1 Computer Experiment 9: Computational NMR and ESR Spectroscopy

1.1 Background - Magnetic Resonance Spectroscopy

Below, a most elementary introduction to magnetic resonance parameters is provided. Experts will undoubtedly know many more details about the analysis of spin-systems, the formalism of the spin-Hamiltonian and the theory behind it.[1]

1.1.1 Magnetic Moments

It is a basic fact that electrons do not only have a charge (one negative elementary charge) and a mass but also an additional degree of freedom that is associated with an intrinsic angular moment of the electron – the *spin*. Since the spin degree of freedom is quantized, it can only assume two values which are loosely referred to as "spin-up" and "spin-down". The two alternatives are given the symbols |α> and |β> (*spin functions*). The immediate consequence of this additional degree of freedom is that the electron does not only behave as a point charge but also as a small bar magnet (Figure 1).

---

[1] Good textbook on EPR: N.M. Atherton "Electron Spin Resonance", Ellis Horwood, New York, **1993**; Advanced methods: A. Schweiger, G. Jeschke *Principles of pulse electron paramagnetic resonance*, Oxford university press, **2001**; General magnetic resonance C.P. Slichter *Principles of magnetic resonance*, Springer, Heidelberg, **1990**; Authoritative theoretical treatments: R. McWeeny: *Molecular Quantum Mechanics*, Academic press, New York, **1992**; J.E. Harriman: *Theoretical Foundation of Electron spin resonance* Academic press, New York, **1978**; Delightful theoretical introduction (highly recommended!): R. McWeeny: *Spins in Chemistry*, Academic Press, New York, **1970** (available e.g. via Amazon). RESEARCH LITERATURE: For a recent edited book see: Kaupp, M.; Bühl, M.; Malkin, V. (Eds) *Calculation of NMR and EPR Parameters. Theory and Applications*. Wiley-VCH; for RECENT EPR REVIEWS see: Neese, F. (**2003**) Quantum Chemical Calculations of Spectroscopic Properties of Metalloproteins and Model Compounds: EPR and Mössbauer Properties. *Curr. Op. Chem. Biol.*, 7, 125-135 (introduction; easy reading!); Neese, F.; Solomon, E.I. (**2003**) Calculation and Interpretation of Spin-Hamiltonian Parameters in Transition Metal Complexes. (Wiley series: Magnetoscience - From Molecules to Materials edited by J.S. Miller and M. Drillon), Volume IV, p 345-466 (coordination compounds); Sinnecker, S.; Neese, F. (**2006**) Theoretical Bioinorganic Spectroscopy, *Current Topics in Chemistry*, Editor M. Reiher, pp 47ff (bioinorganic chemistry) Neese, F. (**2006**) Quantum Chemical Approaches to Spin-Hamiltonian Parameters. *Specialist Periodical Reports on EPR Spectroscopy*, *Vol. 20*, (Ed. B. Gilbert) Royal Society Press, pp 73ff (methodology) Neese, F. (**2007**) Spin Hamiltonian Parameters from First Principles Calculations: Theory and Application, *Mag. Res. Biol.*, Guest Ed. G. Hanson, in press (relatively comprehensive description of the theory).

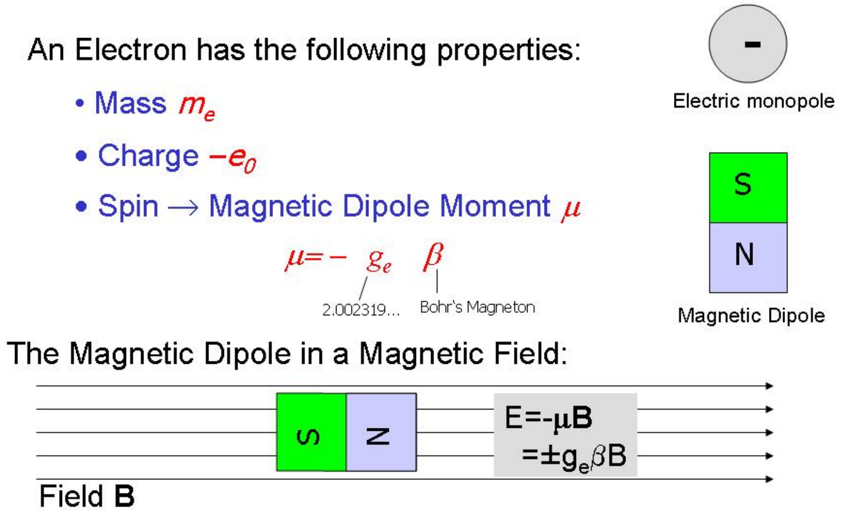


Figure 1: Elementary properties of electrons: point charge, mass and magnetic moment.

In closed-shell molecules all electrons are paired which means that their magnetic moments are aligned antiparallel such that there is no net magnetic dipole moment in the molecule. However, if there is either an odd number of electrons (such as in free radicals), or the molecule exists in a higher spin state (such as in many transition metal complexes or in triplet states of organic molecules), there are unpaired electrons and the molecule develops a magnetic dipole moment. For the sake of simplicity we assume in this course that there is only a single unpaired electron which leads to a total spin of $S = 1/2$. An example of this situation is shown for a typical biologically relevant radical in the figure below (Figure 2).

