

Ensemble Quantum Computing with Nuclear Magnetic Resonance

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During the first year, I have been studying the background of implementing quantum computers with liquid Nuclear Magnetic Resonance (NMR) systems. I have been studying some of the theoretical and experimental tools used in NMR. Moreover, I have looked at the prospects of using para-hydrogen for quantum computing. This first-year report highlights some of the important concepts I have learnt so far, presents some important results and gives a preview of the areas I would like to follow in the coming years.

1. INTRODUCTION

Nuclear magnetic resonance (NMR) is one of the leading technologies in the practical implementation of quantum computers [1–9]. However, there are major problems in scaling-up the system to large numbers of qubits [10, 11]. Many of these problems revolve around the fact that thermal equilibrium states are highly mixed, with small polarizations. The impossibility of preparing pure states for NMR, can be circumvented by assembling pseudo-pure states [12, 13], but this approach is limited by an exponential decrease in sensitivity with the number of qubits. It has been shown that systems below a critical threshold amount of the pure component in a pseudo-pure density matrix can be explained classically, leading some authors to claim that NMR quantum computing is not quantum at all! [14]

For this reason there is a desire to initialize the NMR experiment with non-equilibrium states. One possible solution using liquid-state NMR, at reasonable temperatures and magnetic fields, is to exploit the para-hydrogen induced polarization effect. The para-hydrogen molecule with its pure antisymmetric quantum state, is added to an organometallic compound, dramatically enhancing the polarization of the spins (the PHIP effect) [15, 16].

With colleagues at the University of York we plan to devise experiments to exceed the critical polarization threshold.

2. THERMAL EQUILIBRIUM STATE

2.1. Ensemble of isolated spin- $\frac{1}{2}$ nuclei

Consider an ensemble [12, 19] of isolated 1-qubit systems. Each system is a single spin $\frac{1}{2}$ nucleus. In the presence of an external field \mathbf{B} (conventionally taken to be applied along the z -axis), the energy of the various nuclear spin states is given by the classical relation [17, 18]:

$$E = -\hat{\mu} \cdot \mathbf{B} \quad (1a)$$

The *magnetic moment* $\hat{\mu}$ in (1a) is a quantum mechanical operator related to the *angular momentum operator* $\hat{\mathbf{I}}$ through the *gyromagnetic ratio* γ :

$$\hat{\mu} = \gamma \hat{\mathbf{I}} \quad (1b)$$

So the *Hamiltonian operator* \hat{H} corresponding to the energy in (1a) is given by:

$$\begin{aligned} \hat{H} &= -\gamma \hat{\mathbf{I}} \cdot \mathbf{B} \\ &= -\gamma \hat{I}_z B \\ &= \omega_0 \hat{I}_z \end{aligned} \quad (1c)$$

The operator \hat{I}_z has eigenvalues $m\hbar$ where m is the magnetic quantum number of the corresponding eigenstate, and so (using the correspondence principle) the energy of the nuclear states is given by:

$$E = -\gamma \hbar m B \quad (1d)$$

$$= m \hbar \omega_0 \quad (1e)$$

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The term $\omega_0 = -\gamma B$ in (1c) and (1e) is the *Larmor frequency* of the nucleus (hereafter referred to as simply the “spin”). An isolated spin will precess around the z -axis with this characteristic frequency. For spins with $I = \frac{1}{2}$, m can assume the values $\frac{1}{2}$ and $-\frac{1}{2}$. The spin state corresponding to $m = \frac{1}{2}$ is aligned in the direction of the applied field \mathbf{B} and is generally called the *up* state denoted by $|\alpha\rangle$ or $|0\rangle$. Likewise the state corresponding to $m = -\frac{1}{2}$ is in the *down* state and is labelled as $|\beta\rangle$ or $|1\rangle$. Both of these kets will be eigenkets of the Hamiltonian and are called the *Zeeman* states. The up state is the lower in energy, of the two states for a nucleus with a positive value of γ . The energy difference between the two states is given as:

$$\Delta E = \hbar\omega_0 \quad (2a)$$

$$= \hbar\gamma B \quad (2b)$$

For protons with $\gamma = 267 \times 10^6 \text{ rad s}^{-1} \text{ T}^{-1}$ in a field of $B = 10 \text{ T}$, this difference is only $2.8 \times 10^{-25} \text{ J}$. Compared to the product $k_B T = 4 \times 10^{-21} \text{ J}$ at 300 K, this difference is very small ($\sim 10^{-4}$). The $|\alpha\rangle$ and $|\beta\rangle$ levels will be nearly equally populated and the resulting ensemble will be in a highly *mixed* state [20]. The NMR signal arises because of population **differences** between energy levels and so the thermal equilibrium state will give only a very weak signal. A *pure* state can be represented by the density matrix:

$$\rho_1 = |\psi\rangle\langle\psi| \quad (3a)$$

Another state of interest is:

$$\rho_2 = (1 - \epsilon)\frac{\mathbb{1}}{2} + \epsilon|\psi\rangle\langle\psi| \quad (3b)$$

which will result in the same NMR signal as that obtained from ρ_1 except that its strength would be decreased by a factor of ϵ . The state ρ_2 is an example of a *pseudo-pure* state. Using the argument above, the *maximally mixed state* $\sim \mathbb{1}$ in (3b) will not generate any signal because there is no preferential alignment of the spins in this state and signals from different spins cancel out.

An interesting question to address at this stage is: how could we enhance the sensitivity of the NMR signal? Would it be possible to increase the population difference between the $|\alpha\rangle$ and $|\beta\rangle$ states? There are two obvious ways. First is to increase the energy gap ΔE between the states and the second is to cool the spins. Neither of the methods, however, is practical. For example, suppose we wish to create a population ratio of 1:0.01 between the $|\alpha\rangle$ and $|\beta\rangle$ states at room temperature. This would require a field strength of nearly 145 000 T — something well beyond foreseeable magnet technology. Using conventional fields of order 10 T would not help either as this would require temperatures as low as 0.02027 K. At this temperature, the sample will no longer exist in the liquid state. However, using non-Boltzmann population distributions may give an alternative route to achieve higher sensitivities. I shall discuss this prospect in a later section.

Discounting issues of intensity, the signal from the 1-qubit thermal state would be the same as acquired from a pure ensemble with all spins in the $|\alpha\rangle = |0\rangle$ state. This mixed acts like an “effective” or pseudo-pure state as mentioned before. It is then tempting to suggest that Boltzmann distributions for higher-qubit systems could also serve as pseudo-pure states, but this is not the case.

