Renaissance of the 2nd-order ^{1}H NMR analysis:

a model hamiltonian-based rationalization of benchtop NMR spectra

Technical paper

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1 An Hamiltonian-based rationalization

1.1 The Hamiltonians of NMR in brief

The total Hamiltonian for any spin system is the summation of individual Hamiltonians, which all describe a particular physical interaction.[1] We will here only consider two prominent interactions, The Zeeman Hamiltonian, $\hat{H}_Z$, which accounts for the magnetic interaction of nuclear spins with the static external field of the spectrometer, and the J-coupling Hamiltonian, $\hat{H}_J$, which accounts for the interaction of pairs of nuclear spins through bonding electrons. The total NMR Hamiltonian is expressed as:

$$\hat{H}^{\mathrm{NMR}} = \hat{H}_Z + \hat{H}_J \tag{1}$$

1.2 Nuclear angular momentum and Pauli matrices

We shall first recall that spin is the internal angular momentum of a fundamental particle, associated to the classic picture of a rotating particle. Both the magnitude of the nuclear angular momentum and its z-component are quantized, and confined to the values $\hbar\sqrt{I(I+1)}$ ($I \in [0, \frac{1}{2}, 1, \frac{3}{2}, 2, \frac{5}{2}, ...]$) and $m_I \hbar$ ($m_I \in [-I, I]$)[1]. $\frac{1}{2}$ spin particles thus have an angular momentum of magnitude $(\frac{3}{4})^{\frac{1}{2}}\hbar$ and two possible components $-\frac{\hbar}{2}$ and $\frac{\hbar}{2}$ along the z-axis. It defines the two well-known spin states $|\alpha> = |\frac{1}{2}, \frac{1}{2}>$ and $|\beta> = |\frac{1}{2}, -\frac{1}{2}>$, which are simultaneous eigenstates of $\hat{I}^2$ and $\hat{I}_z$. The eigenvalues equations for the $\hat{I}^2$ and $\hat{I}_z$ operators are

$$\hat{I}^2|I, m_I> = I(I+1)\hbar^2|I, m_I> \tag{2}$$

$$\hat{I}_z|I, m_I> = m_I\hbar|I, m_I> \tag{3}$$

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[1]

- $I = 0$ corresponds to nuclei with no nuclear spin, meaning they have no net nuclear magnetic moment.
- $I = \frac{1}{2}$ is common for nuclei like hydrogen-1, carbon-13 , fluorine-19, etc. Nuclei with $I = \frac{1}{2}$ exhibit two spin states when subjected to an external magnetic field (usually referred to as spin-up and spin-down states)
- $I = 1$ corresponds to certain nuclei like nitrogen-14, chlorine-35, etc. Nuclei with $I = 1$ exhibit three spin states when in an external magnetic field.
- Higher integer or half-integer values for I are also possible, each leading to an increased number of spin states for the nucleus when placed in an external magnetic field

We will later need a general matrix formulation, so now is the good time to express the two spin states under a matrix form

$$\alpha = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \qquad \beta = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \tag{4}$$

All components of the angular momentum can thereby be written from the so-called Pauli matrices[2]

$$\boldsymbol{\sigma}_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad \boldsymbol{\sigma}_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \qquad \boldsymbol{\sigma}_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{5}$$

with

$$\boldsymbol{I}_q = \frac{1}{2}\hbar\boldsymbol{\sigma}_q \quad (q = x, y, z) \tag{6}$$

The shift operators $\hat{I}^+$ and $\hat{I}^-$ operators can as well be expressed as a function of the $\boldsymbol{\sigma}^+$ and $\boldsymbol{\sigma}^-$ Pauli Matrices

$$\boldsymbol{\sigma}^+ = \begin{pmatrix} 0 & 2 \\ 0 & 0 \end{pmatrix} \qquad \boldsymbol{\sigma}^- = \begin{pmatrix} 0 & 0 \\ 2 & 0 \end{pmatrix} \tag{7}$$

It is then straightforward to check by simple matrix algebra that

$$\frac{1}{2}\hbar\boldsymbol{\sigma}^+ \begin{pmatrix} 1 \\ 0 \end{pmatrix} = 0 \quad \frac{1}{2}\hbar\boldsymbol{\sigma}^+ \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \hbar\alpha$$

$$\frac{1}{2}\hbar\boldsymbol{\sigma}^- \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \hbar\beta \quad \frac{1}{2}\hbar\boldsymbol{\sigma}^- \begin{pmatrix} 0 \\ 1 \end{pmatrix} = 0$$

1.3   Nuclei in magnetic fields

The energy of interaction between an hypothetically naked nucleus N that has a magnetic moment $\boldsymbol{\mu}_N$ and an external magnetic field $\boldsymbol{B}_0$ applied along the z-axis can be calculated by considering the Zeeman Hamiltonian, which accounts for the interaction of $\hat{\mu}_z$ and B_0

$$\hat{H}_Z = -\hat{\mu}_z B_0 = -\gamma_N B_0 \hat{I}_z \tag{8}$$

where γ_N is the magnetogyric ratio of nucleus N. Using the relationship between the σ_z Pauli matrix and $\hat{I}_z$ (eq 6), $\hat{H}_Z$ becomes

$$\boldsymbol{H}_Z = -\gamma_N B_0 \frac{\hbar}{2}\boldsymbol{\sigma}_z \tag{9}$$

α and β are eigenstates of $\boldsymbol{H}_Z$ and the associated nuclear spin energies are function of the applied magnetic field

$$-\frac{\gamma_N B_0 \hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = -\frac{\gamma_N B_0 \hbar}{2} \begin{pmatrix} 1 \\ 0 \end{pmatrix} \tag{10}$$

$$-\frac{\gamma_N B_0 \hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = +\frac{\gamma_N B_0 \hbar}{2} \begin{pmatrix} 0 \\ 1 \end{pmatrix} \tag{11}$$

The energy separation between the upper β state and the lower α state is $\Delta E = \gamma_N B_0 \hbar$ (see Figure 1) and absorption occurs with the resonance condition

$$\nu = \frac{\Delta E}{h} = \frac{\gamma_N B_0}{2\pi}$$

2

where ν is the Larmor frequency, which typically lies in the radiofrequency domain of the electromagnetic spectrum, *i.e.* around 500 Mhz.