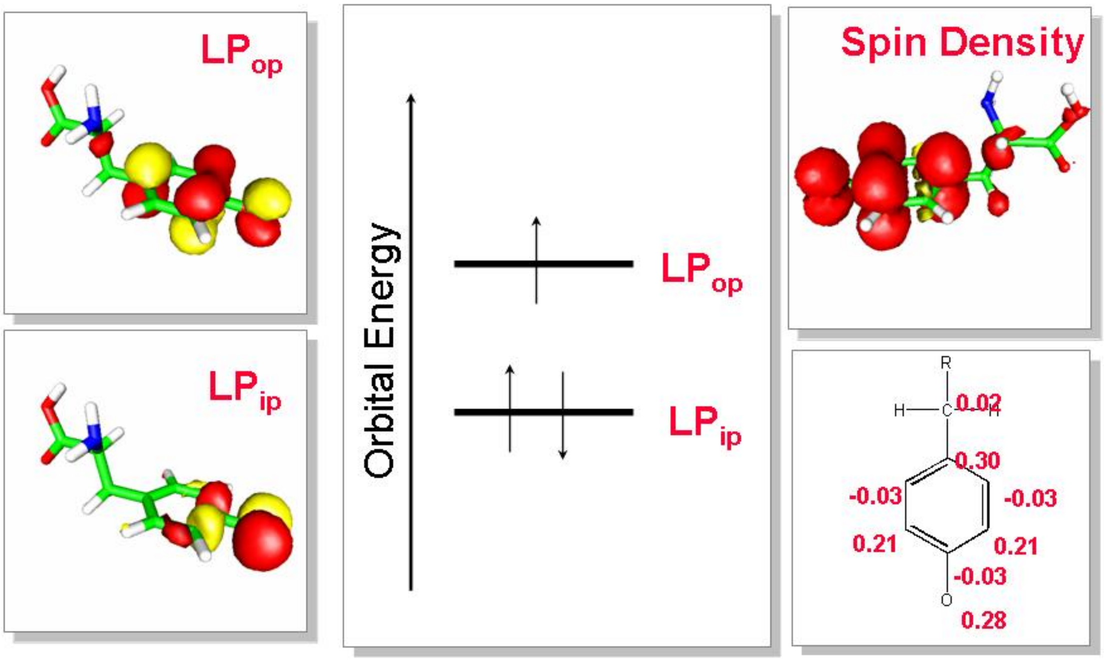
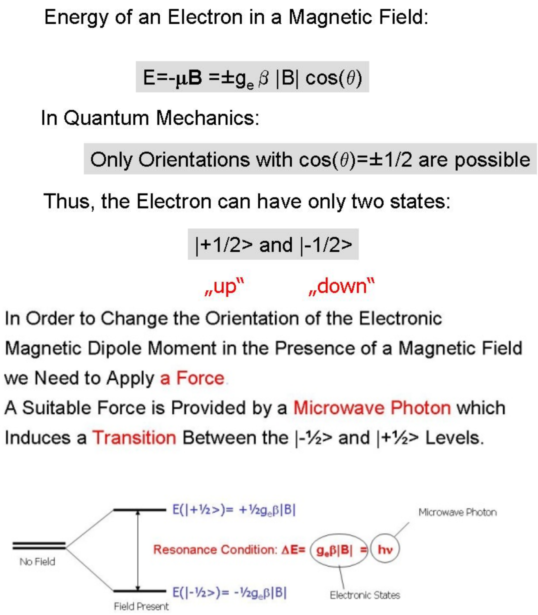


Figure 2: The electronic structure of the tyrosine radical. Left: the out-of-plane and in-plane lone-pair orbitals of the radicalized oxygen; note their delocalization into the π-system, middle: schematic MO diagram showing that in the electronic ground state the in-plane orbital is occupied and the out-of-plane orbital is singly occupied. Right: the total spin density which reflects mainly the shape of the out-of-plane-SOMO orbital; lower right: the spin-populations computed by density functional theory.

In general, a system with spin S = 1/2 can exist in the two states M_S = 1/2 and M_S = -1/2 which correspond to spin-α and spin-β respectively and which are called 'magnetic sublevels' since they arise from a single spatial configuration. In a molecular orbital picture, the two M_S-states simply correspond to the occupation of the singly-occupied MO (SOMO) with a spin-up or a spin-down electron respectively. In the absence of an external magnetic field these two states of the molecule are degenerate.

If a homogeneous magnetic field is turned on, the magnetic dipole moment will start to interact with this field and the two magnetic sublevels will no longer be degenerate. Pictorially speaking, they correspond to parallel and antiparallel alignment of the magnetic dipole with respect to the external magnetic field. In electron spin resonance spectroscopy (ESR) transitions between the two sublevels are induced by photons which happens to fall into the microwave region of the electromagnetic spectrum (Figure 3).



Energy of an Electron in a Magnetic Field:

$E=-\mu\mathbf{B} = \pm g_e \beta |B| \cos(\theta)$

In Quantum Mechanics:

Only Orientations with $\cos(\theta)=\pm 1/2$ are possible

Thus, the Electron can have only two states:

|+1/2> and |-1/2>

„up" „down"

In Order to Change the Orientation of the Electronic Magnetic Dipole Moment in the Presence of a Magnetic Field we Need to Apply a Force

A Suitable Force is Provided by a Microwave Photon which Induces a Transition Between the |-½> and |+½> Levels.

Figure 3: The physical principle of the EPR experiment.

Fortunately, not only electrons behave as bar magnets but nuclei do so too, albeit their magnetic dipole moments are around three orders of magnitude smaller than those of electrons. All nuclei with a nuclear spin $I > 0$ have a nonzero magnetic moment which is measured by their nuclear g-value (g_N) or more commonly by the mgnetogyric ratio $\gamma_N = g_N \beta_N / \hbar$ where β_N is the nuclear magneton ($=5.05082 \times 10^{-27}$ J T^{-1}). This magnetic moment of the nuclei is of course the basis of NMR spectroscopy and also leads to important effects in EPR spectroscopy (see below).