I now derive an exact expression for the equilibrium density matrix ρ_{eq} [19, 21]. ρ_{eq} consists of only populations and all coherences are absent. The fractional populations in the states $|i\rangle$ are given by the Boltzmann distribution [22]:

$$n_i = \frac{e^{-\frac{E_i}{k_B T}}}{Z} \quad (4a)$$

where Z is the appropriate *partition function* and is given by:

$$Z = \sum_j e^{-\frac{E_j}{k_B T}} \equiv \text{Tr} \left\{ e^{-\frac{\hbar\hat{H}}{k_B T}} \right\} \quad (4b)$$

The sum in (4b) is taken over all possible eigenstates and $\text{Tr} \{ \dots \}$ represents the trace operation. In the equations above the term:

$$E_i = -\gamma\hbar m_i B = \hbar\omega_i \quad (4c)$$

is the energy in the i 'th Zeeman state and $\omega_i = m_i \omega_0 = \pm \frac{1}{2} \omega_0$. The exponential factors in (4a) take the form:

$$\exp\left(-\frac{E_\alpha}{k_B T}\right) = \exp\left(-\frac{\hbar\omega_\alpha}{k_B T}\right) = \exp\left(\frac{\gamma\hbar B}{2k_B T}\right) \quad (4d)$$

$$\exp\left(-\frac{E_\beta}{k_B T}\right) = \exp\left(-\frac{\hbar\omega_\beta}{k_B T}\right) = \exp\left(-\frac{\gamma\hbar B}{2k_B T}\right) \quad (4e)$$

Defining the Boltzmann factor as $\mathbb{B} = \frac{\Delta E}{k_B T} = \frac{\gamma\hbar B}{k_B T}$, (4d) and (4e) can be re-written as:

$$\exp\left(-\frac{E_\alpha}{k_B T}\right) = \exp\left(\frac{\mathbb{B}}{2}\right) \quad (4f)$$

$$\exp\left(-\frac{E_\beta}{k_B T}\right) = \exp\left(-\frac{\mathbb{B}}{2}\right) \quad (4g)$$

In the high-temperature limit $k_B T \gg \Delta E \Rightarrow \mathbb{B} \ll 1$, (a condition which would be true even if the temperature is above a few millikelvins), only the first few terms in the exponential factors in (4f) and (4g) need be taken. To first order, these factors can be approximated to:

$$\exp\left(\frac{\mathbb{B}}{2}\right) \simeq 1 + \frac{\mathbb{B}}{2} \quad (4h)$$

$$\exp\left(-\frac{\mathbb{B}}{2}\right) \simeq 1 - \frac{\mathbb{B}}{2} \quad (4i)$$

and the partition function in (4b) simplifies to:

$$Z = \exp\left(\frac{\mathbb{B}}{2}\right) + \exp\left(-\frac{\mathbb{B}}{2}\right) \simeq 2 \quad (4j)$$

Inserting these values into the population terms gives us the following product operator representation [23, 24] of ρ_{eq} :

$$\begin{aligned} \rho_{eq} &\stackrel{highT}{=} \begin{pmatrix} \frac{1}{2} + \frac{B}{4} & 0 \\ 0 & \frac{1}{2} - \frac{B}{4} \end{pmatrix} \\ &= \frac{1}{2}\mathbb{1} + \frac{B}{2}I_z \end{aligned} \quad (5a)$$

The traceless part of ρ_{eq} is called the *deviation matrix*. Multiples of the identity matrix remain unchanged under unitary evolutions and so the deviation matrix is a convenient short-hand, “functional” representation of the state:

$$\rho_{eq} \stackrel{highT}{=} \equiv \frac{B}{4} \{1, -1\} \quad (5b)$$

In (5b), I have represented a diagonal matrix by $\{\dots\}$ with the diagonal elements inside the braces. The population difference between the $|\alpha\rangle$ and $|\beta\rangle$ states is proportional to $\mathbb{B} \sim \Delta E \sim B$. Hence higher fields result in enhanced sensitivity. (For the sake of exactness the fractional population difference between the $|\alpha\rangle$ and $|\beta\rangle$ eigenstates is $\tanh\left(\frac{\hbar\gamma B}{k_B T}\right)$ which approaches 1 in the limit $T \rightarrow 0$).

2.2. Ensemble of multi-qubit systems

The derivation used above can be easily extended to an ensemble of systems with 2 or more spins. Suppose we have two spins I and S with Larmor frequencies ω_I and ω_S respectively. In strong fields, the weak coupling limit $|\omega_I - \omega_S| \gg |\pi J|$ is satisfied where J is the *scalar coupling constant*.

The weak-coupling Hamiltonian in the 2-spin case corresponding to the *Larmor equation* in (1c) is given as:

$$\hat{H} = \omega_I \hat{I}_z + \omega_S \hat{S}_z + \pi J (2 \hat{I}_z \hat{S}_z) \quad (6)$$

The energies of the two-spin energy levels (Zeeman states) can be easily calculated using (6) and (1e). There will be 2^n states for an n -spin system. In the IS system, we shall have the four Zeeman states: $\{|\alpha\alpha\rangle, |\alpha\beta\rangle, |\beta\alpha\rangle, |\beta\beta\rangle\}$. The energy corresponding to the state $|is\rangle$ will be:

$$E_{is} = \hbar m_i \omega_I + \hbar m_s \omega_S + 2\pi J \hbar m_i m_s \quad (7a)$$

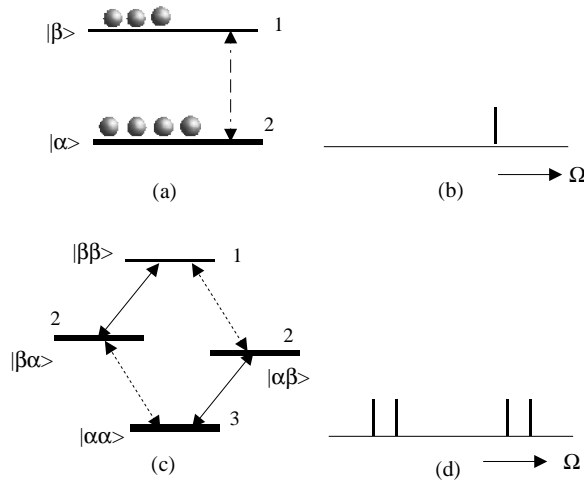


FIG. 1: Energy level diagram for the I (a) and IS (c) spin systems. (b) and (d) show the corresponding NMR spectra. The numbers written next to each energy level represent their relative populations. The $|\alpha\beta\rangle$ and $|\beta\alpha\rangle$ states in (c) are nearly degenerate. In (c), the dotted lines represent I spin and the solid lines represent S spin coherences.

and in analogy with (4c), (7a) can be written as:

$$E_{is} = \hbar\omega_{is} \quad (7b)$$

with the following definition:

$$\omega_{is} = m_I\omega_I + m_S\omega_S + 2\pi Jm_I m_S \quad (7c)$$

As an example, the energy of the state $|\alpha\beta\rangle$ is found out to be:

$$E_{\alpha\beta} = \hbar\left(\frac{\omega_I}{2} - \frac{\omega_S}{2} - \frac{\pi J}{2}\right) \quad (7d)$$

