APL, a powerful research tool in Magnetic Resonance Spectroscopy

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I-Introduction

In spite of its outstanding scientific potential, **APL** is up to now ignored or scarcely exploited by research workers. During 15 years as the head of the Magnetic Resonance Laboratory of the Nuclear Research Center at Saclay, the author has extensively used **APL** in his works [1-3] and continues to promote its scientific applications.

The Magnetic Resonance Spectroscopy (**MRS**) includes two main branches, the Nuclear Magnetic Resonance (**NMR**) and the Electron Spin Resonance (**ESR**) also called Electron Paramagnetic Resonance (**EPR**). The **NMR** is a priviledged method for the identification and conformational analysis of organic and biological molecules and is well known for its medical application, the Magnetic Resonance Imaging. The **ESR/EPR** which is the main subject of this topics, is the specific method for studying paramagnetic molecules i.e. molecules possessing at least one unpaired electron, namely the free radicals resulting from the breaking of a chemical bond, triplet fundamental (e.g. the oxygen of air) or lowest excited states and some metal coordination complexes. Most of these species are very reactive and are initiators or intermediates in a large number of chemical and biological processes : oxidation, combustion, polymerization, radiation damaging, photosynthesis etc… An important application common to the **NMR** and **ESR** is the molecular dynamics which provides thorough information on some physical properties of condensed matter.

II-Principles

Electrons and most of the nuclei possess a spin angular momentum, denoted $\vec{S}$ and $\vec{I}$, respectively, as well as magnetic moments $\vec{\mu}_e = g_e\beta_e\vec{S} = \gamma_e\hbar\vec{S}$ and $\vec{\mu}_I = g_I\beta_n\vec{I} = \gamma_I\hbar\vec{I}$ where g_e and g_I are the spectroscopic factors, the latter being specific of each nucleus, γ_e and γ_I the relevant gyromagnetic ratios, β_e and β_n the Bohr and nuclear magnetons and $\hbar$ the Planck's constant divided by 2π. In a magnetic field $\vec{B}_0$, the spins and magnetic moments undergo a precession of angular frequency $\omega_0 = \gamma B_0$ about $\vec{B}_0$. For a spin quantum number S or I, multiple of ½, the spins and magnetic moments take 2S+1 or 2I+1 orientations defined by the projections $M_S = S, S-1, \ldots 1-S, -S$ or $M_I = I, I-1, \ldots 1-I, -I$ of $\vec{S}$ or $\vec{I}$ on $\vec{B}_0$. To each magnetic quantum number M_S or M_I corresponds an energy level.

A magnetic resonance experiment consists in submitting a small sample (0.1-1 ml) placed in a very strong and homogeneous magnetic field $\vec{B}_0$ to a rotating radiofrequency (**NMR**) or microwave (**ESR**) magnetic field $\vec{B}_1$ perpendicular to $\vec{B}_0$ ($B_1 << B_0$). The resonance phenomenon corresponds to a transition between adjacent energy levels which occurs when the angular frequency of $\vec{B}_1$ is equal to $\omega_0 = \gamma B_0$ and involves the absorption of a photon of energy $h\nu_0 = g\beta B_0$, ν_0 being the spectrometer frequency and h the Planck's constant. For technical reasons, the resonance is obtained by varying ν_0 at constant field (**NMR**) or B_0 at constant frequency (**ESR**) and the **ESR** spectra are usually recorded as the first derivative.

The nuclear and electron spins are seldom isolated and generally experience local magnetic fields due to other spins. The 2S+1 fundamental energy levels of a spin S interacting with a spin I are splitted into 2I+1 sublevels and the resulting (2S+1)(2I+1) levels are :

```
E←(B0×(ge×be×MS)∘.-gn×bn×MI)+a×MS∘.×MI
```

where **a** is the hyperfine coupling constant expressed in energy units. The allowed **ESR** transitions between these levels follow the selection rule $\Delta M_S = \pm 1$, $\Delta M_I = 0$. The above expression is easily extended to any number of spins of any quantum number and is an usual approximation when its first term is much larger than the second one. Figure 1 shows a simple application of these principles to a S=1/2, I=1/2 system, the H• atom, the smallest and one of the most reactive free radical.