1.1.2 Chemical Shift and g-Tensor

Of course, both, EPR and NMR spectroscopy would not be very informative if the resonance position would only depend on the nature of the nucleus or would be a constant of nature in the case of the electron. As a fortunate circumstance for chemical applications, the resonance position is modified by the surrounding the electrons or nuclei such that the EPR and NMR resonances contain information about the geometric and electronic structure of the system being studied. In fact, it is a basic concept from physics that charges in motion create magnetic fields and these fields start to interact with the nuclear and electronic magnetic dipole moments. Thus, both, nuclei and unpaired electrons are reporters of electron or spin-currents that flow through the molecule. The theory of how to calculate such currents is somewhat involved and is not important for the purposes of the present course.[2]

In NMR spectroscopy each resonance position is slightly modified by the molecular surrounding and this phenomenon is referred to as **chemical shift**. The changes of resonance position between different molecules are so small that they have to be measured in parts per million (ppm). A convenient reference molecule which contains the same resonating nuclei is taken as a standard and chemical shift is reported relative to this standard (e.g. tetramethylsilan, TMS, in NMR spectroscopy). However, in computational chemistry we calculate absolute shifts. Such absolute shifts are known for several small molecules but in the context of most practical applications only relative, isotropic shifts are known. Thus, in order to relate our calculations to the measurements we need to do the calculations on the standard molecule (say TMS for protons) too. However, we are free to choose another reference molecule too if its shift relative to TMS is known (for example H_3COH has a chemical shift of 3.35 ppm relative to TMS). Moreover, in computational chemistry we do calculate an entire 3x3 **chemical shift tensor $\boldsymbol{\sigma}$**. In solid state NMR spectroscopy the principal values of this tensor can be determined. However, for rapidly tumbling molecules in fluid solution the anisotropy in the chemical shift is lost, and only its isotropic average ($\delta = \frac{1}{3}\left(\sigma_{xx} + \sigma_{yy} + \sigma_{zz}\right)$) is observed and reported.

Similar concepts apply to EPR spectroscopy. Here, the **g-tensor** measures the resonance position. It is important to understand that the chemical shift tensor is a *local* property which depends on the surrounding of the nucleus that is being probed in the NMR experiment. By contrast, the g-tensor is a *global* property of the molecule since it depends (among other things) on the distribution of the unpaired electron which may be delocalized over substantial parts of the whole molecule (compare Figure 2). As for NMR chemical shifts, the anisotropy in the g-tensor is averaged out for rapidly tumbling molecules but is readily observed in frozen solutions or in single crystals. Since a free electron has an isotropic g-value of 2.002319… typical molecular g-values for a S=1/2 system are centred around g = 2.

---

[2] The course ‘Quantum Chemistry I’ will provide an elementary introduction to the field of molecular properties.

For organic radicals these shifts are usually small, such that a g-shift $\Delta g = g_{iso} - g_e$ is reported in ppm. For transition metal complexes, the g-shifts can become very large (even larger than 1.0=10^6 ppm) and here one usually prefers to report the shifts in ppt or to report the absolute g-value which is determined from the spectrum by $g = h\nu / \beta_e B_{res}$. Here $h\nu$ is the energy of the microwave photon, β_e is the Bohr magneton (=9.27408x10^{-24} JT^{-1}) and B_{res} is the magnetic field (in Tesla) at which resonance is observed.

The mathematical equations for NMR and EPR are very similar. The energies of the two M_S states of a $S = 1/2$ system are:

$$E\left(M_S\right) = M_S \beta B g \tag{1}$$

Leading to the energy difference $\Delta E = E\left(\tfrac{1}{2}\right) - E\left(-\tfrac{1}{2}\right) = \beta_e B g$ and the resonance condition $\beta B g = h\nu$. The only molecular quantity in these equations is the dimensionless g-value and this is the quantity that we are going to calculate below.

For a nucleus with spin I=1/2, the energy levels as a function of $M_I = \pm 1/2$ are:

$$E\left(M_I\right) = -g_N \beta_N \left(1 - \sigma\right) B M_I \tag{2}$$

From which we get the resonance condition:

$$\Delta E = E\left(-\tfrac{1}{2}\right) - E\left(+\tfrac{1}{2}\right) = -g_N \beta_N \left(1 - \sigma\right) B = h\nu \tag{3}$$

The molecular property here is σ and this is the one that we are going to calculate.

1.1.3 Quantum Chemistry of Effective Interactions

It is important to understand, that the numbers g and σ describe *effective* interactions. They allow us to write down the relevant energy levels of the system in extremely simple terms that allow us to easily determine them from measurements. Yet, these numbers are not constants of nature but are of a molecular origin. Thus, these numbers contain a lot of "microscopic" physics that we did not want to deal with in analyzing the experiments. Thus, from an experimental point of view one may say: "*all I do is to determine the values of g and σ by measuring resonance* *positions – I care about the molecular origin of these numbers later or I collaborate with theoreticians who may help to elucidate the connection between molecular geometric and electronic structure of the molecule that I am studying*". Thus, the theoretical challenge is to study the various subtle interactions between electrons, nuclei and fields and come up with theories, algorithms and programs that would allow the prediction of g and σ from *first physical principles* for *arbitrary molecules*. Thus, a lot of thinking, deriving, programming and testing went into the methods that you will use during the course – but the search for better (more accurate, faster, more transparent, …) methods is by no means over and remains a subject of intense theoretical research.

