 & 0 \end{pmatrix} \rightarrow \begin{pmatrix} 0 & \sqrt{3} & 0 & 0 \\ 0 & 0 & 2 & 0 \\ 0 & 0 & 0 & \sqrt{3} \\ 0 & 0 & \sqrt{3} & 0 \end{pmatrix}$$

$$\vec{J}^{-} \rightarrow \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} \rightarrow \begin{pmatrix} 0 & 0 & 0 \\ \sqrt{2} & 0 & 0 \\ 0 & \sqrt{2} & 0 \end{pmatrix} \rightarrow \begin{pmatrix} 0 & 0 & 0 & 0 \\ \sqrt{3} & 0 & 0 & 0 \\ 0 & 2 & 0 & 0 \\ 0 & 0 & \sqrt{3} & 0 \end{pmatrix}$$

Each matrix has 2J + 1 rows and an equal number of columns. The unit matrix has ones along the diagonal and zeros elsewhere. The matrix for J_z is diagonal with elements J, J-1, J-2, . . . , -J from upper left to lower right.

The matrix for J² equals the unit matrix times J(J + 1) and is easily calculated from the expression

$$\vec{J}^2 = \vec{J}_x^2 + \vec{J}_y^2 + \vec{J}_z^2$$

by matrix multiplication ($\vec{J}_x\vec{J}_x$, etc.) followed by matrix addition. These matrices are rather straightforward to form and should present no difficulty for even higher spins J > 3/2).

The x, y and z component matrices obey the usual commutation law:

$$\vec{J}_i\vec{J}j - \vec{J}_j\vec{J}_i = [\vec{J}_i, \vec{J}_j] = \vec{J}_k \sqrt{-1} \text{ (i, j, k cyclic)}$$

as is easily proved by carrying out the matrix multiplication. For example, when J = 1 the commutation law takes the form

$$[\vec{J}_x, \vec{J}_y] = i\vec{J}_z$$

$$\frac{1}{4} \begin{matrix} 0 & \sqrt{2} & 0 \\ \sqrt{2} & 0 & \sqrt{2} \\ 0 & \sqrt{2} & 0 \end{matrix} \quad \begin{pmatrix} 0 & -i\sqrt{2} & 0 \\ i\sqrt{2} & 0 & -i\sqrt{2} \\ 0 & i\sqrt{2} & 0 \end{pmatrix}$$

$$- \begin{pmatrix} 0 & -i\sqrt{2} & 0 \\ i\sqrt{2} & 0 & -i\sqrt{2} \\ 0 & i\sqrt{2} & 0 \end{pmatrix} \begin{pmatrix} 0 & \sqrt{2} & 0 \\ \sqrt{2} & 0 & \sqrt{2} \\ 0 & \sqrt{2} & 0 \end{pmatrix} = i \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

One should note that the matrix for $\vec{J}^2$ automatically has the eigenvalue J(J+1):

$$\begin{matrix} \vec{J}^2 \\ \text{Matrix} \end{matrix} = J(J+1) \begin{matrix} \text{Unit} \\ \text{Matrix} \end{matrix}$$

The Pauli spin matrices, $\vec{\sigma}_i$, are double the spin -½ matrices:

$$\vec{\sigma}_x = \begin{matrix} 0 & 1 \\ 1 & 0 \end{matrix}, \quad \vec{\sigma}_y = \begin{matrix} 0 & -i \\ i & 0 \end{matrix}, \quad \vec{\sigma}_z = \begin{matrix} 1 & 0 \\ 0 & -1 \end{matrix}$$

and they have some special properties not shared by the higher-order matrices. for example, they anticommute in pairs:

$$\vec{\sigma}_i\vec{\sigma}_j + \vec{\sigma}_f\vec{\sigma}_i = 0$$

for any pair i, j = x, y, z. In addition

$$\vec{\sigma}_x^2 = \vec{\sigma}_y^2 = \vec{\sigma}_z^2 = \begin{matrix} 1 & 0 \\ 0 & 1 \end{matrix}$$

which means that $\frac{1}{4} \Sigma_i \sigma_i^2$ also satisfies the eigenvalue equation for J² with J(J + 1) = 3/4 as expected.

The matrices for J_x and J_y and their raising and lowering operator counterparts are less familiar for high spins, and the following mnemonic method is useful for their formation. The only nonzero elements occur adjacent to the diagonal and have values obtained from the following triangle:

J = 1/2 $\quad \sqrt{1}$
J = 1 $\quad \sqrt{2} \quad \sqrt{2}$
J = 3/2 $\quad \sqrt{3} \quad \sqrt{2\cdot 2} \quad \sqrt{3}$
J = 2 $\quad \sqrt{4} \quad \sqrt{3\cdot 2} \quad \sqrt{2\cdot 3} \quad \sqrt{4}$
J = 5/2 $\quad \sqrt{5} \quad \sqrt{4\cdot 2} \quad \sqrt{3\cdot 3} \quad \sqrt{2\cdot 4} \quad \sqrt{5}$
J = 3 $\quad \sqrt{6} \quad \sqrt{5\cdot 2} \quad \sqrt{4\cdot 3} \quad \sqrt{3\cdot 4} \quad \sqrt{2\cdot 5} \quad \sqrt{6}$
J = 7/2 $\quad \sqrt{7} \quad \sqrt{6\cdot 2} \quad \sqrt{5\cdot 3} \quad \sqrt{4\cdot 4} \quad \sqrt{3\cdot 5} \quad \sqrt{2\cdot 6} \quad \sqrt{7}$

The row for a general spin J is

$$\sqrt{(2J)\cdot(1)} \quad \sqrt{(2J-1)\cdot(2)} \quad \sqrt{(2J-2)\cdot(3)}$$
$$\sqrt{(2J-3)\cdot(4)} \quad . \; . \; . \quad \sqrt{(1)\cdot(2J)}$$

One should note that this triangle is symmetrical about its vertical axis. A closer inspection will reveal several obvious methods for generating successive rows for higher spins.

The matrix for J_x is real and symmetric, and contains, adjacent to its diagonal, one half of the numbers in the corresponding row of the triangle. For example, the J = 5/2 matrix has the sequence $\sqrt{5}/2$, $\sqrt{2}$, 3/2, $\sqrt{2}$, $\sqrt{5}/2$ on either side of its diagonal. The matrix for J_y is purely imaginary and is obtained from J_x by multiplying each element to the left below the diagonal by $i = \sqrt{-1}$, and each element to the right above the diagonal by $-i$. The raising operator, J^+, contains this sequence only immediately to the right above the diagonal, while the lowering operator, J^-, contains the same numerical sequence only immediately below and to the left of the diagonal.

The total angular momentum in a system is the vector sum of all other angular momenta:

$$\vec{J} = \Sigma \vec{J}_i$$

In this section we shall treat the case of two angular momenta:

$$\vec{J} = \vec{J}_1 + \vec{J}_2$$

for which the following values of J are allowed:

$$|J_1 - J_2| \leq J \leq J_1 + J_2$$

Since this situation is discussed in standard books on quantum mechanics, only the application of the direct product method to this problem will be presented here.