Owing to the central role played by the Larmor frequency ν in NMR, equation 9 can finally be written as a function of ν

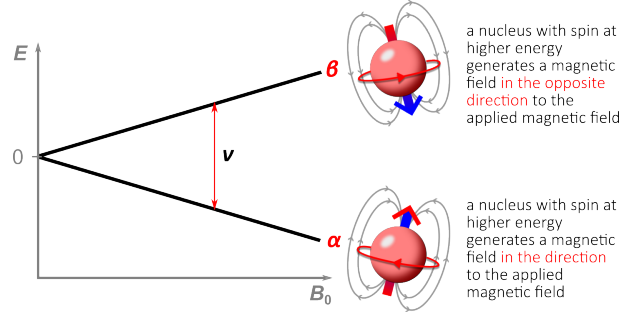$$\boldsymbol{H}_{\mathrm{Z}} = -\frac{\nu h}{2}\boldsymbol{\sigma}_z \tag{12}$$

Figure 1: Zeeman effect for a half-spin nucleus with positive magnetogyric ratio γ_N: nuclear spin energy levels splitting as a function of an electromagnetic field B_0.

Yet, the nuclear angular momentum of a nucleus surrounded by electrons will also interact with a local magnetic field and give rise to a small magnetic field δB_0 which in general is opposite to the applied field B_0, $\delta B_0 = -\underline{\sigma}B_0$, where $\underline{\sigma}$ is the shielding tensor. $\underline{\sigma}$ is a rank 2 tensor, that reduces to a number σ in isotropic liquids ($\sigma = \mathrm{Tr}(\underline{\sigma}/3)$). The Larmor frequency ν now depends on this resulting shielding constant σ

$$\nu = \frac{\gamma_{\mathrm{N}}B_0(1-\sigma)}{2\pi} \tag{13}$$

And the Zeeman Hamiltonian has the same expression as eq. 12, but with the shielding effect of the electrons on the magnetic field $B_0 + \delta B_0$ actually felt by the nucleus.

1.4 Molecules in magnetic fields

Let us now consider a molecule that possesses several spin-$\frac{1}{2}$ nuclei. Firstly, the Zeeman effect will apply to all of them and each non-equivalent nucleus will resonate at its typical Larmor frequency, ν_i. It comes easily from eq. 12 that

$$\boldsymbol{H}_{\mathrm{Z}} = -\frac{h}{2}\sum_{i=1}^{N}\nu_i\boldsymbol{\sigma}_{z_i} \tag{14}$$

Now, dipole fields from nearby spins interact, and resonances can split as multiplets as a result of mutual dipole couplings through bonding electrons. The strength of this coupling is expressed in terms of the scalar coupling J, and a J-coupling Hamiltonian must be introduced to describe this phenomenon

$$\hat{H}_{\mathrm{J}} = \sum_{i=1}^{N}\sum_{j=1}^{i-1}2\pi J_{ij}\hat{\boldsymbol{I}}_i\cdot\hat{\boldsymbol{I}}_j \tag{15}$$

$$= \sum_{i=1}^{N}\sum_{j=1}^{i-1}2\pi J_{ij}\left(\hat{I}_{x_i}\hat{I}_{x_j} + \hat{I}_{y_i}\hat{I}_{y_j} + \hat{I}_{z_i}\hat{I}_{z_j}\right) \tag{16}$$

As it was already the case with the shielding constant σ, $\underline{J}_{ij}$ is actually a rank 2 tensor, but the rapid molecular tumbling in solution averages out $\underline{J}_{ij}$ as a J-coupling constant, J_{ij}. Again, this component of $\hat{H}^{\mathrm{NMR}}$ can be expressed using the Pauli matrices

$$\boldsymbol{H}_{\mathrm{J}} = \frac{h}{4} \sum_{i=1}^{N} \sum_{j=1}^{i-1} J_{ij} \left(\boldsymbol{\sigma}_{x_i} \boldsymbol{\sigma}_{x_j} + \boldsymbol{\sigma}_{y_i} \boldsymbol{\sigma}_{y_j} + \boldsymbol{\sigma}_{z_i} \boldsymbol{\sigma}_{z_j} \right) \tag{17}$$

The NMR spectrum can then be simulated by solving the Schrödinger equation, with $\hat{H}^{\mathrm{NMR}}$ developed in the finite basis set made of the possible spin states. For example, for a two spin-$\frac{1}{2}$ system, there are four spin states, $\{\alpha_1\alpha_2, \ \alpha_1\beta_2, \ \beta_1\alpha_2, \ \beta_1\beta_2\}$, which define an orthonormal basis set S_{spin}. As usual in quantum chemistry, energies - resonance energies in the present case - will be obtained by diagonalizing the matrix representation of $\boldsymbol{H}_{\mathrm{NMR}}$ developed in the system basis set. Eqs. 14 and 17 can conveniently be divided by the Planck contant h, in order to directly obtain resonance frequencies, and $\boldsymbol{H}^{\mathrm{NMR}}$ finally becomes

$$\boldsymbol{H}^{\mathrm{NMR}} = -\frac{1}{2} \sum_{i=1}^{N} \nu_i \boldsymbol{\sigma}_{z_i} + \frac{1}{4} \sum_{i=1}^{N} \sum_{j=1}^{i-1} J_{ij} \left(\boldsymbol{\sigma}_{x_i} \boldsymbol{\sigma}_{x_j} + \boldsymbol{\sigma}_{y_i} \boldsymbol{\sigma}_{y_j} + \boldsymbol{\sigma}_{z_i} \boldsymbol{\sigma}_{z_j} \right) \tag{18}$$

1.5   Application to two strongly coupled $\frac{1}{2}$-nuclei: the AB case

This is a test case, aiming at simulating a two strongly coupled $\frac{1}{2}$-spin system using eq. 18, and at evaluating an AX system as the low J-coupling limit of an AB case. According to the previous developments, the Zeeman and J-coupling components of the Hamiltonian are

$$\boldsymbol{H}_{\mathrm{Z}} = -\frac{1}{2} \nu_{\mathrm{A}} \boldsymbol{\sigma}_{z_{\mathrm{A}}} - \frac{1}{2} \nu_{\mathrm{B}} \boldsymbol{\sigma}_{z_{\mathrm{B}}} \tag{19}$$

$$\boldsymbol{H}_{\mathrm{J}} = \frac{1}{4} J_{\mathrm{AB}} (\boldsymbol{\sigma}_{x_{\mathrm{A}}} \boldsymbol{\sigma}_{x_{\mathrm{B}}} + \boldsymbol{\sigma}_{y_{\mathrm{A}}} \boldsymbol{\sigma}_{y_{\mathrm{B}}} + \boldsymbol{\sigma}_{z_{\mathrm{A}}} \boldsymbol{\sigma}_{z_{\mathrm{B}}}) \tag{20}$$

Using the matrix language of quantum mechanics makes the development of H_{NMR} rather straightforward and easy to achieve using simple matrix operations. It also gives access to computer algebra systems (CAS) for solving the Schrödinger equation in a systematic way. But prior to that, we must recall, if necessary, how to manipulate the direct product of operators. Since we will work on matrix representations of operators, we face the necessity to use Kronecker products.[3] A pedagogical presentation is given in Ref.,[4] with physical applications related to two spin systems and to the interpretation of NMR signals produced by two interacting protons. The following notations are intentionally the same as those used by Fernández[4] in order to allow the reader to become acquainted to these subtle concepts by a joint reading of the present document with Fernández'.