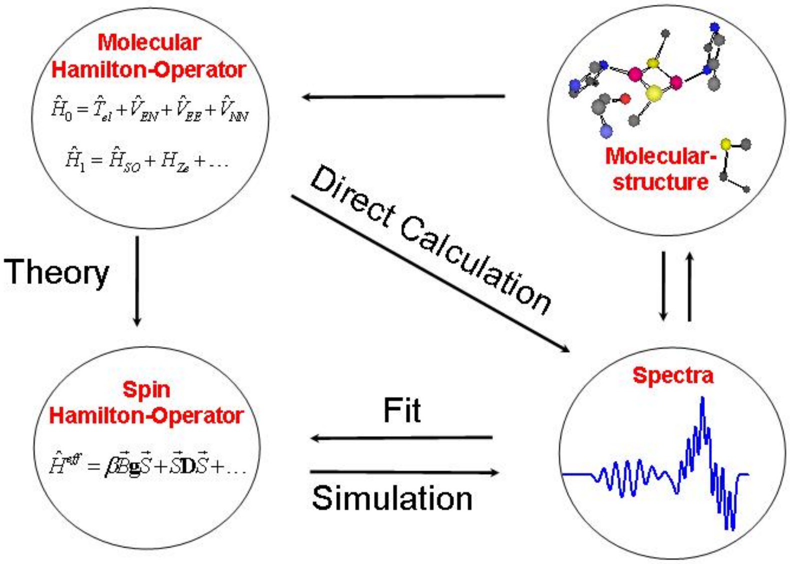


Figure 4: The connection between the Spectrum, the Spin-Hamiltonian, the Molecular Structure and the Microscopic Physics.

In order to at least hint at the way that modern programs predict these spectroscopic properties consider Figure 5. Any electronic structure method produces an approximate solution to the non-relativistic Born-Oppenheimer problem (usually to just one state which most frequently is the ground state). As pointed out in the introduction, the Born-Oppenheimer Hamiltonian includes just the leading electrostatic interactions between the electrons and nuclei. In order to describe magnetic spectra (and in fact many other molecular properties as well), it is necessary to: (a) Include the interaction of the particles in the molecule with the external magnetic field and (b) to include some smaller relativistic effects in the treatment without which one can not arrive at realistic predictions. There is a powerful formalism to approach this problem. Since it is so versatile and so important it has been re-developed in quantum chemistry time and again under different names, some of which are “linear response theory”, “double-perturbation theory” or “analytic derivative theory”. The basic idea is always the same: study the dependence of the approximate energy delivered by the given electronic structure method as a function of the strength of the external perturbation. Since the additional perturbations are usually (but not always) small compared to the strong “internal” interactions in the molecule, it appears to be appropriate to develop the energy in a Taylor series. The first term, is already the most important one and can be related to many molecular properties. The slope of the change of the energy with respect to the strength of the perturbation is called the “linear response” of the system and measures how sensitive the system is to this perturbation. For example, the dipole moment can be represented by the first derivative of the total energy of the system with respect to an external electric field. However, there are many properties – among them practically all EPR and NMR properties – which depend on *two* perturbations at the time (hence the name „double perturbation theory“). In this case, what matters is the mixed second derivative of the energy with respect to the two perturbations. It turns out that the first derivative is usually rather easy to calculate, in particular if the calculations are based on a variational method such as Hartree-Fock or density functional theory. However, the mixed-second derivative is more difficult to approach since it necessarily involves the computation of the change of the orbitals[3] with respect to the perturbation. Such properties are therefore called *response properties*.[4] For example, the polarizability tensor is the second derivative with respect to two components of an external electric field, the nuclear shielding tensor is the mixed second derivative with respect to an external magnetic field and the nuclear magnetic moment, the g-tensor is the mixed second

---

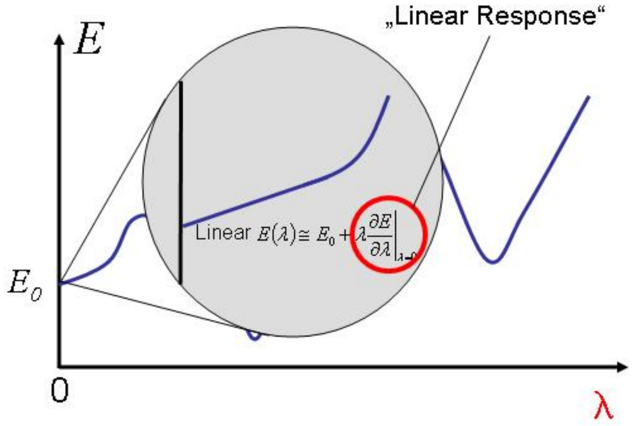
[3] and configuration expansion coefficients in correlated treatments.

[4] The equations that define these changes (to first order) are called the „coupled-perturbed“ SCF equations. They are a large set of linear equations which can, nevertheless, be readily solved.

derivative with respect to the external magnetic field and the electronic magnetic moment and so on. It is thus evident, that the formalism of linear response theory is very general and very powerful – it encompasses many different properties and many different electronic structure methods.[5,6]

Search for Approximate Solutions of: $\hat{H}\Psi = E\Psi$

Which is: $$E\Psi(\mathbf{x}_1\ldots\mathbf{x}_N) = \left(\underbrace{T_e + V_{eN} + V_{NN} + V_{ee}}_{\hat{H}_{BO}} + \underbrace{\lambda V_{electric} + \mu V_{magnetic} + \kappa V_{relativistic}}_{(small)\ \ corrections} \right) \Psi(\mathbf{x}_1\ldots\mathbf{x}_N)$$



Any EPR/NMR/MB Property:

$$\left.\frac{\partial^2 E}{\partial\lambda\partial\kappa}\right|_{\lambda=\kappa=0} = \sum_{\mu,\nu} \frac{\partial P^{\pm}_{\mu\nu}}{\partial\kappa} \left\langle \varphi_\mu \left| \frac{\partial \hat{h}}{\partial\lambda} \right| \varphi_\nu \right\rangle + P^{\pm}_{\mu\nu} \left\langle \varphi_\mu \left| \frac{\partial^2 \hat{h}_{\lambda,\kappa}}{\partial\lambda\partial\kappa} \right| \varphi_\nu \right\rangle$$

Excitation Energies

Search for a time-dependent **E**-field perturbation with frequency ω such that:

$$\frac{\partial^2 E}{\partial\lambda\partial\kappa}(\omega) \to \infty$$

Figure 5: The principle idea of the "linear response" treatment. One studies the first-order change of the energy calculated at a given level of approximation in the presence of time-dependent or time-independent perturbations.