One begins by taking the direct product sum:

$$\vec{J}' = \vec{J}'_x \hat{\vec{i}} + \vec{J}'_y \hat{\vec{j}} + \vec{J}'_z \hat{\vec{k}}$$

$$= \vec{J}_1 \times \vec{\Box}_2 + \vec{\Box}_1 \times \vec{J}_2$$

$$= (\vec{J}_{1x} \times \vec{\Box}_2 + \vec{\Box}_1 \times \vec{J}_{2x})\hat{\vec{i}} + (\vec{J}_{1y} \times \vec{\Box}_2 + \vec{\Box}_1 \times \vec{J}_{2y})\hat{\vec{j}}$$

$$+ (\vec{J}_{1z} \times \vec{\Box}_2 + \vec{\Box}_1 \times \vec{J}_{2z})\hat{\vec{k}}$$

where $\vec{\Box}_1$ and $\vec{\Box}_2$ are unit matrices in the J_1 and J_2 spaces. The components J'_1 have the following explicit forms for $J_1 = J_2 = ½$:

$$\vec{J}'_x = ½ \begin{matrix} 0 & 1 \\ 1 & 0 \end{matrix} \times \begin{matrix} 1 & 0 \\ 0 & 1 \end{matrix} + \begin{matrix} 0 & 1 \\ 0 & 1 \end{matrix} \times \begin{matrix} 0 & 1 \\ 1 & 0 \end{matrix}$$

$$= ½ \begin{pmatrix} 0 & 1 & 1 & 0 \\ 1 & 0 & 0 & 1 \\ 1 & 0 & 0 & 1 \\ 0 & 1 & 1 & 0 \end{pmatrix}$$

$$\vec{J}'_y = ½ \begin{pmatrix} 0 & -i & -i & 0 \\ i & 0 & 0 & -i \\ i & 0 & 0 & -i \\ 0 & i & i & 0 \end{pmatrix}$$

$$\vec{J}'_z = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}$$

The ket vectors, $|m_1 m_2\rangle'$, corresponding to this primed representation are expressed in terms of the $|m_i\rangle$ kets:

$$|1/2\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad |-1/2\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

by the direct product expansion:

$$|1/2\ 1/2\rangle' = \begin{pmatrix}1\\0\end{pmatrix} \times \begin{pmatrix}1\\0\end{pmatrix} = \begin{pmatrix}1\\0\\0\\0\end{pmatrix}$$

$$|1/2\ -1/2\rangle' = \begin{pmatrix}1\\0\end{pmatrix} \times \begin{pmatrix}0\\0\end{pmatrix} = \begin{pmatrix}0\\1\\1\\0\end{pmatrix}$$

$$|-1/2\ 1/2\rangle' = \begin{pmatrix}0\\1\end{pmatrix} \times \begin{pmatrix}1\\0\end{pmatrix} = \begin{pmatrix}0\\0\\1\\0\end{pmatrix}$$

$$|-1/2\ -1/2\rangle' = \begin{pmatrix}0\\1\end{pmatrix} \times \begin{pmatrix}1\\1\end{pmatrix} = \begin{pmatrix}0\\0\\0\\1\end{pmatrix}$$

Thus we have all of the eigenfunctions and angular momentum operators in the $|m_1 m_2\rangle'$ or primed representation.

3c). Perturbation Theory

When an interaction H_p is weak relative to the main energy term H_o then its effect can be calculated by a perturbation approach. Given a Hamiltonian of the form

$$H = H_o + H_p$$

we assume that the eigenvalues of the dominant term H_o are known

$$\langle i|H_o = E_{oi}\langle i|$$

The energy to second order is

$$E_i^{(2)} = E_{oi} + \langle i|H_p|i\rangle + \sum_j{}' \frac{\langle i|H_p|j\rangle\langle j|H_p|i\rangle}{E_{oi}-E_{oj}}$$

and the wave function to the first order is:

$$\psi_i^{(1)} = \psi_{oi} + \sum_j{}' \frac{\langle i|H'|j\rangle}{E_{oi}-E_{oj}}\,\psi_{oj}$$

3d). Transition Probabilities

The line intensity from an initial state $\langle i|$ to a final state $\langle f|$ is calculated using the time varying potential V(t) and either the exact or the perturbation wavefunctions in the following expression for the transition probability.

$$P_{if} = \frac{2\pi}{\hbar^2}\,|\langle f|V(t)|i\rangle|^2\,\delta(\omega_{if} - \omega_o)$$

where the potential

$$V(t) = g\beta\vec{h}(t)\vec{S}$$
$$= g\beta h_x(t)S_x$$

contains the time dependent radiofrequency field $h(t) = h_x(t)$ which is linearly polarized in the x direction. Since only the operator S_x operates on the wavefunctions the transition probability P_{if} is proportional to the expression

$$P_{ij} = K|\langle f|S_x|i\rangle|^2$$

and the relative intensities of various transitions are proportional to the square of the matrix element $\langle f|S_x|i\rangle$.

The operator S_x acts only on the electron spin states so the matrix elements only exist when the nuclear spin quantum number is the same for the ψ_f and ψ_i states. In addition to operator S_x has the following nonzero matrix elements when M_I does not change

$$\langle +m_I|S_x|-m_I\rangle = 1/2$$
$$\langle -m_I|S_x|+m_I\rangle = 1/2$$

The matrix element $\langle f|S_x|i\rangle$ vanishes when the m_S quantum number remains the same, and it also vanishes when m_S changes corresponding to the selection rules

$$\Delta m_S = \pm 1$$
$$\Delta m_I = 0$$

As a result there are only two nonvanishing matrix elements. These results may be summarized as follows:

$$\langle ++|S_x|-+\rangle = 1/2 \qquad \Delta m_S = 1 \; \Delta m_I = 0$$
$$\langle +-|S_x|--\rangle = 1/2 \qquad \Delta m_S = 1 \; \Delta m_I = 0$$

The perturbation wavefunctions together with these matrix elements are used to construct the following transition probability matrix:

$$\begin{array}{ccccc}
 & |++\rangle & \psi_2 & \psi_3 & |--\rangle \\
\langle ++| & 0 & 1/2\varepsilon & 1/2 & 0 \\
\psi_2 & 1/2\varepsilon & 0 & 0 & 1/2 \\
\psi_3 & 1/2 & 0 & 0 & -1/2\varepsilon \\
\langle --| & 0 & 1/2 & -1/2\varepsilon & 0
\end{array}$$

The two allowed ESR transitions have the same intensity (1/2) wherease the NMR transition $\psi\leftarrow 3$ and $1\leftarrow 2$ with the selection rules $\Delta m_S = 0$, $\Delta m_I = \pm 1$ have a much lower intensity.

APPLICATION TO 1 and 2 SPINS

4a) One Spin in a Magnetic Field

The simplest of all cases it is a single spin $S = \frac{1}{2}$ in the presence of a external magnetic field H_o.

The Hamiltonian is given by

$$H = \beta \vec{S} \cdot \overleftrightarrow{g} \cdot \vec{H}$$

or

$$H = \beta g \, S_z \cdot H$$

where the first is for the case of a anisotropic g factor and the second is for the case of isotropic g factor. The eigenvalues are

$$E_1 = g\beta H/2$$
$$E_2 = -g\beta H/2$$

The difference between the first and second case is in the g factor. For the anistropic case is given by

$$g^2 = g_{xx}^2 + g_{yy}^2 + g_{zz}^2$$

which it reduces to the first case when $g_{xx} = g_{yy} = g_{zz}$

A more complex case is considered next

4b Two Interacting Spins in a Magnetic Field

We illustrate the direct product expansion technique by determining the energy for the S = 1/2, I = 1/2 tow spin case with isotropic g-factor and hyperfine terms. We use the following hamiltonian

$$H = g\beta H S_z - g_N\beta_N H I_z + T\vec{S}\cdot\vec{I}$$

and neglect the nuclear Zeeman term, which gives

$$H = g\beta H s_z + T(S_xI_x + S_yI_y + S_zI_z).$$

A unit matrix I in the nuclear spin space is added to the electronic Zeeman term to write it in direct product notation

$$H = g\beta H_z \; S_z \times I + T(S_x \times I_x + S_y \times I_y + S_z \times I_z)$$

First the Zeeman term matrices are expanded to give

$$S_z \times 1 = \begin{array}{c|cccc} & |{+}{+}> & |{+}{-}> & |{-}{+}> & |{-}{-}> \\ \hline <{+}{+}| & 1/2 & 0 & 0 & 0 \\ <{+}{-}| & 0 & 1/2 & 0 & 0 \\ <{-}{+}| & 0 & 0 & -1/2 & 0 \\ <{-}{-}| & 0 & 0 & 0 & -1/2 \end{array}$$

where we use the notation $<m_s m_I|$ and $|m_s m_I>$ for the bra and ket wavefunctions respectively.