By calculating the Zeeman energies in this way and finding the Boltzmann populations (in the high-temperature approximation) as was done for the single-spin, we can derive the following form for ρ_{eq} for the IS case:

$$\rho_{eq} \simeq \left\{ \frac{1}{4} + \frac{\mathbb{B}_I + \mathbb{B}_S}{8}, \frac{1}{4} + \frac{\mathbb{B}_I - \mathbb{B}_S}{8}, \frac{1}{4} - \frac{\mathbb{B}_I + \mathbb{B}_S}{8}, \frac{1}{4} - \frac{\mathbb{B}_I - \mathbb{B}_S}{8} \right\} \quad (8a)$$

$$= \frac{1}{4} + \frac{\mathbb{B}_I}{4} I_z + \frac{\mathbb{B}_S}{4} S_z \quad (8b)$$

The Boltzmann factors for the IS case are defined as $\mathbb{B}_I = \frac{\Delta E}{k_B T} = \frac{\gamma_I \hbar B}{k_B T}$ and $\mathbb{B}_S = \frac{\Delta E}{k_B T} = \frac{\gamma_S \hbar B}{k_B T}$. While writing (8a) I have incorporated the *chemical shift* terms σ_i inside the gyromagnetic ratios γ_i . More precisely, $\gamma_i \equiv \gamma_i(1 - \sigma_i)$. Moreover the J terms are neglected as the J frequencies are generally very small (of the order of hundreds of Hz at the maximum) as compared to the Larmor frequencies (in the MHz range). For homonuclear systems where $\gamma_I \equiv \gamma_S \Rightarrow \mathbb{B}_I = \mathbb{B}_S = \mathbb{B}$, (8b) further simplifies to:

$$\rho_{eq} = \frac{1}{4} + \frac{\mathbb{B}}{4}(I_z + S_z) \quad (8c)$$

$$\sim \frac{\mathbb{B}}{4}\{1, 0, 0, -1\} \quad (8d)$$

Figure 1 shows the *population or energy level diagrams* [18] for the homonuclear 1 and 2 spin cases in thermal equilibrium. The Boltzmann distribution of populations gives a single peak in the single spin case and the familiar pair of doublets at the I and S spin transition frequencies [19].

Using the definition of ω_{is} in (7c), ρ_{eq} is given in exact form as:

$$\rho_{eq} = \begin{pmatrix} \exp(-\frac{\hbar\omega_{\alpha\alpha}}{k_B T}) & 0 & 0 & 0 \\ 0 & \exp(-\frac{\hbar\omega_{\alpha\beta}}{k_B T}) & 0 & 0 \\ 0 & 0 & \exp(-\frac{\hbar\omega_{\beta\alpha}}{k_B T}) & 0 \\ 0 & 0 & 0 & \exp(-\frac{\hbar\omega_{\beta\beta}}{k_B T}) \end{pmatrix} \quad (9a)$$

which can also be expressed in operator notation as:

$$\hat{\rho}_{eq} = \frac{e^{-\frac{\hbar\hat{H}}{k_B T}}}{Z} \quad (9b)$$

(9b) is also valid for a general n -qubit system with the Hamiltonian given as:

$$\hat{H} = \sum_i^n \omega_i \hat{I}_{iz} + \pi J \sum_{k=1}^n \sum_{j<k} 2\hat{I}_{jz}\hat{I}_{kz} \quad (10)$$

In the temperature limit, the density matrix for the generalized homonuclear n -qubit case in (9) becomes:

$$\rho_{eq} = \frac{\mathbb{1}}{2^n} + \frac{\mathbb{B}}{2^n} \sum_i^n I_{iz} \quad (11)$$

3. PSEUDO-PURE PREPARATION

It is a desirable feature in NMR quantum computing, that the computational basis in quantum computing coincides with the Zeeman eigenbasis [25, 26]. If this is the case, the $|\alpha\rangle$ and $|\beta\rangle$ states can be logically labelled as $|0\rangle$ and $|1\rangle$ respectively. Moreover, if NMR is to be of any use in implementing quantum circuits, the system has to be initialized in a known, well-defined state [27]. The initial state commonly used is the $|000\dots 0\rangle$ in which all the n qubits are in the energetic ground or $|\alpha\rangle$ state. For a single qubit system, the problem of initialization is trivial as the thermal state is in itself a pseudo-pure state. The same is not true for higher-qubit systems. Suppose a 2-qubit (or IS) system needs to be brought into the state $|00\rangle$. The density matrix corresponding to this pure state is:

$$\begin{aligned} \rho_{pure} &= |00\rangle\langle 00| \\ &= \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \end{aligned} \quad (12a)$$

$$= \frac{\mathbb{1}}{4} + \frac{I_z + S_z + 2I_z S_z}{2} \quad (12b)$$

$$\sim I_z + S_z + 2I_z S_z \quad (12c)$$

The pure state (12b) does not coincide with the thermal state given in (8c). Starting from this mixed state, a state needs to be assembled that behaves in effectively the same manner as ρ_{pure} . Such a pseudo-pure state would have a deviation matrix equal to the deviation matrix (12c), correct to a scaling factor. Pseudo-pure states can also be expressed in the form given in (3b), each such state with a representative value of ϵ , depending on the initial state and the particular method used in preparing that state.

Different schemes have been proposed to assemble pseudo-pure states from thermal equilibrium. They include the scheme originally invented by Cory *et. al.* [12, 28] involving *spatial averaging*, *temporal averaging* [13] and the more difficult approach of *logical labelling* [29, 30]. All these methods sometimes involve some non-unitary process and hence there is a loss in polarization factor ϵ . Knill *et. al.* [31] have also proposed a more general method of preparing an $(n-1)$ -qubit pseudo-pure state starting from an n -qubit thermal state. This method involves generation of an n -qubit cat state. Such a cat state is an incoherent mixture of n -quantum coherence terms which can be selected using gradients [32] or phase cycling [24].

The polarization factor ϵ represents the pure component in the mixed state. If liquid-state NMR is to become a useful technology for quantum computing, the system needs to be scaled up to a larger number of qubits.

Unfortunately, the amount of pure state, quantified by ϵ , that can be extracted starting from a thermal state falls off exponentially with the number of qubits. The exact value of ϵ depends on the detailed scheme of preparing pseudo-pure states, but we can identify an upper bound on ϵ [10]. For the homonuclear case this bound is:

$$\epsilon \leq \frac{2 \sinh(\frac{n\hbar\omega_0}{2k_B T})}{2^n \cosh^n(\frac{\hbar\omega_0}{2k_B T})} \quad (13a)$$

$$\stackrel{highT}{\simeq} \frac{n\hbar\omega_0}{2^n k_B T} \quad (13b)$$

This exponential decrease in ϵ with the number of qubits, affords critics with two major charges against NMR systems. First, the sensitivity of the signal is reduced exponentially. This is clearly not consummate with the scaling requirements of a quantum computer. Apparently this problem could be resolved by using an exponentially larger number of molecules (bigger volume of sample) but this is contradictory to the resource-economic spirit of quantum information processing [26].

3.1. Entanglement in NMR

The second criticism against NMR systems is more serious and on a more fundamental note: many researchers claim that NMR systems are not quantum mechanical at all!

