Initialization of NMR Quantum Registers using Long-Lived Singlet States

Soumya Singha Roy and T. S. Mahesh
NMR Research Center,
Indian Institute of Science Education and Research (IISER),
Pune 411008, India
(Dated: August 12, 2010)

An ensemble of nuclear spin-pairs under certain conditions is known to exhibit singlet state lifetimes much longer than other non-equilibrium states. This property of singlet state can be exploited in quantum information processing for efficient initialization of quantum registers. Here we describe a general method of initialization and experimentally demonstrate it with two-, three-, and four-qubit nuclear spin registers.

PACS numbers:

I. INTRODUCTION

It has been established theoretically that quantum systems are far more capable than their classical counterparts for certain computational tasks [1]. Although various types of quantum systems are being explored, the realization of a general purpose quantum processor remains a technological challenge [2]. Proof-of-principle type experimental demonstrations have been carried out for several problems including factorization, unsorted database search, and quantum simulations using Nuclear Magnetic Resonance (NMR) [3, 4]. Nuclear spins in an ensemble of molecules present a convenient architecture to simulate a quantum register. The practical demonstrations of Quantum Information Processing (QIP) using such registers are greatly benefited by the long coherence times of nuclear spins and the well developed control techniques of NMR [3, 4].

In order to carry out information processing, a quantum register must satisfy a set of criteria laid out by DiVincenzo [5]. An important criterion is the ability to precisely initialize the register to a desired ket of the computational basis. Nuclear spins in room temperature and at ordinary magnetic fields exist in a highly mixed state and therefore preparing a pure state is not straightforward [6-8]. The spin temperature can nevertheless be reduced by using parahydrogens [6] or by using Dynamic Nuclear Polarization [10]. In future, either or both of these techniques may be available for preparing NMR quantum registers into almost pure states [2]. The existing approach for initializing NMR registers is however based on specially prepared mixed states known as ‘pseudopure states’, which are isomorphic to pure states for several computational problems [11, 12].

Consider an ensemble of identical molecules each having \( n \) spin-1/2 nuclei in a magnetic field. The Zeeman Hamiltonian \( \mathcal{H}_z = h \sum_j \nu_j^0 I_j^z \) is characterized by the frequency \( \nu_0^0 \) of Larmor precession, and the \( z \)-component of the spin angular momentum operator \( I_j^z \) of spins \( j = 1 \ldots n \) [8]. In NMR-QIP, the eigenstates \( \{ \pm 1/2 \} \) of \( \mathcal{H}_z \) are labeled as \( |0 \rangle \) and \( |1 \rangle \) states of a qubit, and the multiplicity eigenbasis \( \{|00 \cdots 00\rangle, |00 \cdots 01\rangle, \cdots \} \) is treated as the computational basis. In thermal equilibrium at ordinary room temperature \( T \), the Boltzmann factor \( kT \) is much larger than the Zeeman energy gaps, so that the density matrix can be expanded as

\[
\rho_{\text{eq}} = 2^{-n} e^{-\mathcal{H}_z/kT} \approx 2^{-n} (1 + \rho_{\Delta}).
\]

Here identity \( 1 \) corresponds to a background of uniformly populated levels and the trace-less part \( \rho_{\Delta} = \sum_j \epsilon_j I_j^z \) is known as the deviation density matrix. The dimensionless numbers \( \epsilon_j = -h\nu^0_0/kT \) have magnitudes \( \approx 10^{-4} \) for protons in currently available magnetic fields at ordinary room temperatures. The deviation density matrix represents the unequal population distribution (over the uniform background) which lead to the observable magnetizations. Thus preparing a pure ground state i.e., \( |00 \cdots 0\rangle \) in an NMR quantum register is rather difficult. Nevertheless, Cory et al [11] and Chuang et al [12] have independently pointed out that often a pure state \( |\psi\rangle \langle \psi| \) can be simulated by the pseudopure state

\[
\rho_{\text{pps}} \approx 2^{-n} \left[ (1 - \epsilon') 1 + 2^n \epsilon' |\psi\rangle \langle \psi| \right].
\]