Next the Hamiltonian matrices of the hyperfine terms are presented:

$$S_x \times I_x = \begin{array}{c|cccc} & |{+}{+}> & |{+}{-}> & |{-}{+}> & |{-}{-}> \\ \hline <{+}{+}| & 0 & 0 & 0 & 1/4 \\ <{+}{-}| & 0 & 0 & 1/4 & 0 \\ <{-}{+}| & 0 & 1/4 & 0 & 0 \\ <{-}{-}| & 1/4 & 0 & 0 & 0 \end{array}$$

$$S_y \times I_y = \begin{array}{c|cccc} & |{+}{+}> & |{+}{-}> & |{-}{+}> & |{-}{-}> \\ \hline <{+}{+}| & 0 & 0 & 0 & -1/4 \\ <{+}{-}| & 0 & 0 & 1/4 & 0 \\ <{-}{+}| & 0 & 1/4 & 0 & 0 \\ <{-}{-}| & -1/4 & 0 & 0 & 0 \end{array}$$

$$S_z \times I_z = \begin{array}{c|cccc} & |{+}{+}> & |{+}{-}> & |{-}{+}> & |{-}{-}> \\ \hline <{+}{+}| & 1/4 & 0 & 0 & 0 \\ <{+}{-}| & 0 & -1/4 & 0 & 0 \\ <{-}{+}| & 0 & 0 & -1/4 & 0 \\ <{-}{-}| & 0 & 0 & 0 & -1/4 \end{array}$$

Finally all of these matrices are combined by addition to give:

$$S_z \times I_z = \begin{array}{c|cccc} & |{+}{+}< & |{+}{-}> & |{-}{+}> & |{-}{-}> \\ \hline <{+}{+}| & g\beta\frac{H}{2}+\frac{T}{4} & 0 & 0 & 0 \\ <{+}{-}| & 0 & g\beta\frac{H}{2}-\frac{T}{4} & \frac{T}{2} & 0 \\ <{-}{+}| & 0 & \frac{T}{2} & -\frac{g\beta H}{2}-\frac{T}{4} & 0 \\ <{-}{-}| & 0 & 0 & 0 & -\frac{g\beta H}{2}+\frac{T}{4} \end{array}$$

which correspond to two 1 x 1 matrices and one 2 x 2 matrix

$$\begin{pmatrix} (1 \times 1) & 0 & 0 \\ 0 & (2 \times 2) & 0 \\ 0 & 0 & (1 \times 1) \end{pmatrix}$$

The 2 x 2 matrix constitutes a quadratic equation which is easily solved in determinant form

$$\begin{vmatrix} \frac{g\beta H}{2} + \frac{T}{4} - \lambda & \frac{T}{2} \\ \frac{T}{2} & -\frac{g\beta H}{2} - \frac{T}{4} - \lambda \end{vmatrix} = 0$$

and the four energies $\lambda = E_j$ are

$$E_1 = \frac{g\beta H}{2} + \frac{T}{4}$$

$$E_2 = -\frac{T}{4} + \frac{1}{2}\left[T^2 + g^2\beta^2H^2\right]^{\frac{1}{2}}$$

$$E_3 = -\frac{T}{4} - \frac{1}{2}\left[T^2 + g^2\beta^2H^2\right]^{\frac{1}{2}}$$

$$E_4 = -\frac{g\beta H}{2} + \frac{T}{4}$$

The coefficients α and γ of the wavefunction are obtained from the expression

$$\begin{pmatrix} \frac{g\beta H}{2} - \frac{T}{4} & \frac{T}{2} \\ \frac{T}{2} & -\frac{g\beta H}{2} - \frac{T}{4} \end{pmatrix} \begin{pmatrix} \alpha \\ \gamma \end{pmatrix} = E_2 \begin{pmatrix} \alpha \\ \gamma \end{pmatrix}$$

which can be evaluated to give

$$\alpha = \{1 + [g\frac{\beta H}{T} - (g^2\frac{\beta^2H^2}{T^2})^{\frac{1}{2}}]^2\}^{-\frac{1}{2}}$$

$$\gamma = \{1 + [g\frac{\beta H}{T} - (g^2\frac{\beta^2H^2}{T^2})^{\frac{1}{2}}]^{-2}\}^{-\frac{1}{2}}$$

and the four eigenfunctions have the form

$$\psi_1 = |++\rangle$$

$$\psi_2 = \alpha|+-\rangle+\gamma|-+\rangle$$

$$\psi_3 = -\gamma|+-\rangle+\alpha|-+\rangle$$

$$\psi_4 = |--\rangle$$

This same case can be handled by perturbation theory, and the zero order result gives two degenerate energies with the following values:

$$E_1 = g\frac{\beta H}{2}$$

$$E_2 = g\frac{\beta H}{2}$$

$$E_3 = -g\frac{\beta H}{2}$$

$$E_4 = -g\frac{\beta H}{2}$$

The first order perturbation solution provides the following energies

$$E_1 = g\frac{\beta H}{2} + \frac{T}{4}$$

$$E_2 = g\frac{\beta H}{2} - \frac{T}{4}$$

$$E_3 = g\frac{\beta H}{2} - \frac{T}{4}$$

$$E_4 = g\frac{\beta H}{2} + \frac{T}{4}$$

The second order of perturbation leaves the upper and lower levels unaffected but shifts the two middle energy levels and also the spectral lines in accordance with the expressions

$$E_1 = g\frac{\beta H}{2} + \frac{T}{4}$$

$$E_2 = g\frac{\beta H}{2} - \frac{T}{4} + \frac{(T/2)^2}{g\beta H}$$

$$E_3 = -g\frac{\beta H}{2} - \frac{T}{4} - \frac{(T/2)^2}{g\beta H}$$

$$E_4 = -g\frac{\beta H}{2} + \frac{T}{4}$$

The perturbation approach provides the approximate values $\alpha = 1$ and $\gamma = T/2g\beta H$ for the coefficients of the wavefunctions.

ANISOTROPIES

5a). Anisotropic g-factor

Until now we have dealt with a hamiltonian which is isotropic which means that the energies are independent of the magnetic field direction. Now we will extend the treatment to the anisotropic case where the energy depends upon the orientation of the magnetic field. We begin by treating the axially symmetric case wherein there is one preferred direction. The Hamiltonian matrix for an electronic spin S = 1/2 in the absence of a nuclear spin is given by:

$$H = \beta \vec{H} \cdot \vec{g} \cdot \vec{S}$$

Using the g factor tensor

$$\vec{g} \qquad \begin{matrix} g_| & 0 & 0 \\ 0 & g_| & 0 \\ 0 & 0 & g_{||} \end{matrix}$$

and the S = 1/2 spin matrices defined above we obtain a 2 x 2 hamiltonian matrix.

The determinant of this Hamiltonian matrix

$$\begin{matrix} 1/2\ g_{||}\ \beta H_z - \lambda & 1/2\ g_|\ \beta(H_x - iH_y) \\ 1/2\ g_|\ \beta(H_x + iH_y) & -1/2\ g_{||}\ \beta H_z - \lambda \end{matrix} = 0$$

is solved to provide the energies

$$\lambda = \pm\ 1/2\ \beta f(\theta)$$

which depend upon the angle θ which the magnetic field makes with the axis of symmetry through the expression

$$f(\theta) = \{[g_|(H_x - iH_y)]^2 + (g_{||}H_z)^2\}^{1/2}$$

If the magnetic field components are expressed in spherical coordinates

$$H_x = H \sin\theta \cos\psi$$

$$H_y = H \sin\theta \sin\psi$$

$$H_z = H \cos\theta$$

then the angular dependence of the energy is made explicit.

$$f(r) = H\{g_|^2 \sin\{\theta + g_{||}^2 \cos^2\theta\}^{1/2}$$

and the energies are given by

$$\lambda = \pm\ 1/2 g\beta H$$

with the angular dependence in the g factor

$$g = (g_|^2 \sin^2\theta + g_{||}^2 \cos^2\theta)^{1/2}$$

5b). Anisotropic Hyperfine Coupling

We have treated the case of an anisotropic g-factor. The hyperfine coupling constant can also be anisotropic, and this can be treated in a similar manner using direct products.

When only the g-factor is anisotropic, the magnetic field positions H_{res} of the doublet lines vary with the orientation but the separation between the lines remains the same.

When only the hyperfine coupling constant T is anisotropic, then the separation of the lines will vary with the orientation in such a manner that the midpoint between them remains at the same magnetic field value.

When the g-factor and the hyperfine interactions are anisotropic, then both the spacing between the lines and their center point will vary with the orientation of the crystal in the magnetic field.

5c Zero Field Tensor

When the unpaired spin has the magnitude S = 1 as occurs in triplet states of hydrocarbon molecules there is an additional hamiltonian term $\vec{S}\cdot\vec{D}\cdot\vec{S}$ called the zero field splitting and we can write

$$H = g\beta\vec{H}\cdot\vec{S} + \vec{S}\cdot\vec{D}\cdot\vec{S}$$

The zero field tensor arises from the dipole-dipole interaction.