1.5.1   An important prerequisite: Kronecker products

Let us consider two linear operators $\hat{A}$ and $\hat{B}$ defined in the same orthonormal basis set, $S_f = \{f_1, f_2, ... f_N\}$, *i.e.* in an *N*-dimensional vector space. It is very easy to manipulate their product or their sum using their matrix representation in this basis set ($\hat{A}\hat{B} \to \boldsymbol{AB}$ and $\hat{A} + \hat{B} \to \boldsymbol{A} + \boldsymbol{B}$). Suppose now that operator $\hat{B}$ is defined in a different basis set, $S_g = \{g_1, g_2, ... g_M\}$. In order to treat this hybrid system, it is necessary to work in a unified orthonormal basis set, $S_{fg} = \{u_{ij} = f_i \otimes g_j, i = 1, 2, ..., N, j = 1, 2, ..., M\}$, where $\otimes$ is the direct product. The scalar product in this vector space is given by

$$< u_{ij}|u_{mn} > = < f_i|f_m > < g_j|g_n > = \delta_{im}\delta_{jn} \tag{21}$$

The operator product for a given vector u_{ij} is now given by $(\hat{A}f_i) \otimes (\hat{B}g_j) = (\hat{A} \otimes \hat{B})u_{ij}$, and the resulting larger matrix representation is denoted by $\boldsymbol{A} \otimes \boldsymbol{B}$, which is the Kronecker product of matrices $\boldsymbol{A}$ and $\boldsymbol{B}$. The construction rule of thumb of the Kronecker product consists in substituting $A_{ij}\boldsymbol{B}$ for every element A_{ij} of $\boldsymbol{A}$. It gives for 2×2 matrices

$$\begin{pmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{pmatrix} \otimes \begin{pmatrix} B_{11} & B_{12} \\ B_{21} & B_{22} \end{pmatrix} = \begin{pmatrix} A_{11}B_{11} & A_{11}B_{12} & A_{12}B_{11} & A_{12}B_{12} \\ A_{11}B_{21} & A_{11}B_{22} & A_{12}B_{21} & A_{12}B_{22} \\ A_{21}B_{11} & A_{21}B_{12} & A_{22}B_{11} & A_{22}B_{12} \\ A_{21}B_{21} & A_{21}B_{22} & A_{22}B_{21} & A_{22}B_{22} \end{pmatrix} \tag{22}$$

1.5.2 A two-spin system

Now comes the difficulty. Let us consider the operator form of the Zeeman Hamiltonian, $\hat{H}_Z = -2\pi\nu_A \hat{I}_{z_A} - 2\pi\nu_B \hat{I}_{z_B}$. Yet, $\hat{H}_Z$ applies to the common spin state space of the AB two nuclei system, which is defined by the S_{spin} basis set

$$S_{\text{spin}} = \{\alpha_A\alpha_B, \alpha_A\beta_B, \beta_A\alpha_B, \beta_A\beta_B\} \tag{23}$$

These four vectors states are eigenvectors of the $\hat{H}_Z$ operator. Let us for example consider the product function $\alpha_A\alpha_B$. It comes that The vector $\alpha_A\alpha_B$ is indeed an eigenvector of the $\hat{H}_Z$ operator, with the eigenvalue $-\frac{\nu_A h}{2} - \frac{\nu_B h}{2}$

$$\hat{H}_Z \alpha_A\alpha_B = [-2\pi\nu_A \hat{I}_{z_A}\alpha_A]\alpha_B + \alpha_A[-2\pi\nu_B \hat{I}_{z_B}\alpha_B] \tag{24}$$

$$= [-\frac{\nu_A h}{2} - -\frac{\nu_B h}{2}]\alpha_A\alpha_B \tag{25}$$

It is interesting to observe that the scalar product between any of these vectors has the form of eq. 21. For example

$$< \alpha_A\beta_B | \alpha_A\alpha_B > = < \alpha_A | \alpha_A > < \beta_B | \alpha_B > = \delta_{\alpha\alpha}\delta_{\beta\alpha} = 1 \times 0 = 0 \tag{26}$$

It means that the product $\alpha_A\alpha_B$ can be written as $\alpha_A \otimes \alpha_B$ and that there is a joint vector space made of the two individual vector spaces of nuclei A and B. But what is the consequence for $\hat{H}_Z$? This operator can now be written in the framework of the cross product notation

$$\hat{H}_Z = -2\pi\nu_A \hat{I}_{z_A} \otimes \hat{1}_B - 2\pi\nu_B \hat{1}_A \otimes \hat{I}_{z_B} \tag{27}$$

where $\hat{1}_A$ is the identity operator defined in the vector space of nucleus A. Let us transpose it to the Pauli matrix formulation

$$\boldsymbol{H}_Z = -\frac{1}{2}\nu_A \boldsymbol{\sigma}_{z_A} \otimes \mathbf{1} - \frac{1}{2}\nu_B \mathbf{1} \otimes \boldsymbol{\sigma}_{z_B} \tag{28}$$

where $\mathbf{1}$ is the identify matrix. Using the definition of the Kronecker product, one finds

$$\boldsymbol{\sigma}_{z_A} \otimes \mathbf{1} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} \tag{29}$$

$$\mathbf{1} \otimes \boldsymbol{\sigma}_{z_B} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} \tag{30}$$

The same approach can be applied to define the J-coupling Hamiltonian

$$\boldsymbol{H}_J = \frac{1}{4}J_{AB}(\boldsymbol{\sigma}_{x_A} \otimes \boldsymbol{\sigma}_{x_B} + \boldsymbol{\sigma}_{y_A} \otimes \boldsymbol{\sigma}_{y_B} + \boldsymbol{\sigma}_{z_A} \otimes \boldsymbol{\sigma}_{z_B}) \tag{31}$$

or, in an abbreviated way

$$\boldsymbol{H}_{\mathrm{J}} = \frac{1}{4} J_{\mathrm{AB}} (\boldsymbol{\Sigma}_{xx} + \boldsymbol{\Sigma}_{yy} + \boldsymbol{\Sigma}_{zz}) \tag{32}$$

with $\boldsymbol{\Sigma}_{qr} = \boldsymbol{\sigma}_{q_{\mathrm{A}}} \otimes \boldsymbol{\sigma}_{r_{\mathrm{B}}}$, $q, r = x, y, z$