Here \( \epsilon' \) is a measure of the magnetization retained in the pseudopure state and it usually gets halved with every additional qubit [12]. The unit background is invariant under the Hamiltonian evolution, does not lead to NMR signal and is ignored [11]. Thus the equilibrium density matrix of a single spin-1/2 nucleus is always in a pseudopure state. Initializing a multi-spin system into a pseudopure state however is essentially a non unitary process [4]. Several methods have earlier been proposed and they involve averaging of magnetization modes over the sample space (called ‘spatial averaging’ [14]) or over spin space (called ‘logical labeling’ [12, 15]) or over several transients (called ‘temporal averaging’ [16]). In some cases subsystem pseudopure states are easier to prepare either by transition selective pulses [17] or by coherence selection using pulsed field gradients [18], but these methods invariably result in loss of a qubit for further computation.

In the next section we propose a different approach that exploits long life-times of certain special states called ‘singlet states’. The following section details the exper-
imental demonstrations on model systems consisting of two, three and four-qubit NMR registers.

II. SINGLET STATES AND REGISTER INITIALIZATION

A. Singlet States

The Hamiltonian for an ensemble of spin-1/2 nuclear pairs of same isotope, in the RF interaction frame, can be expressed as

\[ H_{\text{eff}} = \hbar \left[ \frac{\Delta \nu}{2} I_1^z - \frac{\Delta \nu}{2} I_2^z + J I_1^z I_2^z + \nu_{12} I_{1z}^{1,2} \right]. \] (3)

Here the RF frequency is assumed to be at the mean of the two Larmor frequencies, and \( \Delta \nu \). \( J \) and \( \nu_{12} \) correspond respectively to the difference in Larmor frequencies (chemical shift difference), the scalar coupling constant and the RF amplitude (all in Hz). In the limiting case of \( \Delta \nu \to 0 \), the system is said to have magnetic equivalence, and the singlet state \( |S_0\rangle = (|11\rangle - |10\rangle)/\sqrt{2} \) and the triplet states \( |T_1\rangle = |00\rangle, |T_0\rangle = (|11\rangle + |10\rangle)/\sqrt{2} \), and \( |T_{-1}\rangle = |11\rangle \) form an orthonormal eigenbasis of the internal Hamiltonian \( H_{\text{eq}} = hJI^1 \cdot I^2 \). [8]

The non-equilibrium nuclear spin states decay toward equilibrium state [11] with a time constant called ‘spin-lattice’ relaxation time constant \( T_1 \). [7] Since most of the NMR experiments involve preparation and detection of non-equilibrium spin states, it was generally accepted that the duration of any NMR transient is limited by \( T_1 \), although the theoretical limit of transverse relaxation is \( 2T_1 \). [8] Levitt and co-workers demonstrated that under the Hamiltonian \( H_{\text{eq}} \) the decay constant of singlet state \( |S_0\rangle \) is much larger than \( T_1 \), and hence called it a long-lived state [19, 20]. The phenomenon is akin to the decoherence-free-subspace (DFS) which is well known in QIP [21]. Detailed theoretical analyses of singlet state decay have been provided by Levitt and co-workers [22, 23] and by Karthik and Bodenhausen [24]. The long life times of singlet states have been attributed to the fact that the singlet states are immune to the dominant intramolecular dipole-dipole relaxation mechanism, which is symmetric with respect to the exchange of spin states.