In the principal axis system the off-diagonal terms vanish and the diagonal terms contain an axial part D and a lower symmetry part E as follows

$$\frac{g^2\beta^2}{2} < \frac{r^2-3x^2}{r^5} > = -\frac{1}{3} D + E$$

$$\frac{g^2\beta^2}{2} < \frac{r^2-3y^2}{r^5} > = -\frac{1}{3} D - E$$

$$\frac{g^2\beta^2}{2} < \frac{r^2-3z^2}{r^5} > = \frac{2}{3} D$$

For axial symmetry (E = 0) the zero field tensor in the principal axis system is

$$\vec{D} = \begin{pmatrix} -\frac{D}{3} & 0 & 0 \\ 0 & -\frac{D}{3} & 0 \\ 0 & 0 & \frac{2}{3}D \end{pmatrix}$$

and the hamiltonian has the form

$$H = g\beta H \cdot S + D[S_z^2 - \frac{1}{3}S(S+1)]$$

After rotation through an angle θ around the x axis to a new coordinate system by means of the expression

$$\vec{D}'(\theta) = \vec{R}_\theta{}^x \cdot \vec{D}\, \vec{R}_\theta{}^{x-1}$$

where $\vec{R}_\theta{}^x$ is the notation matrix

$$\vec{R}_\theta{}^x = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\theta & -\sin\theta \\ 0 & \sin\theta & \cos\theta \end{pmatrix}$$

the zero field tensor becomes

$$\vec{D}' = \begin{pmatrix} -\frac{1}{3}D & 0 & 0 \\ 0 & \frac{1}{3}D(2\sin^2\theta - \cos^2\theta) & -D\sin\theta\cos\theta \\ 0 & -D\sin\theta\cos\theta & \frac{1}{3}D(2\cos^2\theta - \sin^2\theta) \end{pmatrix}$$

In this new coordinate system the zero field hamiltonian may be put in the form

$$H_D = -S_x^2\left(\frac{D}{3}\right) + S_y^2\left(-\frac{D}{3}\cos^2\theta + \frac{D}{3}\sin^2\theta\right)$$

$$+S_z^2\left(\frac{2}{3}D\cos^2\theta - \frac{1}{3}D\sin^2\theta\right)$$

$$-(S_yS_z + S_zS_y)D(\sin\theta\cos\theta)$$

This expression provides the angular dependence of the spectral lines. To first order, i.e., when D << gβH, this simplifies to the following approximate equation

$$H_D = D[S_z^2 - \frac{1}{3}S(S+1)]\,(\cos^2\theta - \frac{1}{2}\sin^2\theta)$$

LINESHAPES

6a) Gaussian and Lorentzian Shapes

We have discussed the positions of ESR spectral lines in terms of the hamiltonian and their relative intensities in terms of the transition probability. Additional information about spin systems is provided by the shapes of the spectral lines.

The two main types of lineshapes are the Gaussian which occurs in dipolar broadened solids and the Lorentzian which occurs in liquids and in exchange narrowed solids. The analytic forms of the absorption lineshapes are as follows:

$$Y_{(H)}^{G} = Y_m e^{-0.693\left(\frac{H-H_o}{\frac{1}{2}\Delta H_{\frac{1}{2}}}\right)^2} \qquad \text{(Gaussian)}$$

$$Y_{(H)}^{L} = Y_m \frac{1}{1+[(H-H_o)/\frac{1}{2}\Delta H_{\frac{1}{2}}]^2} \qquad \text{(Lorentzian)}$$

where Y_m is the amplitude at the center of the line where $H = H_o$ and $\Delta H_{\frac{1}{2}}$ in the linewidth between half amplitude points, as shown on Fig. 10.

Ordinarily in ESR experiments we detect first derivatives of the absorption lineshapes given in the following equations for the Gaussian and Lorentzian cases.

$$Y'^{G}_{(H)} = 1.649\, Y'_m \left(\frac{H-H_o}{\frac{1}{2}\Delta H_{pp}}\right) e^{-\frac{1}{2}\left(\frac{H-H_o}{\frac{1}{2}\Delta H_{pp}}\right)^2}$$

$$Y'^{L}_{(H)} = \frac{16\, Y'_m[H-H_o)/\frac{1}{2}\Delta H_{pp}]}{[3+\{(H-H_o)/\frac{1}{2}\Delta H_{\rho\rho}\}^{\neq ♀ \neq}}$$

where the peak to peak amplitude Y'_m is defined on the figure. The peak to peak linewidth ΔH_{pp} defined on this same figure is narrower than its half amplitude counterpart by the following amount.

$$\Delta H_{\frac{1}{2}} = (\ell n2)^{\frac{1}{2}} \Delta pp \qquad \text{(Gaussian)}$$

$$\Delta H_{\frac{1}{2}} = 3^{\frac{1}{2}}\,\Delta\, H_{pp} \qquad \text{(Lorentzian)}$$

6b). Powder Pattern Line Shapes

We have been discussing cases in which the position of the spectral line depends upon the orientation of the sample in themagnetic field. When the sample is a powder the crysallites are oriented randomly and the resulting spectrum is a superposition of spectra from individual crystallites.

To calculate the zero field powder pattern lineshape to first order ($D \ll g\beta H$) we average the hamiltonian term,

$$H_D = D[S_z{}^2 - \frac{1}{3}\, S(S+1)]\ (\cos^2\theta - \tfrac{1}{2}\sin^2\theta)$$

over angles.

The differential dN for the number of crystallites with their axes between θ and $\theta + d\theta$ ralative to the magnetic field direction is proportional to the differential area $dA = 2\pi r \sin\theta\, d\theta$

$$dN \propto dA$$

$$\propto 2\pi r \sin\theta\, d\theta$$

and in terms of the total number N_o of crystallites this becomes

$$dN = \frac{N_o}{2} \sin\theta\, d\theta$$

where θ is restricted to the range of values.

$$0 \le \theta \le \frac{\pi}{2}$$

The energy condition for resonance is

$$\hbar\omega_o = g\beta H_{res} + nD\,(\cos^2\theta - \tfrac{1}{2}\sin^2\theta)$$

where $n = \pm 1$, and there are three resonances with the following magnetic field values and ket vectors

$$H^+_{res} \rightarrow |+1\rangle$$

$$H^o_{res} \rightarrow |0\rangle$$

$$H^-_{res} \rightarrow |-1\rangle$$

If we define

$$\hbar\omega_o = g\beta H_o$$

then we can write the energy condition in the form

$$H = H_o - nD(\frac{3}{2}\cos^2\theta - \tfrac{1}{2}$$

The magnetic field H will be on resonance with some spins between the folowing limits

$$H_{lim} = \begin{array}{ll} H_o - nD & \theta = 0 \\ H_o + \frac{dD}{2} & \theta = \frac{\pi}{2} \end{array}$$

over which the lineshape must be integrated. It is more convenient to integrate the field H than angle θ, so we will change the variable. The derivative $dH/d\theta$

$$\frac{dH}{d\theta} = 3nD\ [\frac{2}{3}\ (\frac{H_o - H}{nD}) + \frac{1}{3}]^{\frac{1}{2}} \sin\theta$$

can be transformed to dN/dH to give the following expression

$$dN = \frac{N_o}{6nD}\ [\frac{2}{3}\ (\frac{H_o - H}{nD}) + \frac{1}{3}]^{-\frac{1}{2}} dH$$

which provides the lineshapes.

DYNAMICAL ASPECTS

7a) Precessing Spins

Until now we have been discussing the static aspects of ESR. To understand the phenomenon of saturation transfer it is also necessary to have some knowledge of the dynamical aspects of this subject, and we will proceed to review them. We begin with a discussion of the Bloch equations.

The magnetization precesses in a magnetic field at a rate determined by the Larmor equation,

$$\frac{d\vec{M}}{dt} = \gamma \vec{M} \times \vec{H}$$

and if it is disturbed from equilibrium, it relaxes back to its equilibrium value M_o in accordance with the expression

$$\frac{dM_z}{dt} = \frac{M_o - M_z}{T_1}$$

where T_1 is the Longitudinal or Spin-Lattice Relaxation time. This equation has the solution

$$M_z = M_o(1-e^{t/T_1})$$

so we see that the magnetization M relaxes exponentially to its equilibrium value M_o.