It is straightforward, albeit tedious, to check that the 4×4 $\boldsymbol{\Sigma}_{xx}, \boldsymbol{\Sigma}_{yy}, \boldsymbol{\Sigma}_{zz}$ matrices are

$$\boldsymbol{\Sigma}_{xx} = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix} \quad \boldsymbol{\Sigma}_{yy} = \begin{pmatrix} 0 & 0 & 0 & -1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 0 \end{pmatrix} \quad \boldsymbol{\Sigma}_{zz} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \tag{33}$$

The most difficult part is now behind us, since the expression of $\boldsymbol{H}_{\mathrm{NMR}}$ is obtained by matrix additions and by multiplications between scalar numbers and matrices

$$\boldsymbol{H}_{\mathrm{Z}} = \begin{pmatrix} \frac{-\nu_{\mathrm{A}} - \nu_{\mathrm{B}}}{2} & 0 & 0 & 0 \\ 0 & \frac{-\nu_{\mathrm{A}} + \nu_{\mathrm{B}}}{2} & 0 & 0 \\ 0 & 0 & \frac{\nu_{\mathrm{A}} - \nu_{\mathrm{B}}}{2} & 0 \\ 0 & 0 & 0 & \frac{\nu_{\mathrm{A}} + \nu_{\mathrm{B}}}{2} \end{pmatrix} \tag{34}$$

$$\boldsymbol{H}_{\mathrm{J}} = \begin{pmatrix} \frac{J_{\mathrm{AB}}}{4} & 0 & 0 & 0 \\ 0 & -\frac{J_{\mathrm{AB}}}{4} & \frac{J_{\mathrm{AB}}}{2} & 0 \\ 0 & \frac{J_{\mathrm{AB}}}{2} & -\frac{J_{\mathrm{AB}}}{4} & 0 \\ 0 & 0 & 0 & \frac{J_{\mathrm{AB}}}{4} \end{pmatrix} \tag{35}$$

Finally

$$\boldsymbol{H}^{\mathrm{NMR}} = \begin{pmatrix} -\frac{\nu_{\mathrm{A}} + \nu_{\mathrm{B}}}{2} + \frac{J_{\mathrm{AB}}}{4} & 0 & 0 & 0 \\ 0 & \frac{\nu_{\mathrm{B}} - \nu_{\mathrm{A}}}{2} - \frac{J_{\mathrm{AB}}}{4} & \frac{J_{\mathrm{AB}}}{2} & 0 \\ 0 & \frac{J_{\mathrm{AB}}}{2} & -\frac{\nu_{\mathrm{B}} - \nu_{\mathrm{A}}}{2} - \frac{J_{\mathrm{AB}}}{4} & 0 \\ 0 & 0 & 0 & \frac{\nu_{\mathrm{A}} + \nu_{\mathrm{B}}}{2} + \frac{J_{\mathrm{AB}}}{4} \end{pmatrix} \tag{36}$$

The eigenvalues of this Hamiltonian can be obtained by diagonalizing this matrix. They correspond to the energies of the spin states of this AB system, whereas the eigenvectors describe these spin states. Actually, do not forget that the NMR Hamiltonian of eq. 18 had been divided by h, so that the energies here are calculated in Hz. The eigenvalues and eigenvectors are

$$E_1 = -\frac{\nu_{\mathrm{A}} + \nu_{\mathrm{B}}}{2} + \frac{J_{\mathrm{AB}}}{4}; \quad \boldsymbol{V}_1 = \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix} \tag{37}$$

$$E_2 = -\frac{1}{2} \left(\sqrt{(\nu_{\mathrm{A}} - \nu_{\mathrm{B}})^2 + J_{AB}^2} \right) + \frac{J_{\mathrm{AB}}}{4}; \quad \boldsymbol{V}_2 = \begin{pmatrix} 0 \\ a \\ b \\ 0 \end{pmatrix} \tag{38}$$

$$E_3 = \frac{1}{2} \left(\sqrt{(\nu_{\mathrm{A}} - \nu_{\mathrm{B}})^2 + J_{AB}^2} \right) - \frac{J_{\mathrm{AB}}}{4}; \quad \boldsymbol{V}_3 = \begin{pmatrix} 0 \\ c \\ d \\ 0 \end{pmatrix} \tag{39}$$

$$E_4 = \frac{\nu_A + \nu_B}{2} + \frac{J_{AB}}{4}; \quad \boldsymbol{V}_4 = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix} \tag{40}$$

The vector coefficients a, b, c, d can be found in several references[4–6] or by implementing these calculations in a CAS software.
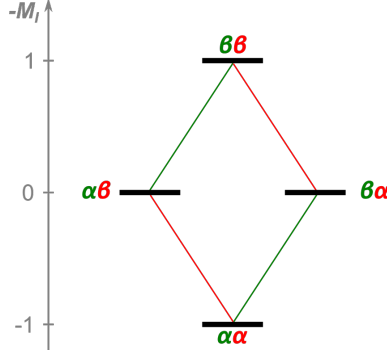

Figure 2: Basis functions for a two-spin system, reported as a function of their total projection of nuclear spins, M_I. Single spin flip transitions are shown (green/red: spin flip on A/B nucleus).

Do not forget that these vectors span the S_{spin} basis set (eq. 23) and note that the four vectors have been arranged with in mind the diagram plot in Figure 2 and the calculated energies. $\boldsymbol{V}_4$ has a component along $\alpha_A \alpha_B$, and it is the less stable state, whereas $\boldsymbol{V}_1$ which has a component along $\beta_A \beta_B$ is the most stable spin state. $\boldsymbol{V}_2$ and $\boldsymbol{V}_3$ are linear combinations of $\alpha_A \beta_B$ and $\beta_A \alpha_B$, which is consistent with the non-zero coupling in the Hamiltonian matrix between the two $M = 0$ basis functions ($\boldsymbol{H}_{23}^{\text{NMR}} = \boldsymbol{H}_{32}^{\text{NMR}} = \frac{J}{2}$). They have intermediate energies. We can now simulate the shape of an AB spectrum.