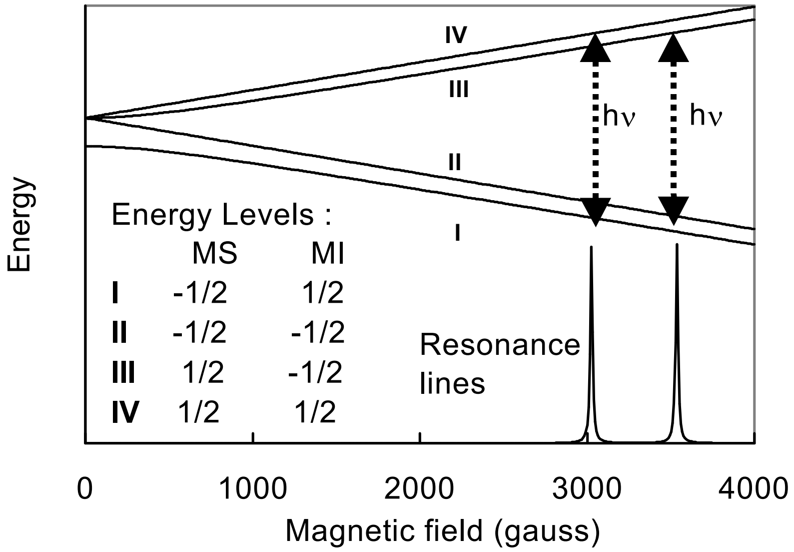


Figure 1 : Energy levels and ESR resonance lines of the hydrogen atom. Hyperfine coupling constant a = 1.42 GHz or 508 gauss (1 gauss = 0.1 mT), spectrometer frequency ν_0 = 9.24 GHz. Allowed transitions : I⇔IV and II⇔III.

III-Applications to the ESR spectroscopy.

The interpretation of the **ESR** spectra in terms of identification of the paramagnetic species we are dealing with, of the hyperfine coupling parameters and sometimes of dynamical behaviour is generally not feasible without the help of computer simulations. A visual comparison of the experimental spectum with the simulated one tell us if the starting assumptions made about this species are likely or not. The **hresol** function listed below is a simplified version for the simulation of high resolution **ESR** spectra of radicals in solution.

```
hresol;⎕IO;A;Y;i
⎕IO←1 ◇ 'Central field (mT) :' ◇ Bc←⎕
'Nuclear spin quantum numbers :' ◇ NS←⍴SN←,⎕
L0:'Hyperfine coupling constants (mT)' ◇ →(NS≠⍴HFC←,⎕)/L0
SW←Bc+⌊0.5+¯1.2 1.2×SN+.×|HFC ⍝Spectral window centered on B
c
'Number of points :' ◇ dH←--/SW÷NPTS←⎕
X0←SW[1],SW[1]+dH×⍳NPTS ◇ DIM1←1+2×SN
DIM2←⍴V←(DIM1⍴¨HFC)×DIM1⍴¨MI←SN,¨SN-⍳¨2×SN ◇ i←0 ◇ HR←Bc
L1:HR←,HR∘.+∊V[i←i+1] ◇ →(i<DIM2)/L1 ◇ INT←+/HR∘.=HR←HR[⍋HR]
MASK←MASK,1↑MASK←(¯1↓HR)≠1↓HR ◇ HR←MASK/HR ◇ INT←MASK/INT
'Linewidth at half-height : '
Y2←Y×Y←HR∘.-X0 ◇ SP←INT+.×¯2×Y÷A×A←Y2+∆HL×∆HL←0.5×⎕
PLOT XY←X0,[1.5]SP←SP÷+/+\SP ⍝Spectrum first derivative
```

The figure 2 shows the spectrum of the benzyl ($C_6H_5-CH_2^\bullet$) radical generated by this function.