7b Bloch Equations

When both longitudinal and transverse relaxation are taken into account the equation of motion of the magnetization has particular forms which are referred to as the Bloch Equations.

$$\frac{dM_x}{dt} = \gamma(\vec{M} \times \vec{H})_x - \frac{M_x}{T_2}$$

$$\frac{dM_y}{dt} = \gamma(\vec{M} \times \vec{H})_y - \frac{M_y}{T_2}$$

$$\frac{dM_z}{dt} = \gamma(\vec{M} \times \vec{H})_z - \frac{M_z - M}{T_1}$$

where T_2 is the Transverse or Spin-Spin Relaxation Time.

$$H_{rf} = 2H_1 e^{-i\omega t}$$

In the x direction for a sinusoidal rf field, the solutions of the Bloch equations give the magnetization components, and the x component M_x is proportional to the complex magnetic susceptibility $\chi(\omega)$

$$M_x = \chi(\omega) H_1$$

which has the real and imaginary parts $\chi'(\omega)$ and $\chi''(\omega)$ respectively

$$\chi(\omega) = \chi'(\omega) - i\chi''(\omega)$$

The solution to the Bloch equations has the real part $\chi'(\omega)$

$$\chi'(\omega) = \tfrac{1}{2}\chi_o \omega_o T_2 \frac{(\omega-\omega_o)\, T_2}{1+(\omega-\omega_o)^2\, T_2{}^2+\gamma^2 H_1{}^2 T_1 T_2}$$

corresponding to the dispersion mode, and the imaginary part $\chi''''(\omega)$

$$\chi''(\omega) = \tfrac{1}{2}\chi_o \omega_o T_2 \frac{1}{1+(\omega-\omega_o)^2\, T_2{}^2+\gamma^2 H_1{}^2 T_1 T_2}$$

corresponding to the absorption mode. In the absence of saturation

$$\gamma^2 H_1{}^2 T_1 T_2 \ll 1$$

we obtain

$$\chi'(\omega) = \tfrac{1}{2}\, \chi_o \omega_o T_2 \frac{1}{1+(\omega-\omega_o)^2 T\, {}_2{}^2}$$

$$\chi''(\omega) = \tfrac{1}{2}\, \chi_o \omega_o T_2 \frac{1}{1+(\omega-\omega_o)^2 T\, {}_2{}^2}$$

In practice, the magnetic field is scanned rather than the frequency and using the expressions

$$\omega = \gamma H \qquad \omega_o = \gamma H_o$$

we can write the susceptibilities as a function of the magnetic field

$$\chi'(H) = \left(\frac{\chi_o H_o}{\Delta H_{\frac{1}{2}}}\right) \frac{\dfrac{H-H_o}{(\frac{1}{2}\Delta H_{\frac{1}{2}})}}{1+\dfrac{H-H_o}{(\frac{1}{2}\delta H_{\frac{1}{2}})}}$$

$$\chi''(H) = \left(\frac{\chi_o H_o}{\Delta H_{\frac{1}{2}}}\right) \frac{1}{1+ \frac{H-H_o}{(\frac{1}{2}\delta H_{\frac{1}{2}})^2}}$$

where

$$T_2 = \frac{2}{\gamma \Delta H_{\frac{1}{2}}}$$

The derivative of the magnetic suseptibility is measured in ESR experiments, and it is obtained from these expressions through differentiation, to give

$$\frac{d_{\chi}'(H)}{dH} = \frac{2\chi_o H_o}{(\Delta H_{\frac{1}{2}})} \frac{\frac{H-H_o}{(\frac{1}{2}\Delta H_{\frac{1}{2}})}}{[1+(\frac{H-H_o}{\frac{1}{2}\delta H_{\frac{1}{2}}})]^2}$$

$$\frac{d_{\chi}''(H)}{dH} = \frac{2\chi_o H_o}{(\Delta H_{\frac{1}{2}})} \frac{\frac{H-H_o}{(\frac{1}{2}\Delta H_{\frac{1}{2}})}}{[1+(\frac{H-H_o}{\frac{1}{2}\delta H_{\frac{1}{2}}})]^2}$$

Experimentally, we ordinarlily measure the quantity $d\chi'(H)/dH$ when we record an ESR spectrum. The above equation gives the shape of the resonance absorption when the lineshape is lorentzian and the power is low so that saturation can be neglected.

7c Saturation

At higher powers where the saturation can be appreciable we write the observed lineshape in the more convenient form

$$Y'_{(H)} = \frac{sH_1 \, Y^{o\,\prime}_m}{\sqrt{3}[1+s(H-H_o)^2\gamma^2 T_2{}^2]^2}$$

where s is the saturation factor defined by

$$s = \frac{1}{1+\gamma^2 H_1{}^2 T_1 T_2}$$

and the rf field H_1 is proportional to the square root of the power.

The spin lattice relaxation time may be found by plotting the signal amplitude $Y_m{}'$ against the square root of the power and determining the maximum point of the curve.

At the maximum point, which satisfies the condition

$$\frac{dY'_m}{dH_1} = 0$$

we have the following value for the saturation factor

$$s = 2/3$$

as may be found carrying out the differentiation.

This maximum point provides the spin lattice relaxation time T_1 from an expression which depends upon a knowledge of the rf magnetic field value H_1 at this point.

$$T_1 = 1.97 \times 10^{-7} \frac{\Delta H^o_{pp}}{g(2H_1)^2}$$

The corresponding expression for T_2 is

$$T_2 = \frac{2}{\sqrt{3}\Delta H^o_{pp}}$$

BIOLOGICAL APPLICATIONS

8a) Radiation Damage

When DNA is irradiated with x-rays, gamma rays or other high energy particles electrons are removed from various atoms or atomic groups to produce primeary free radical cations $\cdot p^+$

$$h\nu + P \rightarrow \cdot P^+$$

The electrons that are released can engage other molecules to produce secondary radical axions $\cdot S^-$

$$e + S \rightarrow \cdot S^+ + 2\ e$$

as they can be captured to produce secondary radical cations

$$e + S \rightarrow \cdot S^-$$

Those paramagnetic species are observed at low temperatures. At room temperature they are that loud and tend to form final more stable radicals by the processes of proton extraction

$$\cdot S^+ + H^+ \rightarrow \cdot SH$$

or hydrox extraction

$$\cdot S^+ + OH^- \rightarrow \cdot SOH$$

from the surroundings.

Some research workers have reported that there is an electron affinity scale for the DNA laser

$$G < A < T < C$$

with uracil (U) similar to thymine (T). This means that in a sample with a mixture of losses radical ions formed from a base at the left side of the seven will interact with bases on the right and transfer their electrons to them. For example, the following reaction is likely to occur

$$\cdot A^- + T \rightarrow A + \cdot T^-$$

Various combinations of samples with mixed base have been studied to show this.

8b Saturation Transfer

We have now completed the survey of background material and are in a position to explain saturation transfer (ST). This phenomenon is based upon the effect of anisotropies in the hamiltonian on the relaxation behaviour of partially saturated free radicals with tumbling times in the range from 10^{-3} to 10^{-7} s.

We should recall that the resonance field of a sample with anisotropic parameters will depend on the angle between a particlular molecular axis of symmetry and the external field. On the other hand, if the sample is made up of molecules undergoing rotational Brownian diffusion in a viscous solvent the ESR spectrum will depend not only on the magnitude of the anisotropy but also in the correlation time τ_2 which is the average time that it takes the molecule to reorient and change the angle θ by an amount equal to one radian (∼ 57°).

As the motion slows down, the spectrum will approach more and more the powder shape, and as the rate increases the anisotropies average out more and more and the spectrum looks like that of a liquid. Intermediate degrees of motion produce spectra with shapes between the extremes. When τ_2 is longer than 10^{-3} s the spectrum looks like a powder and there will not be any difference between the spectrum of a molecule tumbling with a correlation time of 10^{-3} and another tumbling with τ_2 equal, say, to 10^{-2}s. A liquid like spectrum is obtained when τ_2 is less than 10^{-7}s. How we can get information about correlation times in the region of 10^{-7}s to 10^{-3}s?