Entanglement [33] is an important resource for quantum computing [34]. NMR states generally deal with highly mixed states. These states can always be decomposed into product states [35, 36]. For example the maximally mixed state $\frac{\mathbb{1}}{4}$ can be decomposed as a sum of product states:

$$\frac{\mathbb{1}}{4} = \frac{1}{4}(|00\rangle\langle 00| + |01\rangle\langle 01| + |10\rangle\langle 10| + |11\rangle\langle 11|) \quad (14a)$$

This state is clearly *decomposable*¹ and the two spins are clearly not entangled. Since the maximally mixed state is provably non-entangled, it might be possible to model NMR classically. However it has been somewhat difficult to contrive accurate models [14, 37]. This contentious issue is yet to find a conclusive answer.

An additional complication arises when we try to quantify the amount of entanglement in a state. Consider the *pseudo-entangled* state often called the *Werner* state [38]:

$$\rho_W = (1 - \epsilon)\frac{\mathbb{1}}{4} + \epsilon|\phi^+\rangle\langle\phi^+| \quad (15a)$$

$$= \begin{pmatrix} \frac{1+\epsilon}{4} & 0 & 0 & \frac{\epsilon}{2} \\ 0 & \frac{1-\epsilon}{4} & 0 & 0 \\ 0 & 0 & \frac{1-\epsilon}{4} & 0 \\ \frac{\epsilon}{2} & 0 & 0 & \frac{1+\epsilon}{4} \end{pmatrix} \quad (15b)$$

where $|\phi^+\rangle = \frac{1}{\sqrt{2}}(|00\rangle + |11\rangle)$ is one of the four Bell states. At the outset, ρ_W appears to be a mixture of the maximally mixed state and a proportion ϵ of the entangled state. This conjecture is not absolutely correct. The decomposition given in (14a) is not unique. In fact, the maximally mixed state can be decomposed in an infinite number of ways, corresponding to all the possible sets of basis vectors spanning the 4-dimensional Hilbert space. One such possibility involves the decomposition into the 4 Bell basis states, which are the *maximally entangled* states:

$$\frac{\mathbb{1}}{4} = \frac{1}{4}(|\phi^+\rangle\langle\phi^+| + |\phi^-\rangle\langle\phi^-| + |\psi^+\rangle\langle\psi^+| + |\psi^-\rangle\langle\psi^-|) \quad (16)$$

Such a decomposition might raise the entangled component in (15) from its “nominal” value ϵ [26]. A somewhat different decomposition, could therefore increase or decrease the entangled component and there is no special reason to choose one decomposition in favour of the other. Although it may not be currently plausible to quantify the entanglement in a Werner state, Werner derived the important result that ρ_W would *always* be separable for $\epsilon < \frac{1}{3}$ [38].

¹ A state ρ is said to be decomposable or *separable* if it can be written as a convex sum of direct product states $\rho = \bigotimes_k \lambda_k |\psi_k\rangle\langle\psi_k|$

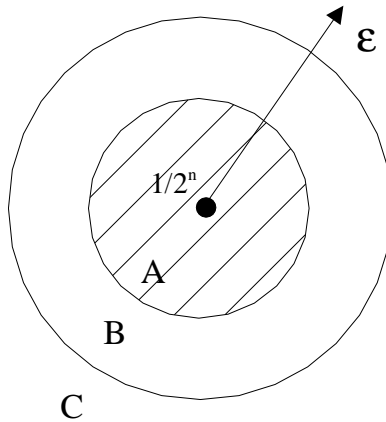


FIG. 2: Bounds on ϵ . A, B and C are the regions in the neighbourhood of the maximally mixed state $\frac{1}{2^n}$. The region A is where the state is provably separable and C is where it is provably non-separable. Present-day NMR implementations work in the area A.

Braunstein *et. al.* [37] formulated and improved the upper and lower bounds on ϵ to establish the separability or otherwise, of a general state of the form given in (3b). ρ can be shown to be separable for sufficiently small values of ϵ :

$$\epsilon \leq \frac{1}{1+2^{2n-1}} \xrightarrow{n \rightarrow \infty} \frac{2}{4^n} \quad (17a)$$

If, on the other hand, ϵ exceeds the upper bound, the state is non-separable. This upper bound is given by:

$$\epsilon \geq \frac{1}{1+2^{\frac{n}{2}}} \xrightarrow{n \rightarrow \infty} \frac{2}{2^{\frac{n}{2}}} \quad (17b)$$

Figure 2 schematically represents these two bounds. Current NMR implementations have so far approached 7 qubits. With realistic high-temperature estimates of the polarization factor ϵ (13b) $\sim 3 \times 10^5$, we find that the states presently used in NMR all lie within the region A. If we fix ϵ at this current value, we can *expect* entangled states only for 13 or more qubits. All present-day NMR protocols are explicitly separable and this motivates the claims that current NMR technologies are not quantum in the first place. However, this question must follow another more fundamental question: what makes a quantum process really “quantum”!

3.2. Methods of enhancing polarization

The way out of this bleak scenario for NMR, it seems, is to somehow enhance the polarization co-efficient ϵ . Different schemes have been tested in this respect. They include optical pumping of electronic spin states in noble gases and the subsequent transfer to the nuclear spins [39], the nuclear Overhauser effect (NOE) [40, 41] and chemically induced dynamic nuclear polarization (CIDNP) [42]. These techniques, however, all perform poorly in the liquid state.

The one most promising area in this regard is exploiting the high polarization offered by para-hydrogen (p-H₂). The non-Boltzmann distribution of para-hydrogen, at least theoretically, offers the possibility of achieving very nearly pure states ($\epsilon \sim 1$).

4. PARAHYDROGEN

4.1. Di-hydrogen nuclei in the singlet state

A para-hydrogen molecule is a di-hydrogen molecule H₂ in which the two nuclei are in a singlet state. Suppose we have two spins (nuclei) A and B in a diatomic molecule such as in H₂. Each spin being simply a proton has a *spin quantum number* of $\frac{1}{2}$, $s_A = s_B = \frac{1}{2}$. Adding these spin quantum numbers to find the *total angular momentum* is like the traditional problem in quantum mechanics of the addition of two angular momenta [21]. The spin quantum number s for the composite two-spin molecule can take on the values $s = |s_1 - s_2|, |s_1 - s_2| + 1, \dots, s_1 + s_2 - 1, s_1 + s_2$.