1.1.4 Spin-Spin Coupling and Hyperfine Structure

Both, NMR and EPR spectra have a much richer structure than implied by the simple chemical shift and g-value considerations described above. This is due to the interactions between the magnetic moments of the nuclei and (unpaired) electrons. In NMR spectroscopy, the interaction between the magnetic moments of nuclei give rise to the phenomenon of **spin-spin coupling** which gives rise to the fine structure of NMR spectra. In EPR spectroscopy, the interaction of unpaired electrons with nuclear magnetic moments gives rise to the phenomenon of **hyperfine coupling.**

---

[5] The "mechanics" of the calculations differ from method to method, but the common meeting point is the computation of the effective density matrix (for correlated methods these are the so-called "relaxed" densities) and its response to the external perturbation (the so-called "response" densities).

[6] The computations are not restricted to time-independent external perturbations. In fact, the more general time-dependent formalism leads to treatments that allow the computation of excitation spectra of various kinds without ever calculating the excited states themselves! This is the basis of "time-dependent DFT" and the "random-phase approximation" in Hartree-Fock theory.

For a given pair of nuclei in a given geometrical arrangement the interaction is measured by a so-called **spin-spin coupling tensor**. Once more, averaging leads to a single isotropic coupling constant. In order to describe the system we now have to take into account the four possibilities of arranging the magnetic moments of the two magnetic nuclei: ($\uparrow\uparrow, \uparrow\downarrow, \downarrow\uparrow, \downarrow\downarrow$ corresponding to the four combinations of M_{I1}, M_{I2}). Mathematically, the energies of the four arrangements may be

$$E\left(M_{I1}, M_{I2}\right) = -g_N \beta_N \left(1-\sigma\right) B M_{I1} - g_N \beta_N \left(1-\sigma\right) B M_{I2} + J_{12} M_{I1} M_{I2} \quad (4)$$

Here J_{12} is the molecular quantity of interest which measures the strengths of the magnetic interaction between the two nuclei. This coupling is very weak and is usually quoted in units of Hz.

A similar argument applies to EPR spectroscopy. Here the energy of the four energy levels as a function of the electron spin orientation (M_S) and the nuclear spin orientation (M_I) is given by:

$$E\left(M_S, M_I\right) = \beta_e B g M_S + a M_S M_I \quad (5)$$

Where a is the so-called hyperfine coupling constant (HCC). Its size can be anywhere between a fraction of a MHz and several hundred MHz. It is thus typically much stronger than the spin-spin couplings observed in NMR. In reality the hyperfine coupling is also represented by 3x3 tensor and only its isotropic average is observed in fluid solution.

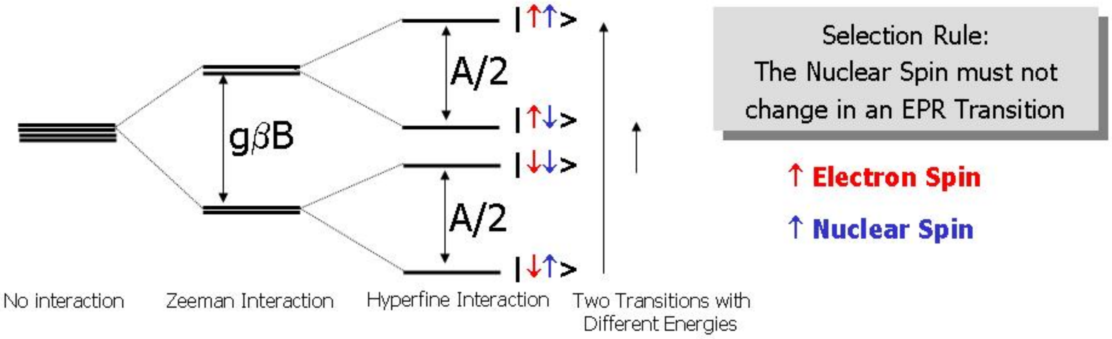


Figure 6: The level splittings induced by the hyperfine coupling.

The physical origin of the observed couplings is fairly complex. In fluid solution, the direct magnetic dipole-magnetic dipole interactions between nuclei or electrons and nuclei averages to zero. What remains in ESR spectroscopy is the so-called Fermi-contact interaction which states that the HCC is proportional to the spin-density at the nucleus in question. The spin-density is simply the density of unpaired electrons. The indirect spin-spin coupling is usually dominated by the same mechanism but now the Fermi contact interaction is 'propagated' through bond electrons to neighbouring nuclei which explains why it is so much smaller than the hyperfine coupling.

There are many ways in which the J and a values can be related to the geometric and electronic structure of the molecules in question. Two famous relations in EPR spectroscopy are due to Harden McConnell and will be studied in the actual computer experiment below. The first relation deals with the hyperfine coupling of protons that lie in the plane of an aromatic π-system which carries an unpaired electron. Since the proton is situated in a node of the singly occupied π-orbitals it was mysterious at the time why it can have an isotropic hyperfine coupling since this requires the presence of unpaired spin-density at the location of the proton. This led to the concept of ***spin-polarization***. This is a rather complicated phenomenon that will not be analyzed in depth here. Briefly, the repulsion between electrons of the same spin is weaker than those between electrons of opposite spin. Thus, for a single spin-up electron in the π-system, the spin-up electron in the adjacent C-H σ-bond is less repelled than the spin-down electron in the same bond. Thus, on average, the spin-up electron is closer to the aromatic carbon while the spin-down electron is closer to the hydrogen. Consequently, there is a slight ***negative spin density*** induced at the position of the hydrogen and this can be observed as a hyperfine splitting in ESR experiments. McConnell analyzed this situation in detail and found that he could, to a good approximation, relate the magnitude of the hyperfine coupling to the spin-population at the adjacent carbon atom that was, at the time, calculated on the basis of Hückel MO calculations. The agreement with experiment was quite pleasing and the relation has been used for many years in order to deduce semi-empirical values of spin-populations from ESR measurements. (thus, ESR spectroscopists have been claiming to 'see' the shape of the SOMO orbital). Quantitatively, McConnell's equation reads:[7]

$$a_H = Q\rho_C$$

(6)

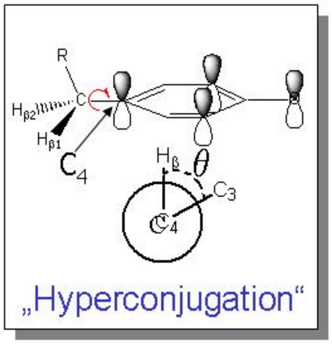
McConnell found that the proportionality constant Q should be on the order of -63 MHz in order to explain the experimental data. You will find below that its value depends upon the method of population analysis used in modern MO theory.