To analyze this problem in greater detail we will consider the ESR spectra produced by paramagnetic nitroxides. These free radicals called spin lables attach themselves to macromolecules and produce an equal intensity triplet due to the hyperfine interaction of the unpaired electron with the nuclear spin I = 1 of the nitrogen. The g-factor is close to isotropic, and the hyperfine interaction is axially symmetric. As a result each molecule oriented at a particular angle θ will produce resonance absorption at a particular magnetic field, and the intensity of the absorption at that magnetic field strength will be proportional to the probability that a molecule will be so oriented. We can see that various lines are at different resonant fields, that is to say two lines belong to two molecules that make different angles with the external field. The importance of this is the following: for certain angles θ a small change in angle will produce a large change in the resonant field and for certain other angles the same change in angle will produce little or no change in the resonant field.

Suppose that we have a sample with paramagnetic molecules (i.e. molecules with nitroxide radicals attached). If we scan through the spectrum at very low power its shape will not be affected by the power level. A priori it will look like all the molecules will also be equally affected by saturating powder levels, and that a spectrum with a tumbling time of 10^{-7}s will not be distinguished from one of 10^{-4}s by its behaviour under saturation. A more careful examination will tell us that this is not so.

During the measurement of time all of the molecules will tumble at the same average rate but not all will be making the same angle with the field. The key to understand saturation transfer is based in the fact that the two lines mentioned before are not at the same resonance field and we require analytical expressions for the dependence of the resonance field on the hyperfine interaction angle of orientation.

In the case of nitroxides the anisotropy in the hyperfine coupling is constant but is is convenient to use the zero field term expressions that we

already have derived since the idea is the same. Thus we have

$$\frac{dH_{res}}{d\theta} = 3ND\left[\frac{2}{3}\left(\frac{H_o-H}{D}\right) + \frac{1}{3}\right]^{\frac{1}{2}} \sin\theta$$

The two extreme values of H_{res} for $\theta = 0$ and $\theta = \pi/2$ are

$$H_{res}\ (0) = H_o - D$$

$$H_{res}\ (\pi/2) = H_o + \frac{D}{2}$$

and at these extreme points we have

$$\left.\frac{dH_{res}}{d\theta}\right|_{\theta = 0} = 0$$

$$\left.\frac{dH_{res}}{d\theta}\right|_{\theta = \frac{\pi}{2}} = 0$$

If we consider a molecule which makes an angle close to 0 or $\pi/2$, a small change of angle will not alter its resonant field since $dHres/d\theta = 0$ for $\theta = 0$, $\pi/2$ and so the molecule will remain saturated and the signal will be high. When a second molecule is oriented at an angle different from 0 or $\pi/2$ where $dH_{res}/d\theta$ is large and it moves to another resonant field it "transfers" its saturation. The saturation behavior at its new angle will not be the same as that at its original angle of orientation. This change in saturation is reflected in the spectral line shape, and it provides us with information about the rate of tumbling.

How is this information obtained? Researchers have used the Bloch equations which were discussed above and also the Density Matrix method both of which are rather equivalent to each other. The basic idea is to stimulate spectra under the condition of partial saturation taking into account tumbling in the presence of anisotropic interactions. The resulting lineshapes compare fairly well with experiments.

We have been discussing saturation transfer in terms of the conventional absorption spectrum and its derivative. We examined the changes that occured in the regular absorption signal that is in phase with the modulation reference signal, and we showed how the observed spectrum varies with the rate of tumbling. The spectrometer settings used for recording spectra of this type are not the best ones for detecting small changes in tumbling rates. Therefore we will pause briefly to describe the modes of detection that are most suitable for studying ST and then we will show how to characterize and analyze the resulting spectra.

To specify different types of spectra, a conventional notation has been accepted and before we continue with the description of ST we will describe this notation:

The letter U indicates dispersion

The letter V indicates absorption

The index 1 or 2 indicates first harmonic (first derivative) and second harmonic (second derivative) detection

Primed or Unprimed indicate out of phase or in phase respectively.

The normal spectrum recorded with a conventional spectrometer is a V_1 type, that is to say absorption, first harmonic, in phase. Nevertheless, with two choices of a harmonic and phase there are a total of 8 possibilities. All of these were tried and the two which give the highest sensitivity for ST, are U_1' which is the best, and V_2' which is the second best.

The mode that is used regularly is V_2' because it is much simpler from the point of view of instrumentation. Modern E.P.R. instruments with conventional 100 kHz modulation have a switch that converts to second harmonic detection. Under this condition the modulation is at 50 kHz and detection is at 100 kHz.

The prime in V_2' indicates out of phase and we all know that one of the rules for obtaining good spectra, expecially if there is a sensitivity problem, is to be sure that the phase is set correctly. In fact a perfect out of phase setting should give zero signal, but in practice the out of phase signal is 1% of the in phase one.

The best way to be sure that we are out of phase is to operate at low power and look for the signal in phase, maximize it, change the phase by 90°, increase the gain as much as possible and adjust the phase to minimize the signal.

It seems paradoxical that we take so much trouble in being out of phase where the signal is, zero, or almost zero, but it happens that if now an intermediate saturation power is applied a stronger signal appears! And this signal is very sensitive to the rate of tumbling as we explained before.

How much modulation? time constant? power? must we apply? For better or for worst no definite rule can be established and so the actual value of τ_2 can not always be determined with also precision as is the case in the measurement of the absolute number of spins, but rather a good accuracy can be obtained if relative measurements are made. For example we vary the tumbling rate by changing the solvent, viscosity or temperature.

About the best way to set the power, modulation, etc., is to follow the review of Hyde and Thomas (1980). For the people that have a Varian E Line instrument the manual is reasonably good and explicit. From my experience it is very important to be careful with the phase setting and the method that I described earlier is a small modification of what is called the self null method. It must be emphasized that during the search for a null signal or out of phase spectrum the power whould be very low, of the order of 1 mW. That poses a problem because very seldom is the signal to noise very high and so the reduced power practically kills the signal, but life is full of problems.

The experiment is performed in more or less the following sequence. Find the null phase according to the technique explained earlier, applying an intermediate saturation power. There is no rule for this, and trial and error and experience can tell you what is best. Record the spectra and measure the parameters that have been already adopted by convention, namely the ratios H"/H, L"/L and C"/C. The graphs of Hyde and Thomas give the correlation time τ_2 in terms of the values of these ratios.

FRACTALS

9a) Definitions

There is a rather big field of research called Automata Theory that covers a wide range of subjects from biological problems to computer models. It has been applied to neural model cellular automata, L systems etc. (L system is called the language theory).

Here we do not intend to go in any deep way in any of these directions, rather we plan to give a pedestrian view of cellular automata: simple definitions, its relation with fractals, and specifically an application to the determination of the radius of gyration of proteins by means of Electron Spin Resonance.

It appears that the basic laws of physics relevant to everyday phenomena are now known. Yet there are many everyday natural systems whose complex structure and behavior have so far defied even qualitative analysis. For example, the laws that govern the freezing of water and the conduction of heat have long been known, but analyzing their consequences for the intricate pattern of snowflake growth has not yet been possible. Many components that make up the whole system act together to yield very complex behavior.

In some cases this complex behavior may be simulated numerically with just a few components, but in most cases the simulation requires too many components, and this direct approach fails. One must instead attempt to distill the mathematical essence of the process by which complex behavior is generated. The hope in such an approach is to identify fundamental mathematical mechanisms that are common to may different natural systems. Such commonality would correspond to universal features in the behavior of very different complex natural systems.

To discover and analyze the mathematical basis for the generation of complexity, one must identify simple mathematical systems that capture the essence of the process. Cellular automata are a candidate class of such systems. Cellular automata promise to provide mathematical models for a wide variety of complex phenomena, especially biological growth.

Cellular Automata are simple mathematical models of natural systems. They are made up of a simple lattice of discrete identical sites. At each site there will be a set of integer numbers and these numbers evolve in time according with some rather simple rule. One of the simplest examples of this cellular automata is the following: Our lattice will be a line of equally spaced sites and the set of integer numbers is 0 and 1. The evolution in time is obtained when a new line is derived from the previous one by the simple rule

$$A_i^{(t+1)} = A_{i-1}^{(t)} + A_{i+1}^{(t)} \mod 2$$

We have then the simplest lattice of equally spaced points in one dimension; the simplest set of integers: 0 and 1 and probably the simplest rule of evolution. In the equation for the evolution, mod 2 indicated that the value could be either 0 or 1, whichever is the remainder after division by two (this is equivalent to the Boolean algebra, 'exclusive or').