For H_2 the possible values of s are 1 and 0. Associated with each s there will be $2s+1$ *degenerate states* with *magnetic quantum numbers* $m = -s, -s+1, \dots, s-1, s$. In the H_2 molecule, the following values of the total spin and magnetic moment are possible:

$$\begin{aligned} s = 1; & \quad m = 1, 0, -1 \\ s = 0; & \quad m = 0 \end{aligned} \tag{18}$$

The states in (18) with $s = 1$ are called the *triplets* T_1, T_0 and T_{-1} respectively. The state in (18) with $s = 0$ is the *singlet* S_0 . The singlets and triplets form a 4-dimensional angular momentum *basis*. This basis is generally called the *singlet-triplet*, ST or the *symmetrical basis*, denoted by $\{|s_A, s_B; s, m\rangle\}$. The triplet states are symmetrical and the singlet is *anti-symmetrical* under exchange of the nuclei. These states are related to the eigenstates in the *direct product basis* $\{|s_A, s_B; m_A, m_B\rangle\}$ in the following way:

$$\begin{aligned} T_1 &= |\alpha\alpha\rangle \\ T_0 &= \frac{1}{\sqrt{2}} (|\alpha\beta\rangle + |\beta\alpha\rangle) \\ T_{-1} &= |\beta\beta\rangle \\ S_0 &= \frac{1}{\sqrt{2}} (|\alpha\beta\rangle - |\beta\alpha\rangle) \end{aligned} \tag{19}$$

A state vector $\vec{\mathbf{u}}$ written in the direct product basis can be expressed in the ST basis as $\vec{\mathbf{v}}$ by multiplying it with the transformation matrix P i.e., $\vec{\mathbf{v}} = P \cdot \vec{\mathbf{u}}$. The transformation between the two bases is given by the orthogonal matrix:

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

It is assumed that the eigenvectors in the direct and total angular momentum bases are taken in the order $\{|\alpha\alpha\rangle, |\alpha\beta\rangle, |\beta\alpha\rangle, |\beta\beta\rangle\}$ and $\{T_1, T_0, S_0, T_{-1}\}$ respectively. Clearly, the elements in P are the *Clebsch-Gordon coefficients* $\langle \frac{1}{2}, \frac{1}{2}; s, m | \frac{1}{2}, \frac{1}{2}; m_A, m_B \rangle$ [21]. It is interesting to note that the strong coupling hamiltonian $\hat{H}_J = \pi J 2 \mathbf{I} \cdot \mathbf{S}$ is diagonal only in the ST basis and not in the direct product basis. However, in the limit of weak coupling, the hamiltonian is diagonal in both bases.

Returning to the case of para-hydrogen, the two spins are in the singlet state $S_0 = \frac{1}{\sqrt{2}} (|\alpha\beta\rangle - |\beta\alpha\rangle)$. The total magnetic quantum number for this state is 0. In quantum computing notation (and dropping the normalization factor) pure para-hydrogen is simply the state $|01\rangle - |10\rangle$, which is also one of the four Bell states, $|\psi^-\rangle$. The exact density matrix for para-hydrogen can therefore be written as:

$$\begin{aligned} \rho &= |\psi^-\rangle\langle\psi^-| \\ &= \frac{1}{2} (|01\rangle - |10\rangle) (\langle 01| - \langle 10|) \\ &= \frac{1}{2} \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 1 & -1 & 0 \\ 0 & -1 & 1 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \end{aligned} \tag{20a}$$

$$= \frac{1}{4} \mathbb{1} - \frac{1}{2} (2 I_x S_x + 2 I_y S_y + 2 I_z S_z) \tag{20b}$$

$$= \frac{1}{4} \mathbb{1} - \frac{1}{2} (2 I_z S_z) - ZQ_x \tag{20c}$$

$$= \frac{1}{4} \mathbb{1} - \mathbf{I} \cdot \mathbf{S} \tag{20d}$$

where (20a) is the para-hydrogen density matrix in the Zeeman basis; (20b) is its representation in the product operator basis and (20c) shows that it is a mixture of zero quantum coherence and longitudinal two-spin order terms. The deviation matrix which is of interest in unitary evolutions is the *isotropic term* $\mathbf{I} \cdot \mathbf{S}$ in (20d). Notwithstanding the fact that the singlet is anti-symmetric *with respect to exchange of the nuclei*, it is symmetrically invariant under

total rotations. By total rotations, I mean rotations that act on the joint Hilbert space of the spins and not just the sub-space of individual spins. In operator notation, these rotations are of the form $\mathcal{D}(\hat{\mathbf{J}}) \otimes \mathbf{1} + \mathbf{1} \otimes \mathcal{D}(\hat{\mathbf{J}})$. The isotropic term is a *scalar*² as it commutes with the operator $\sum_k \hat{F}_{ku}$ where k is the number of spins (2 in our case) and $u = x, y$ or z . The isotropic term commutes with the total angular momentum operators in all three directions:

$$\begin{aligned} [\mathbf{I} \cdot \mathbf{S}, \hat{I}_x + \hat{S}_x] &= 0 \\ [\mathbf{I} \cdot \mathbf{S}, \hat{I}_y + \hat{S}_y] &= 0 \\ [\mathbf{I} \cdot \mathbf{S}, \hat{I}_z + \hat{S}_z] &= 0 \end{aligned} \quad (21)$$

The relations in (21) indeed show that the para-hydrogen state is unaffected by *hard pulses*, defined as pulses which equally affect both spins. If only hard pulses act on pure para-hydrogen and all kinds of selective rotations or free precessions are prevented, para-hydrogen preserves its isotropic character. Preserving this rotationally symmetric, isotropic state is one important issue in quantum computing with para-hydrogen.

The density matrix for ortho-hydrogen ρ_{ortho} (pure in the mixture sense) can be calculated in a similar manner:

$$\rho_{ortho} = \frac{\mathbf{1}}{3} + \frac{1}{3} \mathbf{I} \cdot \mathbf{S} \quad (22)$$

4.2. Para-hydrogen from a statistical mechanistic perspective

The *symmetrization postulate* of quantum mechanics [43] states that the total wavefunction of a system ψ_t must be even (symmetric) under the exchange of bosons (integer spins) and odd (anti-symmetric) under the exchange of fermions (half-integer spins). For the case of the hydrogen molecule H_2 the nuclei are protons which are fermions. So upon exchange of the nuclei, ψ_t must be an odd function. Since H_2 is a linear diatomic molecule, this exchange can be visualized as a 180° rotation: $(r, \theta, \phi) \mapsto (r, \pi - \theta, \phi + \pi)$ [44]. The overall wavefunction ψ_t can be written as a product of independent wavefunctions including contributions due to the electronic, translational, vibrational, rotational and the nuclear spin degrees of freedom:

$$\psi_t = \psi_{elec} \psi_{tr} \psi_{vib} \psi_{rot} \psi_{ns} \quad (23)$$

The parity of the individual wavefunctions must be such that the overall wavefunction becomes odd. ψ_{elec}, ψ_{tr} and ψ_{vib} are all even under exchange of the nuclei, and so the product of ψ_{rot} and ψ_{ns} must be odd. The rotational wavefunction ψ_{rot} itself is a spherical harmonic and its parity depends on the angular momentum quantum number j :

$$Y_{j,m}(\pi - \theta, \phi + \pi) = (-1)^j Y_{j,m} \quad (24)$$

so ψ_{rot} will be odd or even depending on whether j is odd or even:

$$\psi_{rot} = \begin{cases} \text{even} & j = 0, 2, 4, \dots \text{ } j \text{ is even} \\ \text{odd} & j = 1, 3, 5, \dots \text{ } j \text{ is odd} \end{cases} \quad (25)$$