A second important relation was found when McConnell was studying the hyperfine interactions of radicals of the form $Ar^{\bullet}$-$C_{\alpha}H_2$-R, where R is some substituent and $Ar^{\bullet}$ is an aromatic radical. In such radicals, the hyperfine splittings of the H_{α} protons depend sensitively on the orientation of the protons relative to the aromatic ring. This orientation may be measured by the dihedral angle θ defined by the H-C_{α}-C_{ring}-p_z orientation, where 'p_z' denotes the orientation of the spin-carrying π-orbital of $Ar^{\bullet}$ which is oriented perpendicular to the plane of the aromatic ring. The hyperfine couplings where shown to have a dependence on this angle of the form:

$$a_{H_{\alpha}} = B\rho_C \cos^2\theta$$

(7)

Where *B* is a suitable constant. Thus, if B is known for a class of compounds and ρ_C can be estimated, it is possible to deduce θ, that is – structural information, from the EPR spectra.



---

[7] McConnell, H.M. J. Chem. Phys. (**1958**), <u>28</u>, 1188; McConnell, H.M.; Chestnut, D.B. J. Chem. Phys. (**1958**), <u>28</u>, 107 Bersohn, R. J. Chenm. Phys. (**1956**), <u>24</u>, 1066; McConnell, H.M. J. Chem. Phys. (**1956**), <u>24</u>, 764

Figure 7: The mechanism of "hyperconjugation" and the definition of the dihedral angle that enters McConnel's relation

1.1.5 Summary

EPR and NMR spectroscopy can be described in terms of a small set of numerical parameters that are called spin-Hamiltonian parameters. Of these, the g-value (g) is a global measure which is specific to the entire molecule. It represents the interaction between the unpaired electrons and the external magnetic field. The other parameters are local and associated with magnetic nuclei. The chemical shift δ measures the interaction between the nuclear spin and the external magnetic field, the indirect spin-spin couplings (J_{12}) measures the magnetic interactions between nuclei and the hyperfine coupling (a) measures the interactions between unpaired electrons and magnetic nuclei.

The spin-Hamiltonian parameters are a convenient meeting place for experimentalists and theoreticians. The experimentalist determines the values of the SH parameters from analyzing the spectra while the theoretician tries to compute these numbers from first physical principles for the molecules of interest. This is what we are going to do next.

1.2 Description of the Experiment

1.2.1 Calculation of NMR chemical shifts.

PART 1: Optimize the geometries of the following molecules using the BP86 functional and the TZVP basis set (their experimental absolute ^{1}H shieldings in ppm are given below)[8]

• CH_4	: 30.6
• NH_3	: 32.4

---

[8] (Source of data: mainly Cramer 'Introduction to computational chemistry', table 9.5, page 312) except C_2H_6, C_2H_4, HCN which are from Ditchfield Mol. Phys. (1974), 4, 789-807; H_2S from Ruud et al. J. Chem. Phys. (1994), 100, 8178; H_2CNN is a CCSD(T) calculation from Gauss and Stanton (1996) J. Chem. Phys., 104, 2574; HCl from Specialist Periodic Report in NMR Vol 29 (2000), p 41ff; C_6H_6 from Patchkovskii, Autschbach and Ziegler (2001), J. Chem. Phys, 115, 26

- H_2O : 30.1
- HF : 28.7
- C_2H_2 : 29.3
- C_2H_4 : 25.4
- C_2H_6 : 29.8
- CH_3F : 26.6
- HCN : 27.8
- H_2CNN : 28.4
- H_2CO : 18.3
- C_6H_6 : 23.5
- HCl : 31.1 (use the IGLO-II basis set for Cl)
- H_2S : 30.5 (use the IGLO-II basis set for S)

The ORCA job for calculating chemical shieldings with the BP86/IGLO method would look like:

```
! RKS BP86 EPR-II TightSCF
* xyz 0 1
  c                       0.000000    0.000000    0.000000
  h                       0.629312    0.629312    0.629312
  h                      -0.629312   -0.629312    0.629312
  h                      -0.629312    0.629312   -0.629312
  h                       0.629312   -0.629312   -0.629312
*
%eprnmr nuclei = all { shift };
        origin IGLO
        end
```

Now:

- Plot the experimental versus the experimental shieldings

- Calculate the parameters of a linear regression analysis. How reliable are your predictions using this 'model chemistry'? What is your mean deviation from experiment, what is your maximum deviation?

- Discuss the trends in the calculated shieldings in chemical terms, i.e. how do the shieldings vary with electronegativity of the atom that the hydrogens are bonded to. How do they correlate with, say, calculated Natural Atomic Charges (NPA keyword)?