To start we fix a seed, for example, along a line one site is selected as 1 and all the others are 0. To evolve in time we go to a line below and the number at each site is the sum, mod 2 of two sites from the previous line, one before and one after, as shown below.

0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	1	0	1	0	0	0	0	0	0	0
0	0	0	0	0	0	1	0	0	0	1	0	0	0	0	0	0
0	0	0	0	0	1	0	1	0	1	0	1	0	0	0	0	0
0	0	0	0	1	0	0	0	0	0	0	0	1	0	0	0	0
0	0	0	1	0	1	0	0	0	0	0	1	0	1	0	0	0
0	0	1	0	0	0	1	0	0	0	1	0	0	0	1	0	0
0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0
1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1

After a long time the system starts to show striking regularities and one of them is 'self-similarity,' that is to say, if we magnify part of the pattern it can not be distinguished from the whole. Another way of putting is is to say that the pattern is invariant under length scaling.

This type of self similarity pattern is called fractal. The reason for the name fractal is because if we think of a square and change the length to, say twice the previous one, the area will be 2^2 times bigger and we say that the square is a two dimension system. On the other hand if we look at figure 1 the area of the number ones is 29 in a rectangle of dimensions 17 x 9. If we double the length and width to 2 x 17 and 2 x 9 the area of number ones will not be 2 x 29 but rather $2^{1.585}$ x 29 and we say that it is a fractal with dimension 1.585. We see that this simple model generates self similarity; in addition it has another property which is even more striking, the property of self-organization. This can be put in evidence if we start with a random line of zeros and ones as shown in the figure.

After some time the cellular automata starts to organize itself. There are some mollusks with shells that actually show a similar pattern indicating that the growth of this shell could follow cellular automaton rules. In systems that follow conventional thermodynamics, the second law implies a progressive degradation of any inital structure with the well known property that systems which evolve in time increase their entropy, that is to say, the system evolves toward disorder. On the other hand biological systems evolve in the opposite direction: they generate structures even when they start from disorder.

The cellular automata is one, very simple, example that belongs to the second class. That is to say, even starting from disorder it generates structure. Another interesting feature is the following: given a particular state the next state is completely defined, for example

state i   0 1 0 1 1 0 1 0
state i + 1   0 0 1 1 0 0

But given state i + 1 we do not know for sure which is the predecessor, we could reach the same i + 1 from other previous states, for example

state j   1 0 1 0 0 1 0 1
state i + 1   0 0 1 0 0 0

This tells us that the evolution is irreversible. In fact we can start with any state, proceed by evolution, and never reach a similar state. To check this it is more convenient to use finite systems with periodic boundaries, like in a circle.

The few states toward which the system converges are called attractors. The possibility of such structures is a result of irreversibility.

Conventional thermodynamics treats systems which are intrinsically reversible. The irreversibility comes from the statics, where each state is practically defined by a chain of predecessors. In the cellular automata the irreversibility is intrinsic and the difference makes one case increase its energy and the other decrease it.

This brief description of the cellular automata gives us an idea of the possibility of the existance of objects of fractional dimension called fractals. Examples in every day life are snowflakes, broccoli etc. that are shown in the color slides. The main feature is the self similarity.

9b) Protein Dimensions

Now we will take a look at some proteins which are polymers made up of dimers. Some are more linear than others depending on how twisted they are. Several definitions are given in relation with its dimensions:

Average end to end dimension is

$$h_{av} = (\overline{H^2})^{\frac{1}{2}}$$

where h is the distance between the ends of a given configuration and the average is over all configurations

Average radius of gyration R

$$R_G = (\overline{R^2})^{\frac{1}{2}}$$

$$= (\overline{\sum_i m_i r_i{}^2 / \sum_i m_i})^{\frac{1}{2}}$$

and if the masses are the same, then

$$R_G = \frac{1}{N} \ (\Sigma \ \overline{r_i{}^2})^{\frac{1}{2}}$$

If each dimer of length ℓ were located one after the other in a line the end to end length h would be given by

$$h = N\ell$$

for N dimers.

On the other hand if these dimers were allowed to move in any direction, each step will be equivalent to a random walk and in this case

$$h = N^{\frac{1}{2}}\ell$$

Further we must realize that the molecule can not occupy two sites simultaneously. When this is taken into account we obtain what is called a self avoiding random walk that gives the following end to end distance for a two and three dimensional space.

$$h = N^{4/3}\ell$$

and

$$h = N^{5/3}\ell$$

From the above expressions N can be obtained as follows

$$N = (h/\ell)^{\overline{d}}$$

where $\overline{d}$ is the fractal dimension. For the case of a polymer in a line h is proportional to N for a given ℓ making $\overline{d} = 1$, for a random walk N is proportional to h^2 making $\overline{d} = 2$, etc. From crystallographic x-ray information we can determine $\overline{d}$.

For each structure a sphere is drawn and all carbons along the backbone of the protein are counted. In this way for every configuration we will have a sphere of radius h_i, and N_i carbons. An average is taken and fit to the equation $N = (\frac{h}{\ell})^{\bar{d}}$ from which $\bar{d}$ is obtained. The values obtained range between $1.2 < \bar{d} < 1.8$ indicating the possibility of determining structural information.

As we have seen, in each case we need to take an average since we do not have the regularity required for the definition of a fractal: self similarity (two objects close but not equal do not actually have similarity).

The definition can, however, be extended to irregular figures through the concept of statistical self similarity, when some statistical distribution function describing the properties of the object exhibits self similarity rather than the object itself. In our case the components of the vectors connecting points on a random walk of N steps are Gaussian random variables of mean zero and standard deviation $\sigma(N) = \ell N^{\frac{1}{2}}$ where ℓ is the step size.

It can be shown that the standard deviation of $\frac{N}{n}$ steps of length ℓ is the same as the standard deviation of N steps of length ℓ/s with $s = n^{\frac{1}{2}}$, or

$$\begin{aligned}\sigma_1(N) &= \sigma_0(N/n)\\ &= n^{\frac{1}{2}}\,\sigma_0(N)\end{aligned}$$

To probe the first we notice that

$$\begin{aligned}\sigma_1(N) &= \frac{\ell}{s}\,N^{\frac{1}{2}}\\ &= \ell(\tfrac{N}{n})^{\frac{1}{2}}\\ &= \sigma_0(\tfrac{N}{n})\end{aligned}$$

The second results again from the definition

$$\sigma_0(\tfrac{N}{n}) = \ell\,(\tfrac{N}{n})^{\frac{1}{2}}$$

$$\sigma_0(N) = \ell\,N^{\frac{1}{2}}$$

$$\alpha\sigma_0(N) = \sigma_0\,(N/n)$$

$$\alpha = \frac{1}{n^{\frac{1}{2}}}$$

$$\sigma_0\,(\tfrac{N}{n}) = \frac{\ell}{s}\,(\tfrac{N}{n})^{\frac{1}{2}}$$

A rather similar way of defining a fractal is the following: the fractal dimension, d and the number of copies n of a scaled object needed to cover the original to the scale factor s are related by

$$n = s^d$$

and from this expression we have

$$\begin{aligned}d &= \ell n\ n/\ell n\ s\\ &= \ell n\ n/\ell n\ n^{\frac{1}{2}}\\ &= \frac{\ell n\ n}{\frac{1}{2}\ell n\ n}\\ &= 2\end{aligned}$$

9c) Relaxation Times

Now we will describe an interesting use of fractals in relation to the end to end length of proteins.

First we need to revise the concept of relaxation time.

As it was mentioned before when a system of spins is perturbed, it returns to equilibrium with a characteristic time T_1 called the spin-lattice relaxation time. Many complications appear when one wants to calculate T_1 which among other things has a strong temperature dependence.

Basically when a spin flips at low temperature where there is a sufficient number of phonons of the proper energy it either gives or receives a kick from the lattice creating or annihilating a phonon, and the process is called direct. At higher temperatures where there is a wide band of phonons it is more probable that one phonon collides with the spin, making it flip, and a new phonon is produced. So two phonons of frequencies ν_1 and ν_2 are involved in such a way that the energy is conserved.

$$g\beta H = h(\nu_1 - \nu_2)$$

The general expression for T_1 is

$$\frac{1}{T_1} = A' \coth \left(\frac{h\nu}{2\beta T}\right) + CT^9$$

$$\cong AT + CT^9$$

where the first term corresponds to the direct process and the second to the Raman or two phonon process. In fact things are more complicated than this because in addition there could be bottleneck which, in turn, could be normal, intermediate, or full. There also could be cross relaxation, an Orbach process, a tunneling process, etc.