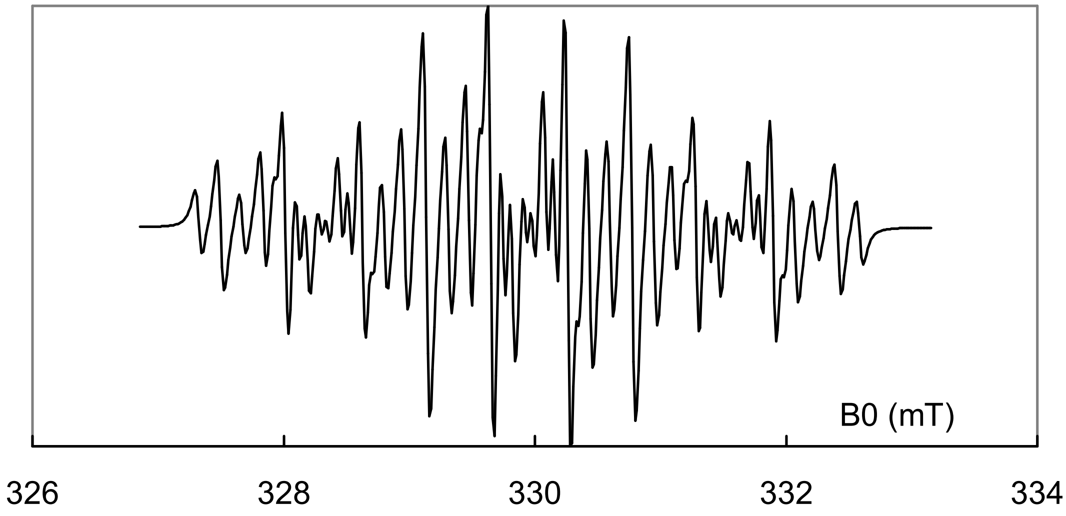


Figure 2. Simulated ESR spectrum (first derivative) of the $C_6H_5-CH_2^\bullet$ radical in fluid solution. The electron spin is coupled to 3 pairs of equivalent protons and a single proton.

The interactions between the spins and the magnetic field and between the spins are of the form $\vec{B}_0.\mathbf{g}.\vec{S}$ and $\vec{S}.\mathbf{A}.\vec{I}$, respectively, where **g** and **A** are symmetric second rank tensors whose components are the sum of an isotropic term (g factor and hyperfine coupling constant) and an anisotropic one. In fluids, the latter is averaged to zero by fast molecular motions but is partially or not averaged in anisotropic systems as solids and liquid crystals.

The functions for fitting the spectra of spin S=1/2 species (free radicals, copper and vanadyl ions) in anisotropic media proceed by the following steps :

1 - Parameters

Invariant : spectrometer frequency, spectral width and nuclear spin quantum numbers.

Adjustable : principal values of **A, g** and **σ** (linewidth) tensors, width of Gaussian line broadening and rate of rotational motion if any.

2 – Angular dependence of the transitions probabilities $P(\theta, \varphi, M_I)$ and linewidths $\sigma(\theta, \varphi, M_I)$, the angles θ and ϕ defining the orientation of $\vec{B}_0$ in the frame of the **g** tensor.

3 – Calculation of resonance fields $B_r(\theta, \varphi, M_I)$.