Moreover the nuclear spin wavefunctions corresponding to the triplet states T_1, T_0 and T_1 given in (19) are even and the wavefunction for the singlet state S_0 is odd. Therefore, the triplets can only be combined with the $j = 1, 3, 5, \dots$ rotational states and the singlet with the $j = 0, 2, 4, \dots$ rotational states. Such a combination makes the total wavefunction odd. The H_2 molecules in the odd rotational states are conventionally called *ortho-hydrogen* and the molecules in the even rotational states are termed as *para-hydrogen*.³

The combined partition function for the rotational and the spin states becomes:

$$Z = 3 \sum_{j=1,3,5,\dots} (2j+1) e^{\frac{-j(j+1)\hbar^2}{2Ik_B T}} + \sum_{j=0,2,4,\dots} (2j+1) e^{\frac{-j(j+1)\hbar^2}{2Ik_B T}} \quad (26)$$

² A scalar is defined as an operator that is invariant under the rotation $\hat{R}(\vec{\mathbf{u}}, \delta\alpha)$ of the system, where the infinitesimal rotation operator $\hat{R}(\vec{\mathbf{u}}, \delta\alpha)$ about the axis $\vec{\mathbf{u}}$ through an infinitesimal angle $\delta\alpha$ is defined as: $\hat{R}(\vec{\mathbf{u}}, \delta\alpha) = 1 - i(\delta\alpha/\hbar)\hat{\mathbf{J}} \cdot \vec{\mathbf{u}}$. A scalar operator \hat{A} , satisfies the relationship: $[\hat{A}, \hat{J}_u] = 0 \quad \forall u$.

³ Note that the terms singlet and triplet refer to nuclear spins only and not to the molecules themselves. Para-hydrogen molecules would be in even rotational states with their nuclear spins in the $S_0 = \frac{1}{\sqrt{2}}(|\alpha\beta\rangle - |\beta\alpha\rangle)$ state.

where I is the moment of inertia of the H_2 molecule. The factor of 3 in (26) indicates that there are three times as many triplet states than there are singlet nuclear states. This effectively gives a 3-fold degeneracy to the odd rotational terms in (26). The factor $\frac{\hbar^2}{2Ik_B}$ in (26) can be replaced by θ_r , which has dimensions of temperature and is conventionally called the *rotation temperature*:

$$Z = 3 \sum_{j=1,3,5,\dots} (2j+1) e^{-\frac{j(j+1)\theta_r}{T}} + \sum_{j=0,2,4,\dots} (2j+1) e^{-\frac{j(j+1)\theta_r}{T}} \quad (27)$$

For the H_2 molecule, θ_r has a value of 82 K which is the highest amongst gases. The relative ratios of para and ortho molecules in a mixture of H_2 gas is a function of temperature and is given as:

$$\frac{N_{para}}{N_{ortho}} = \frac{\sum_{j=0,2,4,\dots} (2j+1) e^{-\frac{j(j+1)\theta_r}{T}}}{3 \sum_{j=1,3,5,\dots} (2j+1) e^{-\frac{j(j+1)\theta_r}{T}}} \quad (28a)$$

In the high-temperature limit $T \gg \theta_r$, the spacing of the rotational energy levels is very small as compared to $k_B T$ and the summations over the rotational states can be computed by standard integrals:

$$Z_{rot} = \sum_{j=0}^{\infty} (2j+1) e^{-\frac{j(j+1)\theta_r}{T}} \mapsto \int_{x=0}^{\infty} 2x e^{-\alpha x^2} dx \quad (28b)$$

where $x^2 = j(j+1)$ and $\alpha = \frac{\theta_r}{T}$. the integral in (28b) is a standard integral with the solution:

$$\int_{x=0}^{\infty} 2x e^{-\alpha x^2} dx = \frac{1}{\alpha} = \frac{T}{\theta_r} \quad (28c)$$

Moreover summations over *only* the odd or even rotational states in the high-temperature approximations yield the integrals:

$$\sum_{j=even} (2j+1) e^{-\frac{j(j+1)\theta_r}{T}} = \sum_{j=odd} (2j+1) e^{-\frac{j(j+1)\theta_r}{T}} \mapsto \frac{1}{2} \int_{x=0}^{\infty} 2x e^{-\alpha x^2} dx = \frac{1}{2} \frac{1}{\alpha} = \frac{1}{2} \frac{T}{\theta_r} \quad (28d)$$

Using these approximations in (28d) at a temperature of 300 K, simply gives a $\frac{N_{para}}{N_{ortho}}$ ratio of 1:3.

At lower temperatures $T \ll \theta_r$ or $T \sim \theta_r$, the spacing between the rotational states is no longer small compared to $k_B T$ and the explicit summations as in (28a) must be carried out. However, the series rapidly converges for small values of T and only the first few terms need to be taken:

$$\frac{N_{para}}{N_{ortho}} \mapsto \frac{1 + 5e^{-\frac{6\theta_r}{T}} + 9e^{-\frac{20\theta_r}{T}} + \dots}{3(3e^{-\frac{2\theta_r}{T}} + 7e^{-\frac{12\theta_r}{T}} + 11e^{-\frac{30\theta_r}{T}} + \dots)} \quad (28e)$$

The percentage of para-hydrogen in a mixture with ortho-hydrogen at different temperatures is shown in Figure 3 and Table (I). The low-temperature assumption has been used in calculating these values and only the first three terms in the sums in (28e) have been used. There is a 1:1 ortho-para mixture at a temperature of about 75 K. At temperatures near 20 K, we can virtually remove all the ortho molecules from the mixture and obtain a nearly pure state.

The rotational ground state with $j = 0$ is a para-hydrogen state. This state will be preferred at lower temperatures. The ortho to para conversion at such low temperatures can also be catalyzed in the presence of a paramagnetic material like Fe_2O_3 . The catalyst dissociates the H_2 molecule, which then recombines favourably in this lower energy state. If the catalyst is then removed and the para-hydrogen is left to warm, the conversion to the ortho form will be very slow as both the rotational and nuclear spin symmetries need to be broken. Practically, a cylinder of p- H_2 can be stored for weeks without any ‘‘degradation’’ into the ortho form.

TABLE I: Percentage of para-hydrogen in para-ortho mixture as a function of temperature

Temperature T (K)	% age of para-hydrogen
300	25.05
200	25.77
150	28
100	37
80	46
60	63
40	87
20	99

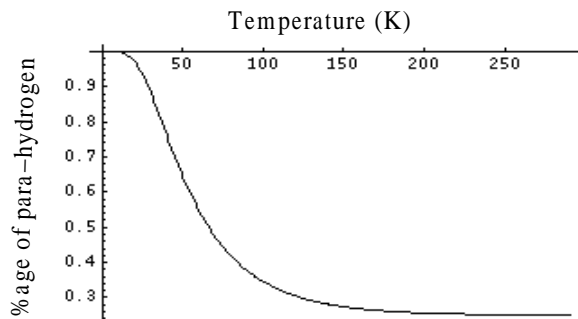


FIG. 3: The percentage of para-hydrogen as a function of temperature.