1.5.3 An AB spectrum

The selection rule in NMR states that only one spin flip is achieved in a transition.[6] In other words only the transitions between states 1-2, 1-3, 2-4 and 3-4 are allowed. The frequencies of the four NMR peaks of an AB system can be easily calculated from the differences $E_2 - E_1$, $E_3 - E_1$, $E_4 - E_2$ and $E_4 - E_3$. It is also possible to calculate the transition intensities by explicitly developing the relationship at the basis of the selection rule. It consists in calculating the probabilities of the transitions induced by the radiofrequency field B_x (with $B_x \ll B_0$), which is orthogonal to the applied magnetic field. For a N-spin system, this rule is actually governed by transition probabilities, which are integrals of the form[7]

$$(\gamma_N B_x)^2 \left| < \psi_j | \sum_{i=1}^{N} \hat{I}_{x_i} | \psi_i > \right|^2 \tag{41}$$

where the ψ_i are the spin states of the system, *i.e.* those that make diagonal the $\hat{H}_{\text{NMR}}$ Hamiltonian. Using the Pauli matrix formulation, relative intensities in the AB system can be calculated as proportional to

$$I = \left[\boldsymbol{V}_i^T (\boldsymbol{I}_{x_A} \otimes \boldsymbol{1} + \boldsymbol{1} \otimes \boldsymbol{I}_{x_B}) \boldsymbol{V}_j \right]^2 \tag{42}$$

It is interesting to analyze the transition matrix, $\boldsymbol{T} = \boldsymbol{I}_{x_A} \otimes \boldsymbol{1} + \boldsymbol{1} \otimes \boldsymbol{I}_{x_B}$, which is

$$\begin{pmatrix} 0 & 1 & 1 & 0 \\ 1 & 0 & 0 & 1 \\ 1 & 0 & 0 & 1 \\ 0 & 1 & 1 & 0 \end{pmatrix} \tag{43}$$

It turns out that, as well known in NMR, the only non-zero transitions are between spin states that differ by one spin flip, *i.e.* $\Delta M = \pm 1$.

Let's consider now two protons that resonate at $\nu_A = 180$ Hz and $\nu_B = 220$ Hz and that are coupled by $J_{AB} = 7$ Hz. Using a CAS software and after implementation of the key previous equations, it becomes easy to diagonalize $\boldsymbol{H}^{\mathrm{NMR}}$ (in frequency units, see also Figure 3a), as well as to compute transition frequencies ($\boldsymbol{\nu}$) and transition intensities ($\boldsymbol{I}$) matrices

$$
\boldsymbol{E} = \begin{pmatrix} -198.2 & 0.0 & 0.0 & 0.0 \\ 0.0 & -22.1 & 0.0 & 0.0 \\ 0.0 & 0.0 & 18.6 & 0.0 \\ 0.0 & 0.0 & 0.0 & 201.7 \end{pmatrix}
$$

$$
\boldsymbol{\nu} = \begin{pmatrix} 0.0 & 176.2 & 216.8 & 0.0 \\ 176.2 & 0.0 & 0.0 & 223.8 \\ 216.8 & 0.0 & 0.0 & 183.2 \\ 0.0 & 223.8 & 183.2 & 0.0 \end{pmatrix} \qquad \boldsymbol{I} = \begin{pmatrix} 0.0 & 0.8 & 1.2 & 0.0 \\ 0.8 & 0.0 & 0.0 & 0.8 \\ 1.2 & 0.0 & 0.0 & 1.2 \\ 0.0 & 0.8 & 1.2 & 0.0 \end{pmatrix}
$$

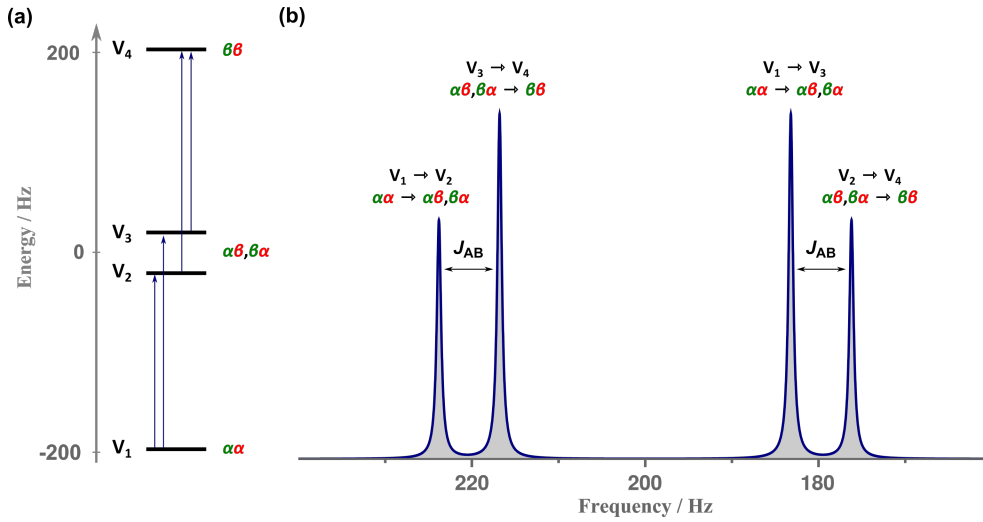an then to simulate the spectrum reported in Figure 3b.

Figure 3: (a) Energy level diagram for an AB system (in frequency unit, with: $\nu_A = 180$ Hz, $\nu_B = 220$ Hz, $J_{AB} = 7$ Hz); (b) simulated ^{1}H NMR spectrum.

1.5.4 The weakly coupled two spin-$\frac{1}{2}$ AX system

Hamiltonians. This case is nothing else than first-order NMR. The S_{spin} basis set (eq. 23) and the Zeeman Hamiltonian (eqs. 19 and 28) are the same as for the AB system. However, it can be shown that the $\hat{I}_x$ and $\hat{I}_y$ terms in the product $\hat{I}_A \hat{I}_B$ of the J-coupling Hamiltonian do not contribute to any first-order energies, and for the AX system, $\boldsymbol{H}_J$ (eq. 31) becomes

$$
\boldsymbol{H}_J = \frac{1}{4} J_{AB}(\boldsymbol{\sigma}_{z_A} \otimes \boldsymbol{\sigma}_{z_B}) \tag{44}
$$

The Zeeman Hamiltonian developed in the S_{spin} basis set has the same form as its AB counterpart

$$
\boldsymbol{H}_Z = \begin{pmatrix} \frac{-\nu_A - \nu_X}{2} & 0 & 0 & 0 \\ 0 & \frac{-\nu_A + \nu_X}{2} & 0 & 0 \\ 0 & 0 & \frac{\nu_A - \nu_X}{2} & 0 \\ 0 & 0 & 0 & \frac{\nu_A + \nu_X}{2} \end{pmatrix} \tag{45}
$$

but now the J-coupling Hamiltonian is more simple since it does not have off-diagonal components

$$
\boldsymbol{H}_{\mathrm{J}} = \begin{pmatrix} \frac{J_{\mathrm{AX}}}{4} & 0 & 0 & 0 \\ 0 & -\frac{J_{\mathrm{AX}}}{4} & 0 & 0 \\ 0 & 0 & -\frac{J_{\mathrm{AX}}}{4} & 0 \\ 0 & 0 & 0 & \frac{J_{\mathrm{AX}}}{4} \end{pmatrix}
\tag{46}
$$