If we consider just Raman terms we can use the following theoretical expression for the value of T_1.

$$\frac{1}{T_1} = \int_0^{\nu_D} \frac{\nu^4\rho^2(\nu)e^{h\nu/\beta T}}{(e^{h\nu/\beta T}-1)^2} \, d\nu \qquad \text{(Raman)}$$

where $\rho(\nu)$ is the density of vibrational states and ν_D is the Debye or cutoff frequency. The definition of $\rho(\nu)$ tells us that the number of vibrational states between the frequencies ν and $\nu + d\nu$ is $\rho(\nu)d\nu$. The ν_D is chosen so that the total number of vibrational modes equals the number of degrees of freedom of the system.

For a regular lattice of dimension d (Euclidean) with constant sound velocity v_s it is known that

$$\rho(\nu) \, \alpha \, \nu^{d-1} \qquad 0 \leq \nu \leq \nu_D$$

$$\rho(\nu) = 0 \qquad \nu > \nu_D$$

For a fractal structure it is tempting to use scaling agruments, that is to say,

$$\rho(\nu) \, \alpha \, \nu^{\tilde{d}-1} \qquad 0 \leq \nu \leq \nu_D$$

$$\rho(\nu) = 0 \qquad \nu > \nu_D$$

The reason why we write $\tilde{d}$ instead of $\bar{d}$ will be explained later. Now the following expression for T_1

$$\frac{1}{T_1} = \int_0^{\nu_D} \nu^{2+2\tilde{d}} \frac{e^{h\nu/\beta T}}{(e^{h\nu/\beta T}-1)^2} \, d\nu$$

with the change in variable $Z = h\nu/\beta T$ gives

$$\frac{1}{T_1} = \left(\frac{\beta T}{h}\right)^{3+2\tilde{d}} \int_0^{Z_D} \frac{Z^{2+2\tilde{d}}e^Z dZ}{(e^Z-1)^2}$$

If $\nu_D/T \geqq 333$ GHz/K or for example $\nu_D = 4000$ GHz and T = 12 K, then we can replace Z_D by ∞ where

$$\int_0^{Z_D} f(Z) \, dz \neq f(T)$$

and so

$$\frac{1}{T_1} \, \alpha \, T^{3+2\tilde{d}} \qquad \text{(Raman)}$$

if $\tilde{d} = 3$ (Euclidean space) then

$$\frac{1}{T_1} \alpha \, T^9$$

but if $\tilde{d} < 3$ as in proteins then the exponent could be less than 9 as the experiment actually shows.

To measure this requires some care, especially since other contributions can produce the T^n Raman behavior. Two techniques can be used, one, continuous saturation and the other pulse and recovery. The first technique is simpler and basically every instrument has the capability to do the work. A pulse and recovery spectrometer is a more sophisticated instrument which requires some intrumentation experience to design it and to later operate it.

Relaxation times are usually very short and low temperatures are required to increase the time to a long enough value so it can be measured; typical temperatures range from 1.5 K to 25 K. Between 1.5 K and 4.2 K the temperature is obtained by pumping on liquid helium, the lower the pressure the lower the temperature. Between 4.2 K and 25 K the temperature is obtained either by means of a cold finger or by circulating helium vapor.

The value $\tilde{d}$ is called the spectral dimension and the value $\bar{d}$ is the fractal dimension, and they are related. To see this relation we can use the fact that

$$N(R) = s^{\bar{d}}\ N(R/s)$$

which it is obtained from the previous definition

$$N(R) = \left(\frac{R}{\ell}\right)^{\bar{d}}$$

and

$$N\left(\frac{R}{s}\right) = \left(\frac{R}{s\ell}\right)^{\bar{d}}$$

$$= \frac{1}{s^{\bar{d}}}\ \left(\frac{R}{\ell}\right)^{\bar{d}}$$

$$= N(R)/s^{\bar{d}}$$

The density of vibrational states in the larger object (R) is the sum of the constituents' densities:

$$\rho_R(\nu) = s^{\bar{d}}\ \rho_{R/s}\ (\nu)$$

then

$$\rho_R(\nu_R) = \frac{d\nu_{R/s}}{d\nu_R}\quad \rho_{R/s}\ (\nu_{R/s})$$

where ν_R and $\nu_{R/s}$ are the fundamental (normal) modes.

If the low frequency scaling obeys the following expression

$$\nu_{R/s} = s^a\ \nu_R$$

then

$$s^{\bar{d}}\ \rho_{R/s}\ (\nu_R) = s^a\ \rho_{R/s}\ (s^a \nu_R)$$

and

$$\tilde{d} = \bar{d}/a$$

a range between 1 and $\bar{d}$. The experimental results agree very nicely with the theoretical predictions.

I will describe a completely different approach used to calculate some properties of a polymer like the average end to end length and the ratio between an average monomer and its "radius." The end to end and monomer length were already defined. The radius mentioned here is the radius of a hypothetical sphere attached to the monomer. This sphere represents, depending on the point of view, a repulsive potential or the size of the molecule or a simple device to restrict the bending of the molecule.

This model is called "pearl-necklace." There are $N_o + 1$ hard spheres of diameter h, indexed from 1 to $N_o + 1$ which are connected by N_o bonds of length ℓ. The end to end correlation length R which is a function of N_o, h_o and ℓ_o is given by

$$R(N_o,\ h_o,\ \ell_o) = \langle r_1 - r\ N_o + 1)^2\rangle^{\frac{1}{2}}$$

where the r_i are the coordinates of the center of the sphere.

We already have written the scaling law for the length. A slightly more sophisticated expression is given by

$$R(\ell_o,\ h_o,\ N_o) = \ell_o N_o{}^{\nu} t\ f(N_o(\frac{h_o}{\ell_o})^{d/\phi_f})$$

where d is the dimension, ν_t is the tricrital exponent and ϕ_t is the crossover exponent. In the mean field approximation

$$\nu_{MF} = \phi_{MF} = \tfrac{1}{2}$$

and with this value we have $R(\ell_o, h_o, N_o) = A\ell_o\delta_o^c N^\nu$.

The basic idea is how, knowing N_o, ℓ_o, and h_o we can calculate the fractal dimension. One of the techniques is Renormalization Group, another one is Monte Carlo Renormalization Group, etc. I will describe briefly the latter approach. Given N_o, ℓ_o, and h_o and using the Monte Carlo method, a chain is generated, then we use what is called a block transformation and redefine the bonds replacing by two consecutives by one, in this way the number of bonds N_o is reduced to $\frac{N_o}{2}$, in general to $\frac{N_o}{s}$ if s is the number of bonds replaced by one. It is required that after the renormalization

$$R(\ell_o, h_o, N_o) = R(\ell_1, h_1, N_{o/s})$$

The new ℓ_1 is obtained by

$$\ell_1 = \langle (r_j - r_{j+s})^2 \rangle^{\frac{1}{2}}$$

With ℓ, and $N_1 = N_{o/s}$ we pick some h_1 and run a Monte Carlo chain, h_1 is repeatedly adjusted until $R\ (\ell_o, h_o, N_o) = R(\ell_1, h_1, \frac{N_o}{s})$. The process is repeated and the block bonds have the following behavior

$$\ell_k \cong A\ell_o\ \delta_k^c\ s^{\nu k}$$

and

$$\frac{\ell_{k+1}}{\ell_k} = s^\nu\ (\frac{\delta_k}{\delta k+1})^c$$

with $\delta_k \rightarrow \delta_{k+1} \rightarrow \delta^*$ where δ^* is the fixed point.

After some math it results

$$R(\ell, h, N) = \ell\ (\frac{\delta}{\delta^*})^c\ N^\nu$$

Details on Monte Carlo calculations, computer programs and actual calculation steps will be given in a session in the afternoon for people that are interested.

SUGGESTED READING

For Static Topics

"Electron Spin Resonance," J. E. Wertz and J. R. Bolton, McGraw-Hill, New York (1972).

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