<u>PART 2:</u> Below there are a few elementary chemical problems that can be addressed with the help of chemical shift calculations. In fact, most of them could be solved from inspection already but it might be instructive to try to solve them quantum chemically (all shifts relative to TMS; thus you need to calculate TMS first!). HINT: run these calculations including the COSMO(water) model.

a) The ester H_3C-CO-O-CH_3 has two resonances at δ=3.6 ppm and δ=2.03 ppm in the 1H NMR spectrum. Assign the two resonances two the two groups of protons

b) A substance with the sum formula C_2H_6O could either belong to ethanol or to dimethylether. In the ^{1}H-NMR spectrum one observes resonance at δ=5.1 ppm, δ=3.7 ppm and 1.22 ppm. Assign the correct structure on the basis of chemical shift calculations.

c) The structure of Feist's acid has been under dispute for a long time. The ^{1}H-NMR spectrum shows resonances at δ=11.0 ppm, δ=5.5 ppm and δ=4.0 ppm. Discern between the two alternatives shown below on the basis of chemical shift calculations.

1.2.2 Calculation of ESR g-Values and Hyperfine Couplings.

PART 1: Next we will calculate the g-values and hyperfine couplings for a few small radicals . First optimize the structures of the following radicals (all with S=1/2; use the BP86 functional and the TZVP basis set)[9]

- H_2O^+ : g_{iso}= 7930 ppm A_{iso}(H)=-72.1 MHz A_{iso}(O)=-83.2 MHz
- MgF : g_{iso}=-1430 ppm
- C_3H_5 : g_{iso}= 400 ppm A_{iso}(H)=12, -41,-39 MHz A_{iso}(C)=-48,61 MHz
- CN : g_{iso}= -1330 ppm A_{iso}(N)=-12.6 MHz A_{iso}(C)=588 MHz
- CO^+ : g_{iso}= -1600 ppm
- BS : g_{iso}=-5600 ppm
- NO_2 : g_{iso}=-2560 ppm A_{iso}(N)=153 MHz A_{iso}(O)=$\sim$-50 MHz
- H_2CO^+ : g_{iso}= 1330 ppm A_{iso}(H)=371 MHz A_{iso}(C)=-109 MHz
- HCO : g_{iso}=-2000 ppm
- NF_2 : g_{iso}= 2970 ppm
- CH_3 : $g_{iso}$$\sim$500 ppm A_{iso}(H)=-65 MHz A_{iso}(C)=121 MHz
- CH : A_{iso}(H)=58 MHz A_{iso}(C)=47 MHz
- H_2CN : A_{iso}(H)=233MHz A_{iso}(C)=-81 MHz A_{iso}(N)=26 MHz
- OH : A_{iso}(H)=-26 MHz A_{iso}(O)=-30 MHz

Calculate the EPR properties of the radicals using the ORCA program, the B3LYP functional and the EPR-II basis set. Note that the experimental data contain considerable uncertainties and that they show very large anisotropies. Thus, individual tensor components may differ substantially in magnitude in sign.

A typical input file may be:

---

[9] The g-values were mainly taken from the compilation in Schreckenbach and Ziegler, J. Phys. Chem. A, (**1997**), 101, 3388. The hyperfine couplings were mainly taken from the review of Engels and Erikson, Adv. Quant. Chem. (**1996**), 27, 297. Much of this data is also found in the appendix of Weltner's book: Weltner W (**1983**) Magnetic Atoms and Molecules, Dover publications Inc., New York.

```
! UKS B3LYP EPR-II TightSCF
* int 1 2
    C(1)  0 0 0 0.00   0     0
    O(2)  1 0 0 1.20    0     0
    H(3)  1 2 0 1.10  120     0
    H(3)  1 2 3 1.10  120   180
*
%eprnmr nuclei= all { aiso,adip }
        gtensor true
        end
```

- Plot the experimental versus the experimental parameters.

- Calculate the parameters of a linear regression analysis. How reliable are your predictions using this ‘model chemistry’? What is your mean deviation from experiment, what is your maximum deviation?

PART 2: Perform a calculation on the naphthalene anion. This is a “famous” EPR spectrum which is shown below.

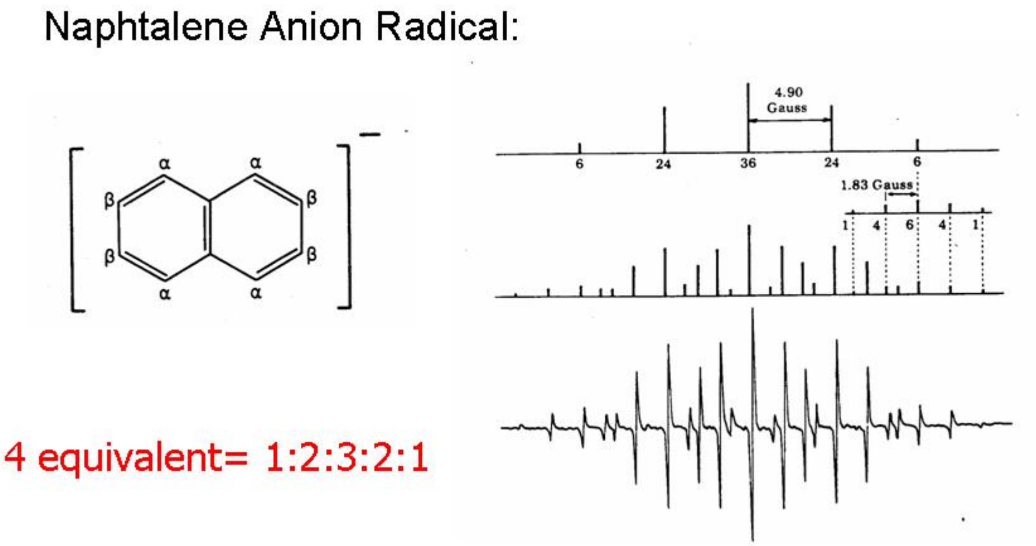


Figure 8: The EPR spectrum of the naphthalene anion-radical together with the explanation of the observed hyperfine splittings.

While it has a rather complicated appearance there are basically only two types of proton hyperfine couplings contributing to this spectrum.

- First optimize the geometry using the BP86 functional and SV(P) basis set.