4.3. Creating an “artificial” isotropic state

At sufficiently low temperatures, most of the H_2 molecules will be in the para form and we can expect a high polarization co-efficient ϵ . However, before we actually perform any experiments with para-hydrogen we can “artificially” generate the isotropic state $\mathbf{I} \cdot \mathbf{S}$ in a two-spin homonuclear system AB⁴ starting with the thermal equilibrium state

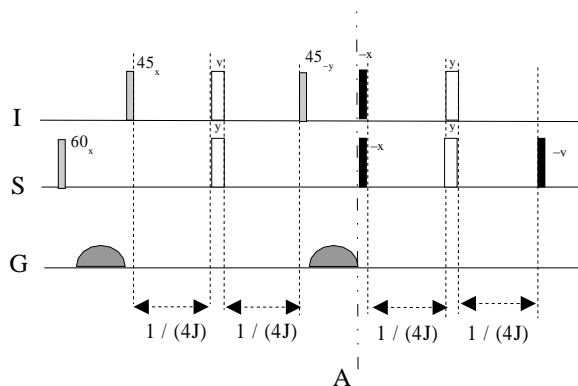


FIG. 4: Pulse sequence for generating isotropic state in an AB system. White boxes represent 180° pulses, black represent 90° pulses whereas light grey indicates pulses with other angles. The phase of each pulse is written with the corresponding box.

⁴ A two-spin system can be broadly classified as an AB or AX type depending on the relative magnitudes of the difference in chemical shifts $|\Delta|$ of the species and the scalar coupling J between them. In NMR jargon, letters further apart in the alphabet, such as A and X, are used if Δ is large in comparison to J and letters closer together in the alphabet, like A and B, are used if the two parameters are comparable in their magnitudes. The relative sizes of Δ and J also determine whether the system is weakly or strongly coupled. An

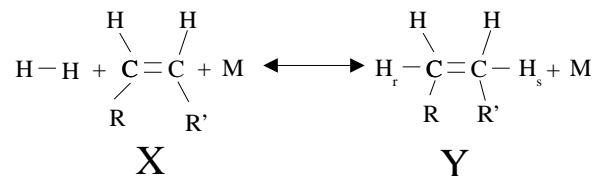


FIG. 5: Simple model of hydrogenation with para-hydrogen. \mathbf{M} is the metal catalyst, \mathbf{X} and \mathbf{Y} are the reactant and product molecules. H_r and H_s are the spins derived from the p- H_2 molecule.

$\sim I_z + S_z$. This state will have a pure component equal to $\mathbf{I} \cdot \mathbf{S}$ albeit with much lower polarizations. The simplified pulse sequence shown in Figure 4 centers around an initial preparation of the pseudopure state $\sim |11\rangle\langle 11|$ at stage A followed by a cat-preparation stage $|11\rangle\langle 11| \mapsto (|01\rangle - |10\rangle)(\langle 01| - \langle 10|)$. The pulse sequence was simplified from the original concept using the notion of abstract reference frames [26, 31] and selective excitations using the jump-rotate sequence [45, 46].

4.4. Para-hydrogen induced polarization

Bryndza in 1981 discovered strange anti-phase signals on the products of hydrogenation of tricobaltalkylidene complexes [47]. At that time, this was attributed to the CIDNP effect. However, Bowers and Weitekamp showed the possibility of signal enhancement when H_2 enriched gas was allowed to hydrogenate an unsaturated organic compound in the presence of a metal catalyst [15]. Since then, the polarization enhancement effect called the *para-hydrogen induced polarization* (PHIP) has been used as a diagnostic tool in many important organic reactions, especially the identification of reaction intermediates and possible reaction pathways in various catalyzed hydrogenation reactions [16, 48, 49].

H_2 is a symmetric molecule. It does not have an NMR signal of its own ($m = 0$). This symmetry can be broken if it is added onto a non-symmetric substrate molecule \mathbf{X} to form the product molecule \mathbf{Y} as shown in Figure 5. This figure represents but a simple choice of the reactant \mathbf{X} . I am assuming that this reaction is taking place in the presence of a strong field (inside the magnet) and that the reaction is instantaneous. As soon as \mathbf{Y} is formed, the p- H_2 spins H_r and H_s acquire different chemical shifts Ω_I and Ω_S and the placid symmetry of the molecule is broken. Such a sudden breach of symmetry falls in the so-called PASADENA (**P**arahydrogen and **S**ynthesis **A**llow **D**ramatically **E**nanced **N**uclear **A**lignment) category.

The origin of the PHIP lies in the selective population of the singlet spin state in the product molecule \mathbf{Y} . Assuming formation of \mathbf{Y} at time $t = 0$, the density matrices of the product state ρ_Y is given as the instantaneous product of the reactants [20]:

$$\rho_Y(0) = \rho_{para}(0) \rho_X(0) \quad (29a)$$

$$\stackrel{dev.}{\equiv} \frac{1}{2^{n-2}} (\hat{\mathbf{I}}_1 \otimes \hat{\mathbf{I}}_2 \otimes \hat{\mathbf{I}}_3 \otimes \hat{\mathbf{I}}_4 \otimes \dots \otimes \hat{\mathbf{I}}_n) \quad (29b)$$

where $\rho_{para}(0)$ is the isotropic state given in (20) and we assume that the $n - 2$ active spins in \mathbf{X} are in the maximally mixed state: $\rho_X(0) = \frac{1}{d_{n-2}}$ where d_{n-2} is the dimension of the $(n - 2)$ -spin Hilbert space. The energy levels populated in \mathbf{Y} are shown in Figure 6. An upper bound to the enhancement factor η can be derived from first principles [16]. Relative to the NMR signal strength of an equal number of spins at thermal equilibrium, η is given as:

$$\eta = \frac{k_B T (1 - 4a)}{6\gamma\hbar B} \quad (30)$$

where (30) T is the experimental temperature and a is the ratio of para to ortho molecules. Enhancement factors well above several thousand can be obtained, at workable temperatures.

AX system is an example of a weakly coupled system and an AB system exemplifies the latter.

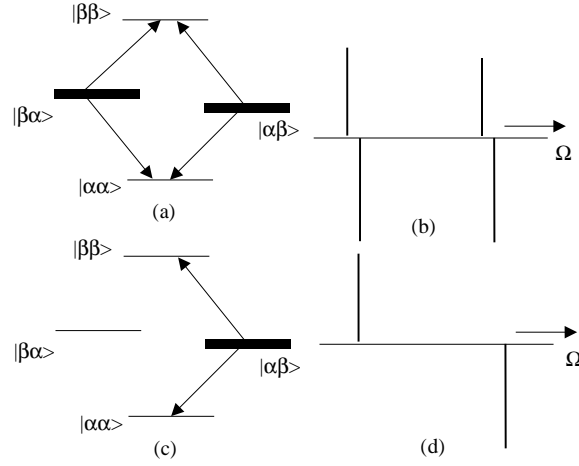


FIG. 6: Population diagrams for the PASDENA (a) and ALTADENA (c) and corresponding spectra (b) and (d) respectively. For the PASADENA case only the singlet state is preferentially populated giving rise to strong anti-phase signal.