Finally, $\boldsymbol{H}^{\mathrm{NMR}}$ does not have to be diagonalized since it is already diagonal

$$
\boldsymbol{H}^{\mathrm{NMR}} = \begin{pmatrix} -\frac{\nu_{\mathrm{A}}+\nu_{\mathrm{X}}}{2} + \frac{J_{\mathrm{AX}}}{4} & 0 & 0 & 0 \\ 0 & \frac{\nu_{\mathrm{X}}-\nu_{\mathrm{A}}}{2} - \frac{J_{\mathrm{AX}}}{4} & 0 & 0 \\ 0 & 0 & -\frac{\nu_{\mathrm{X}}-\nu_{\mathrm{A}}}{2} - \frac{J_{\mathrm{AX}}}{4} & 0 \\ 0 & 0 & 0 & \frac{\nu_{\mathrm{A}}+\nu_{\mathrm{X}}}{2} + \frac{J_{\mathrm{AX}}}{4} \end{pmatrix}
\tag{47}
$$

The eigenvalues and eigenvectors are simply

$$
E_1 = -\frac{\nu_{\mathrm{A}} + \nu_{\mathrm{X}}}{2} + \frac{J_{\mathrm{AX}}}{4}; \quad \boldsymbol{V}_1 = \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix}
\tag{48}
$$

$$
E_2 = \frac{\nu_{\mathrm{X}} - \nu_{\mathrm{A}}}{2} - \frac{J_{\mathrm{AX}}}{4}; \quad \boldsymbol{V}_2 = \begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \end{pmatrix}
\tag{49}
$$

$$
E_3 = -\frac{\nu_{\mathrm{X}} - \nu_{\mathrm{A}}}{2} - \frac{J_{\mathrm{AX}}}{4}; \quad \boldsymbol{V}_3 = \begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \end{pmatrix}
\tag{50}
$$

$$
E_4 = \frac{\nu_{\mathrm{A}} + \nu_{\mathrm{X}}}{2} + \frac{J_{\mathrm{AX}}}{4}; \quad \boldsymbol{V}_4 = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix}
\tag{51}
$$

Although the $\hat{I}_x$ and $\hat{I}_y$ terms in the product $\hat{I}_{\mathrm{A}}\hat{I}_{\mathrm{B}}$ of the J-coupling Hamiltonian do not contribute to $\hat{H}_{\mathrm{J}}$, the transition probability is still given by eq. 41 and the transition matrix is the same as eq. 43.

An AX spectrum. Let's consider now two protons that resonate at $\nu_{\mathrm{A}} = 150$ Hz and $\nu_{\mathrm{X}} = 250$ Hz and that are coupled by $J_{\mathrm{AB}} = 7$ Hz. Using again a CAS software, the energies ($\boldsymbol{E}$) transition frequencies ($\boldsymbol{\nu}$) and transition intensities ($\boldsymbol{I}$) matrices are calculated to be

$$
\boldsymbol{E} = \boldsymbol{H} = \begin{pmatrix} -198.2 & 0.0 & 0.0 & 0.0 \\ 0.0 & 48.25 & 0.0 & 0.0 \\ 0.0 & 0.0 & -51.75 & 0.0 \\ 0.0 & 0.0 & 0.0 & 201.7 \end{pmatrix}
$$

$$
\boldsymbol{\nu} = \begin{pmatrix} 0.0 & 246.5 & 146.5 & 0.0 \\ 246.5 & 0.0 & 0.0 & 153.5 \\ 146.5 & 0.0 & 0.0 & 253.5 \\ 0.0 & 153.5 & 253.5 & 0.0 \end{pmatrix} \qquad \boldsymbol{I} = \begin{pmatrix} 0.0 & 1.0 & 1.0 & 0.0 \\ 1.0 & 0.0 & 0.0 & 1.0 \\ 1.0 & 0.0 & 0.0 & 1.0 \\ 0.0 & 1.0 & 1.0 & 0.0 \end{pmatrix}
$$

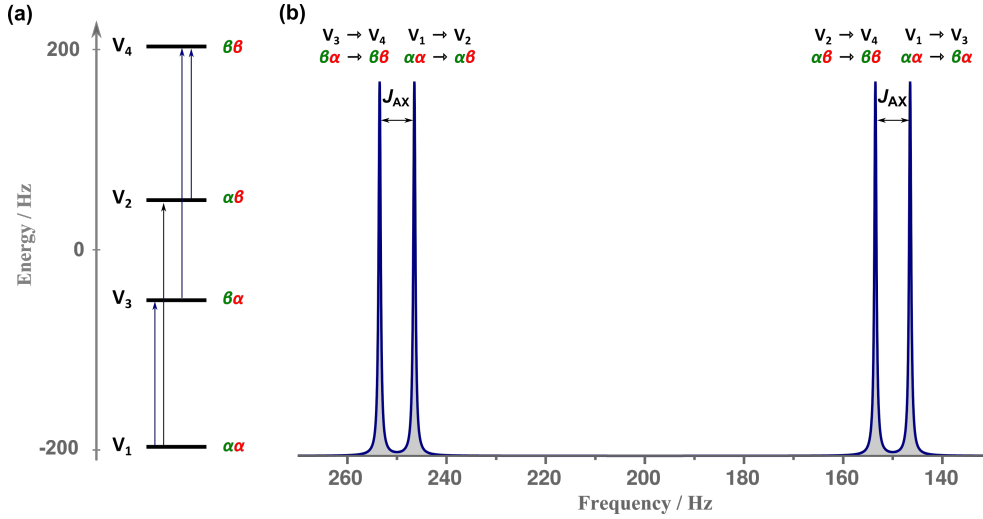The energy level diagram as well as the AX simulated spectrum are reported in Figure 4.

Figure 4: (a) Energy level diagram for an AX system (in frequency unit, with: $\nu_A = 150$ Hz, $\nu_B = 250$ Hz, $J_{AB} = 7$ Hz); (b) simulated ^{1}H NMR spectrum.