- Then use the EPR-II basis set for a single point calculation with the B3LYP functional and predict the hyperfine structure of the radical. (the experimental values are 4.9 and 1.8 Gauss)
- Calculate the McConnel constant from your computational data and compare it to the accepted value of -63 MHz. Is the Löwdin, Mulliken or NPA analysis to be preferred for this task?
- Plot the spin-density distribution of the radical. Discuss regions of positive and negative spin-density. How does the calculated hyperfine structure reflect the calculated couplings? How does spin-polarization work in this radical?

<u>PART 3:</u> A second famous relation in EPR spectroscopy is McConnell's relation for the dependence of the isotropic hyperfine coupling of C_α-protons bound to an aromatic radical. We have chosen a simply phenoxyl-radical as shown below (note the atom numbering)

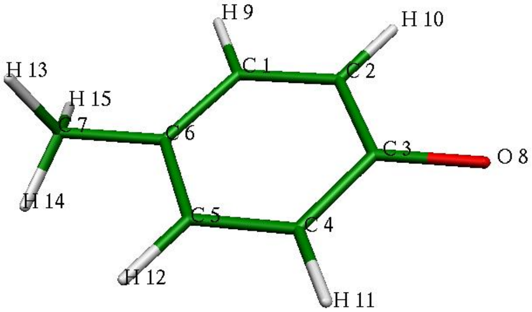


Figure 9: The radical studied in this experiment together with the atom numbering (NOTE: the numbers are incremented relative to the ORCA output by one since ORCA starts counting at zero!).

We are interested in the isotropic hyperfine coupling of the H_{13} proton as a function of the dihedral angle H_{13}-C_7-C_6-C_5. In order to conform to McConnell's definition of θ, we have to add 90° to this angle in order to make 0° corresponding to the situation, where the C_7-H_{13} bond is parallel to the spin-carrying π-orbital. We will use a "rigid scan" calculation in order to obtain a qualitatively correct property surface (e.g. a_{iso}

plotted versus the angle θ). The input for ORCA is shown below. Only standard geometrical parameters have been used which is sufficient for the present purposes.

```
#
# Check McConnell’s relation for Cα-protons
#
! UKS B3LYP EPR-II SlowConv SmallPrint
%method reduceprint false end
%paras theta = 0,180,19 end

* int 0 2
 C     0   0   0   0.000000     0.000     0.000
 C     1   0   0   1.396000     0.000     0.000
 C     2   1   0   1.396000   120.000     0.000
 C     3   2   1   1.396000   120.000     0.000
 C     4   3   2   1.396000   120.000     0.000
 C     5   4   3   1.396000   120.000     0.000
 C     6   5   4   1.510000   120.000   180.000
 O     3   2   1   1.360000   120.000   180.000
 H     1   2   3   1.100000   120.000   180.000
 H     2   1   3   1.100000   120.000   180.000
 H     4   3   2   1.100000   120.000   180.000
 H     5   4   3   1.100000   120.00    180.000
 H     7   6   5   1.090000   109.4712   {theta+ 90}
 H     7   6   5   1.090000   109.4712   {theta+330}
 H     7   6   5   1.090000   109.4712   {theta+210}
*

%eprnmr nuclei = 13 { aiso }
        end
```

The program will make 19 steps between 0 and 180°. For each angle theta there will be separate B3LYP calculation and an evaluation of the hyperfine coupling. The output will look something like:

```
------------------------------------------------------------------------
----
                                ORCA EPR/NMR CALCULATION
------------------------------------------------------------------------
----

GBWName                       ... Phenoxyl-Radical-01.gbw
Electron density file         ... Phenoxyl-Radical-01.scfp.tmp
Spin density file             ... Phenoxyl-Radical-01.scfr.tmp
Spin-orbit integrals          ...
Multiplicity                  ... 2
g-tensor                      ... 0
D-tensor                      ... 0
Number of nuclei for epr/nmr  ... 1
   Nucleus:  12H
```

```
       I=   1.000 P= 533.551 Q=    0.003 Zeff=   1.000
       rho(0)=N f(grad)=N a(iso)=Y a(dip)=N a(orb)=N sigma(nmr)=N

-----------------------------------------
ELECTRIC AND MAGNETIC HYPERFINE STRUCTURE
-----------------------------------------

 -----------------------------------------------------------
 Nucleus  12H : I=  1.0 P=533.5514 MHz/au**3 Q=  0.0029 barn
 -----------------------------------------------------------
 Raw HFC matrix (all values in MHz):
            36.2391       0.0000       0.0000
             0.0000      36.2391       0.0000
             0.0000       0.0000      36.2391

 A(FC)      36.2391      36.2391      36.2391
         ----------   ----------   ----------
 A(Tot)     36.2391      36.2391      36.2391 A(iso)=    36.2391
 Orientation:
  X       0.0000000    1.0000000    0.0000000
  Y       0.0000000    0.0000000    1.0000000
  Z       1.0000000    0.0000000    0.0000000
```

At each angle θ. The value that you are interested in is printed in bold here. From the output file you have to extract A(iso) as a function of θ. You will also need the spin-population at the C_6 carbon as a function of θ.[10,11] This is all the information you need in order to determine McConnell's constant B. Do you also need an offset to fit the data (e.g. $a_{H_\alpha} = A + B\rho_C \cos^2\theta$)? If yes, what is your interpretation in chemical terms? How does the hyperconjugation mechanism work in producing spin density at the proton position? Does your value for B depend on the method of population analysis (Löwdin or Mulliken) to a noticeable extent?

---

[10] Note a subtlety here: the ORCA program starts counting with 0. Thus, it prints 12H which is nucleus number 13 in your figure. Likewise you have to look for the spin population of C5 and not C6 in the output!

[11] Note that we used the „ReducePrint false" command in order to not suppress the printing of the populations after the first step of the trajectory.