4.5. The para-hydrogen experiment

p-H₂ offers hope to achieving a nearly pure state, with high ϵ and thus circumventing the scaling problem associated with NMR systems and also crossing the entanglement threshold. Suppose the hydrogenation reaction is allowed to proceed for a time τ_h such that:

$$\tau_h \ll \frac{1}{|\Omega_I - \Omega_S|} \quad (31)$$

then the initial state (29), the density matrix remains unchanged:

$$\rho_Y(\tau_h) = \rho_Y(0) \quad (32)$$

The condition stated in (31) implies that the precursor molecules \mathbf{X} in the volume must all be hydrogenated nearly concurrently⁵. Such a condition is not to be confused with the additional constraint that both spins adding onto one molecule of \mathbf{X} must come from the same p-H₂ molecule: a condition sometimes termed as the *pairwise addition* of spins.

To understand why (31) needs to be fulfilled, one has to look at the dynamics of the state $\rho_Y(\tau)$ for $0 \leq \tau \leq \tau_h$. Assuming that the $(n-2)$ NMR-active spins in \mathbf{X} have been decoupled and so we have a two spin system (of AX or AB type depending on $\frac{\Omega_I - \Omega_S}{J}$), the relevant rotating frame Hamiltonian is given as:

$$\hat{H} = \begin{cases} \Omega_I \hat{I}_z + \Omega_S \hat{S}_z + \pi J 2 \hat{I}_z \hat{S}_z & \text{AX type} \\ \Omega_I \hat{I}_z + \Omega_S \hat{S}_z + \pi J 2 \mathbf{I} \cdot \mathbf{S} & \text{AB type} \end{cases} \quad (33a)$$

For the AX case, \hat{H} can be expressed as a sum of two mutually commuting parts \hat{H}_1 and \hat{H}_2 [16, 50]:

$$\hat{H}_1 = \Sigma (\hat{I}_z + \hat{S}_z) + \pi J 2 \hat{I}_z \hat{S}_z \quad (33b)$$

$$\hat{H}_2 = \Delta (\hat{I}_z - \hat{S}_z) \quad (33c)$$

with $\Sigma = \frac{\Omega_I + \Omega_S}{2}$ and $\Delta = \frac{\Omega_I - \Omega_S}{2}$. The working for the AB case, which I am omitting for the sake of brevity, is seen to be similar. $\rho_Y(0)$ commutes with \hat{H}_1 . So, the state $\rho_Y(0)$ evolves only under the Hamiltonian \hat{H}_2 :

$$e^{-i\hat{H}_2\tau} e^{-i\hat{H}_1\tau} \rho_Y(0) e^{i\hat{H}_1\tau} e^{i\hat{H}_2\tau} \quad (34a)$$

$$= e^{-i\hat{H}_2\tau} \rho_Y(0) e^{i\hat{H}_2\tau} \quad (34b)$$

⁵ I find it useful differentiating between the concepts of concurrence and instantaneity.

I have already shown that $\rho_Y(0)$ is a mixture of ZQ_x and $2I_zS_z$ terms (20c). The longitudinal spin order term commutes with \hat{H}_2 whereas ZQ_x evolves as:

$$ZQ_x \xrightarrow{\Delta(\hat{I}_z - \hat{S}_z)} ZQ_x \cos 2\Delta + ZQ_y \sin 2\Delta \quad (34c)$$

Thus the $\mathbf{I} \cdot \mathbf{S}$ state in $\rho_Y(0)$ is not preserved and (32) does not hold in general. Instead $\rho_Y(0)$ approaches I_zS_z (correct to a scaling factor) and ϵ is compromised. A smaller value for Δ compared to τ_h automatically translates to the condition (31).

4.6. Isotropic mixing

Typical values of $|\Omega_I - \Omega_S|$ lie in the KHz range whereas τ_h is of the order of a few seconds. So with current set-ups (31) is definitely not satisfied. Therefore it is necessary to apply an *isotropic mixing sequence* [51, 52]. Isotropic mixing sequences are extensively used in traditional NMR for a variety of purposes including *magnetization transfer* amongst coupled or uncoupled spins, *decoupling*, *purge pulses* or suppression of free precessional effects (i.e. removal of terms in \hat{H} containing single spin terms such as I_z and S_z). It is in this latter sense, that we apply an appropriate mixing sequence during τ_h . *Multiple pulse sequences* are routinely used [53] which replace the offsets with effective offsets $\Omega_{I,eff}$ and $\Omega_{S,eff}$ with $|\Omega_{I,eff} - \Omega_{S,eff}| \rightarrow 0$ and thus satisfying (31). In the language of the *average hamiltonian theory* [24], the objective is to design an *average Hamiltonian* \hat{H}_{av} containing only the bilinear terms:

$$\hat{H}_{av} = \pi J 2 I_z S_z \quad (35)$$

The absence of chemical shift terms also means that the *Hartmann-Hahn* condition $\Omega_I = \pm\Omega_S \Rightarrow \Omega_{I,eff} = \Omega_{S,eff}$ is satisfied and so such pulse sequences are collectively termed as HOHAHA or HEHAHA (**H**omo/**H**eteronuclear **H**artmann-**H**ahn) sequences [53].

Various multiple-pulse sequences have been developed which achieve the energy-matching condition; all with their many quality indices such as *bandwidths*, *off-resonance* and *pulse length error compensation* properties, *power* and complexity. Amongst others I have investigated the MLEV-16 *supercycle* sequence which is given as: RR \bar{R} \bar{R} \bar{R} RR \bar{R} \bar{R} RR \bar{R} RR \bar{R} \bar{R} (time from left to right) with R= $90_x 180_y 90_x$ and the bar indicates a phase inversion $\bar{R} = 90_{-x} 180_{-y} 90_{-x}$. Numerical simulations in Mathematica show that the MLEV-16 sequence fares extremely well in preserving the $\rho_Y(0)$ state with *fidelity factors* approaching unity. This sequence, with a nutation frequency $\frac{\omega_1}{2\pi} \simeq 10$ KHz produces negligible effective offsets in a frequency range of ± 11.5 KHz. This range seems to be large enough to cover the offset frequencies in our sample molecules.

Conclusions and Further Work

Hübblér and co-workers have exploited the PHIP effect [54] by hydrogenating the Vaska's catalyst with H₂ enriched with the para form. They implemented the famous Deutsch algorithm with their p-H₂ based 2-qubit quantum computer. However, the value of ϵ obtained was quite low at 0.1. In the coming months, I would like to start my experimental work with p-H₂ based systems, with our colleagues at York University. I shall be working with them in devising technological modifications that could help cool the system to lower temperatures; the precise control of hydrogenation times using laser-induced photolysis. I also intend to strengthen my understanding of the complete characterization of states using *quantum state tomography* [26]. Moreover, I am currently looking at purification pulses that could suppress the undesirable terms in the p-H₂ state. Tomography would also help in quantifying error terms generating from dissipative processes, all lowering the measured value of ϵ . Superoperator techniques [24, 25, 55] in NMR would help me understand the ϵ -lowering mechanisms such as relaxation and chemical exchange. The prime objective at this stage, however, remains at crossing the entanglement threshold.

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