1.6 Outlook: rationalization of more complex NMR systems

The same formalism can be used for more complex systems. As the reader knows from its basic NMR knowledge, the overall NMR spectrum of a molecule can usually be divided in several non-coupled sub-systems. The definition of the proper Hamiltonian for each sub-system should first be done, depending on the first- or second-order couplings for a given NMR spectrometer with characteristic resonance frequency ν_0, which is defined according to protons

$$\nu_0 = \frac{\gamma_H B_0}{2\pi} \tag{52}$$

The first- or second-order coupling between two sets of magnetically equivalent protons i and j connected by the coupling constant J_{ij} is given by the ratio $\nu_0 \Delta \delta_{ij}/J_{ij}$, where $\Delta \delta_{ij} = |\delta_j - \delta_i|$. First order interpretation will be employed when the ratio $\nu_0 \Delta \delta_{ij}/J_{ij}$ is large (10 is usually considered as a relevant threshold), whereas if $\nu_0 \Delta \delta_{ij}$ is of the same order of magnitude of the coupling constant J_{ij}, a second-order analysis must be applied. For an hybrid sub-system with both strongly and weakly coupled sets of magnetically equivalent nuclei, the J-coupling Hamiltonian is made of two different parts. According to eq. 18 and to the discussion in section 1.5.4, the general expression for $\boldsymbol{H}^{\mathrm{NMR}}$ using the Pauli matrices is

$$\boldsymbol{H}^{\mathrm{NMR}} = -\frac{1}{2} \sum_{i=1}^{N} \nu_i \boldsymbol{\sigma}_{z_i} \tag{53}$$

$$+ \frac{1}{4} \sum_{i=1}^{n} \sum_{j=1}^{i-1} J_{ij} \left(\boldsymbol{\sigma}_{x_i} \boldsymbol{\sigma}_{x_j} + \boldsymbol{\sigma}_{y_i} \boldsymbol{\sigma}_{y_j} + \boldsymbol{\sigma}_{z_i} \boldsymbol{\sigma}_{z_j} \right) \tag{54}$$

$$+ \frac{1}{4} \sum_{i=1}^{m} \sum_{j=1}^{i-1} J_{ij} \left(\boldsymbol{\sigma}_{z_i} \boldsymbol{\sigma}_{z_j} \right) \tag{55}$$

where n is the total number of strongly coupled nuclei ($\nu_0 \Delta \delta_{ij}/J_{ij} \sim 1$), m is the total number of weakly coupled nuclei ($\nu_0 \Delta \delta_{ij}/J_{ij} \gg 1$) and N is the total number of sets of magnetically equivalent nuclei (i.e. $N = n + m$).

The $\boldsymbol{H}^{\mathrm{NMR}}$ matrix will then be diagonalized after transposition under the form that uses the Kronecker product. It provides the nuclear spin states $\boldsymbol{V}$ and their energies $\boldsymbol{E}$. Intensities can be obtained by calculating the transition probability matrix

$$\boldsymbol{I} = \left[\boldsymbol{V}^T \boldsymbol{T} \boldsymbol{V} \right]^2 \tag{56}$$

where $\boldsymbol{T}$ is the transition matrix

$$T = I_{x_1} \otimes 1... \otimes 1 + 1 \otimes I_{x_2} \otimes 1... \otimes 1 + ... + 1... \otimes 1 \otimes I_{x_N} \tag{57}$$

It is convenient to calculate the frequency matrix ν, which can be obtained by taking advantage of the conditional evaluation operator available in CAS softwares

$$\nu_{i,j} \leftarrow \begin{cases} |E_i - E_j| \text{ if } I_{i,j} \neq 0 \\ \qquad 0 \text{ if } I_{i,j} = 0 \end{cases}$$

We are now going to illustrate this on ABX systems.

1.7 ABX systems

It will now be rather easy to investigate three-spin ABX systems. As indicated by the notation, the A and B nuclei are strongly coupled and have similar chemical shifts, whereas nucleus X resonates in a different domain and is weakly coupled to A and B. This occurs frequently in trisubstituted aromatics or in vinyl systems. ABX NMR spectra usually exhibit an unsymmetrical 8-peak AB part and a 6-peak X part. The primary intent of the present approach is to show that with the help of a CAS software and thanks to the Kronecker product algebra, it becomes quite easy to plot a typical ABX spectrum and to understand its shape, in association with NMR textbooks[5,6] or seminal scientific articles.[8]

1.7.1 The Hamiltonian

Using Kronecker products, the Zeeman and J-coupling components of the NMR Hamiltonian are

$$H_Z = -\frac{1}{2}\nu_A \sigma_{z_A} \otimes 1 \otimes 1 - \frac{1}{2}\nu_B 1 \otimes \sigma_{z_B} \otimes 1 - \frac{1}{2}\nu_X 1 \otimes 1 \otimes \sigma_{z_X} \tag{58}$$

$$H_J = \frac{1}{4}J_{AB}(\sigma_{x_A} \otimes \sigma_{x_B} \otimes 1 + \sigma_{y_A} \otimes \sigma_{y_B} \otimes 1 + \sigma_{z_A} \otimes \sigma_{z_B} \otimes 1) \tag{59}$$

$$+ \frac{1}{4}J_{AX}(\sigma_{z_A} \otimes 1 \otimes \sigma_{z_X}) + \frac{1}{4}J_{BX}(1 \otimes \sigma_{z_B} \otimes \sigma_{z_X}) \tag{60}$$

The dimension of the H^{NMR} matrix is 8×8, in agreement with the 8 product functions of the three-spin system. Using again the Kronecker product, the product functions given in Table 1 can directly be obtained by calculating

$$\begin{pmatrix} \alpha_A \\ \beta_A \end{pmatrix} \otimes \begin{pmatrix} \alpha_B \\ \beta_B \end{pmatrix} \otimes \begin{pmatrix} \alpha_X \\ \beta_X \end{pmatrix} \tag{61}$$

	A	B	X	M_I
ψ_1	α	α	α	$3/2$
ψ_2	α	β	α	$1/2$
ψ_3	β	α	α	$1/2$
ψ_4	β	β	α	$-1/2$
ψ_5	α	α	β	$1/2$
ψ_6	α	β	β	$-1/2$
ψ_7	β	α	β	$-1/2$
ψ_8	β	β	β	$-3/2$

$$H : \begin{pmatrix} H_{11} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & H_{22} & H_{23} & 0 & 0 & 0 & 0 & 0 \\ 0 & H_{32} & H_{33} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & H_{44} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & H_{55} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & H_{66} & H_{67} & 0 \\ 0 & 0 & 0 & 0 & 0 & H_{76} & H_{77} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & H_{88} \end{pmatrix}$$

Table 1: Product functions of the ABX system, sorted to highlight the bloc-diagonal shape of the Hamiltonian matrix and the existence of two ab subspectra. Red/Green: α/β spin states for X.