4 – For each transition, summation of spectra over all orientations :

$$S(B, M_I) = \frac{1}{N} \int_0^{\pi/2} \int_0^{\pi} P(\theta, \phi, M_I) F\left(B - B_r(\theta, \phi, M_I), \sigma(\theta, \phi, M_I)\right) \sin\theta \, d\theta \, d\phi$$

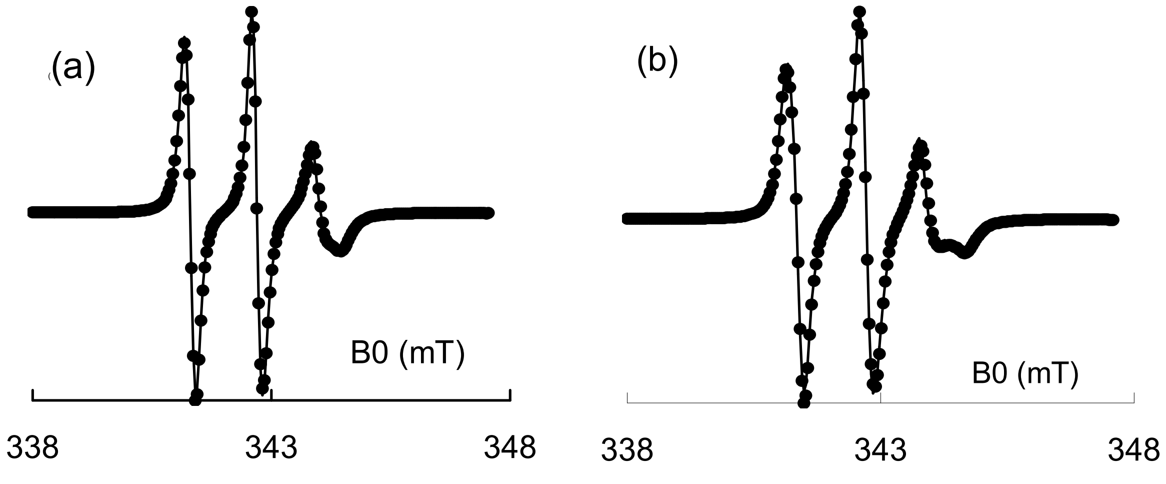
where B is the scanning magnetic field, F the form function and N the normalization factor. For a Lorentzian form function $F(x) = 1/(1+x^2)$, the relevant APL expression is :

```
(d1 d2 d3)←ρ¨B th phi
U←B∘.-,Br ◇ F←÷∆U×1+U×U←U÷∆U←(d1ρ1)∘.×,sigma
S←S÷+/S←F+.×,P×(1○th)∘.×d3ρ1
```

5 – The overall spectrum obtained by summing $S(B, M_I)$ over M_I is convoluted by a Gaussian and derived numerically.

6 – If the agreement with the experimental spectrum is not satisfactory, return to **1** to reajust the parameters. This step may be automated by means of an optimization function based on the Levenberg-Marquardt's algorithm [4] to minimize the variance between the experimental and computed spectra.

Figure 3 shows an example of an automated fitting using the method outlined above.



.Figure 3. Experimental (solid line) and computed (•••••) spectra of an ESR spin-probe, a nitroxide radical, in a model phospholipid membrane before (a) and after (b) addition of cholesterol. This membrane is constituded by phospholipid bilayers separated by water and behaves as a liquid crystal.The broadening and increased asymmetry of the lines from (a) to (b) are significant of an increase of the membrane rigidity and molecular ordering upon cholesterol addition, which may be quantitavely estimated [5].

IV-Conclusion

The theory of magnetic resonance is for a large part founded on matrix algebra, one of the strong points of **APL**, making quite easy the programming of spectral simulations and fitting of experimental data. For this reason the author has chosen **APL** rather than other programming languages currently used by the scientific community (Fortran, Basic, C, Pascal) in spite of its small diffusion and of some problems of portability.

The Magnetic Resonance software is written in APL2 (IBM) and APL+WIN (APL2000). Descriptions of the workspaces are given in the sites www.garpe.org and ftp://ierc.scs.uiuc.edu/pub/SoftwareDatabase.

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