1.7.2 An example of ABX system

Let us consider the triptophan molecule, which vinyl protons are characterized at high field ^{1}H NMR to lie at *ca.* δ_A: 3.3 ppm, δ_B: 3.5 ppm, δ_X: 4.05 ppm. The coupling constants are found to be: J_{AB}: 15.3 Hz, J_{AX}: 8.1 Hz, J_{BX}:

4.7 Hz. According to the $\nu_0\delta_{ij}/J_{ij}$ criterion, an ABX spectrum is indeed expected to be found with low-frequency NMR spectrometers. For example, the second-order coupling effect cannot be neglected between nuclei A and B with a 200 MHz equipment ($\nu_0\delta_{AB}/J_{AB}$: 2.6, $\nu_0\delta_{AX}/J_{AX}$: 18.5, $\nu_0\delta_{BX}/J_{BX}$: 23.4). After sorting the energies and NMR states under the canonical order given in Table 1, the frequency and intensity matrices are found to be

$$\nu = \begin{pmatrix}
0 & 647.1 & 695.9 & 0 & 808.3 & 0 & 0 & 0 \\
647.1 & 0 & 0 & 711.2 & 0 & 816.0 & 852.9 & 0 \\
695.9 & 0 & 0 & 662.4 & 0 & 767.1 & 804.0 & 0 \\
0 & 711.2 & 662.4 & 0 & 0 & 0 & 0 & 811.7 \\
808.3 & 0 & 0 & 0 & 0 & 654.7 & 691.7 & 0 \\
0 & 816.0 & 767.1 & 0 & 654.7 & 0 & 0 & 707.0 \\
0 & 852.9 & 804.0 & 0 & 691.7 & 0 & 0 & 670.0 \\
0 & 0 & 0 & 811.7 & 0 & 707.0 & 670.0 & 0
\end{pmatrix}$$

$$I = \begin{pmatrix}
0 & 0.687 & 1.313 & 0 & 1.000 & 0 & 0 & 0 \\
1.313 & 0 & 0 & 1.313 & 0 & 0.003 & 0.997 & 0 \\
0.687 & 0 & 0 & 0.687 & 0 & 0.997 & 0.003 & 0 \\
0 & 0.687 & 1.313 & 0 & 0 & 0 & 0 & 1.000 \\
1.000 & 0 & 0 & 0 & 0 & 0.586 & 1.414 & 0 \\
0 & 0.997 & 0.003 & 0 & 0.586 & 0 & 0 & 0.586 \\
0 & 0.003 & 0.997 & 0 & 1.414 & 0 & 0 & 1.414 \\
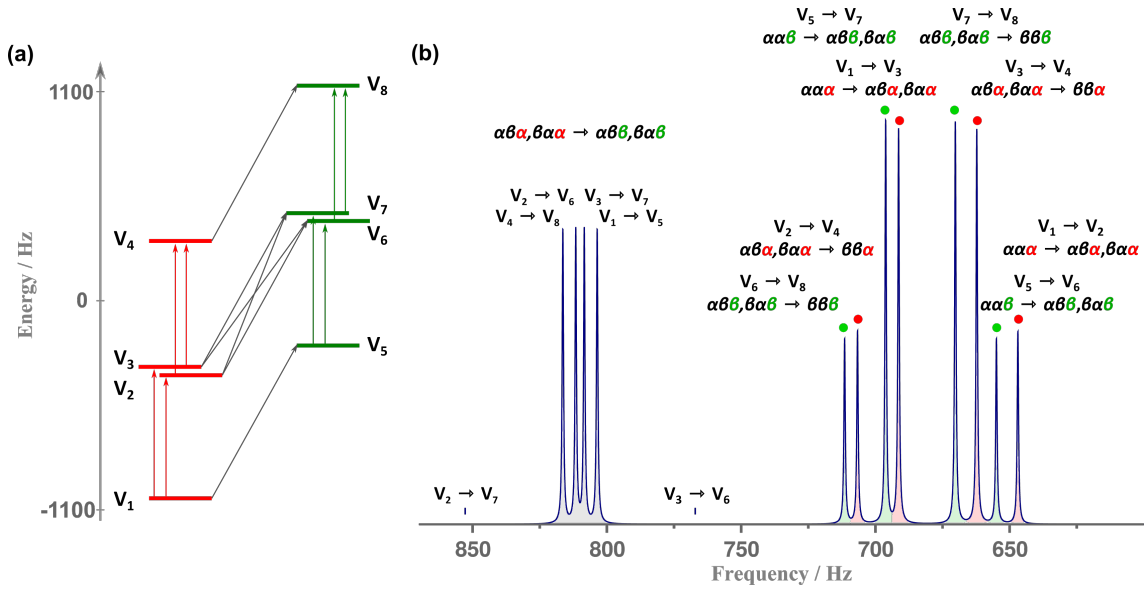0 & 0 & 0 & 1 & 0 & 0.586 & 1.414 & 0
\end{pmatrix}$$

Figure 5: (a) Energy level diagram for an ABX system (in frequency unit) with ν_A: 660 Hz, ν_B: 700 Hz, ν_X: 810 Hz, J_{AB}: 15.3 Hz, J_{AX}: 8.1 Hz, J_{BX}: 4.7 Hz. Red/green energy levels: ab subspectra with X in its α/β spin state, respectively; (b) simulated ^{1}H NMR spectrum.
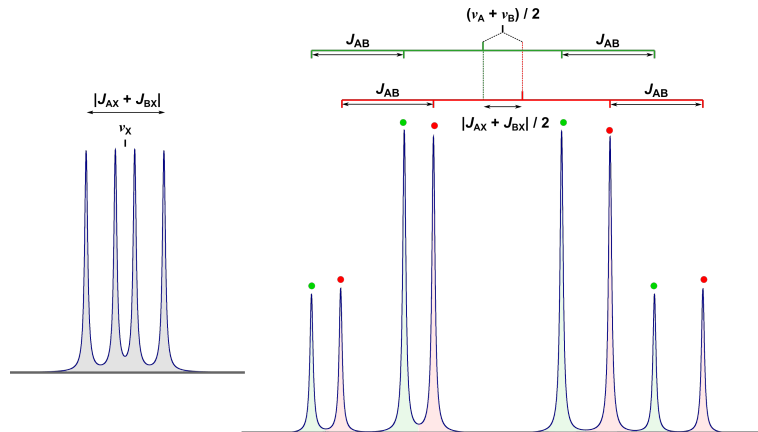

Figure 6: Same ABX spectrum as Figure 5.

2 Implementation with python and the SymPy library

see the pyPhysChem github repository.

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