Experimentally, singlet decay constants up to \( 36T_1 \) have been reported [25], and in another instance singlet lived till about half an hour [26]. Overcoming the \( T_1 \) limit has motivated a number of novel applications including studying slow molecular dynamics and transport processes [23, 27], precise measurements of NMR interactions [28], the transport and storage of hyper polarized nuclear spin order [29, 31], homogeneous line narrowing in spectroscopy [32], and determining molecular torsion angles [33]. Recently we had reported that high-fidelity singlet states can be easily prepared and characterized in two-spin systems under various experimental conditions [37]. In the following we describe the preparation and detection of singlet states and then elucidate the initialization of quantum registers.

B. Preparation and detection of singlet states

The state \(|S_0\rangle\langle S_0| - |T_0\rangle\langle T_0|\) can be easily prepared from the equilibrium density matrix \( I_1^2 + I_2^2 \) by using the propagator

\[ U_{1,2}^{1,2} = e^{-i\pi I_{1z}^{1,2}} e^{-i\pi I_{1z}^{1,2}} e^{-i\pi I_{1z}^{1,2}} e^{-i\pi I_{1z}^{1,2}}. \] (4)

With certain approximations the above propagator can be constructed from the Hamiltonians similar to the one in [39]. The equivalence Hamiltonian \( H_{\text{eff}} \) may be realized by suppressing the chemical shift \( \Delta \nu \) either by vanishing the Zeeman field [19], or by using a ‘spin-lock’ [20, 39]. In this work we employ the latter technique. The spin-lock may be achieved by applying a long low-power unmodulated RF [20], or by specially designed phase modulated sequence which were originally used for spin-decoupling [39].

The singlet states by themselves are inaccessible to macroscopic observables, but can be indirectly detected by removing the equivalence and transforming to observable single quantum coherence using the propagator [19, 20]

\[ U_{1,2}^{1,2} = e^{-i\pi I_{1z}^{1,2}} e^{-i\pi I_{1z}^{1,2}}. \] (5)

Alternatively, a more detailed and quantitative analysis of singlet states may be carried out using density matrix tomography [37].

C. Initializing NMR Registers

The circuit for initializing a 2-qubit NMR register via singlet states is shown in Fig. I. An initially imperfect singlet density matrix gets purified during the spin-lock period as a result of the long life time, while the artifact coherences are destroyed by relaxation process as well as the inhomogeneities in the spin-lock itself. There exist optimal spin-lock conditions at which one obtains singlet states with high fidelity [37]. Once the singlet state is prepared with high fidelity, the conversion \(|S_0\rangle \to |01\rangle\) can be easily achieved by the propagator

\[ U_{2}^{1,2} = e^{-i\pi I_{1z}^{1,2}} e^{-i\pi I_{1z}^{1,2}} e^{-i\pi I_{1z}^{1,2}}. \] (6)

Finally a pulsed field gradient \( G_r \) can be used to destroy the residual single and multiple quantum coherences. If necessary, other pseudopure states can be obtained simply by applying NOT gates.

This procedure of initialization can be extended to multiqubit systems, since it is known that a spin-pair
spin-lock of multiple singlet pairs can be achieved using sophisticated modulated RF sequences as described in the next section.

III. EXPERIMENTS

The following experiments are carried out in Bruker 500 MHz NMR spectrometer at an ambient temperature of 300 K. We used strongly modulated pulses for designing high fidelity local gates as well as cNOT gates [40, 41]. The spin-lock was achieved by WALTZ-16 - a phase modulated RF sequence, which is routinely used in broadband spin decoupling [37]. Spectra corresponding to pseudopure states are obtained by linear detection scheme using small flip angle RF pulses. Since the pseudopure states have one energy level more populated than the equal distribution in all others, the spectrum should consist ideally of only one transition per qubit in each case. Quantitative analyses of the pseudopure states are carried out using extended versions of density matrix tomography described in reference [37]. Finally, the success of the experimental state \( \rho \) in achieving a target pseudopure state \( \rho_{pp} \) is measured by calculating the correlation [40].

\[
\langle \rho_{pp} \rangle = \frac{\text{trace} \left[ \rho \cdot \rho_{pp} \right]}{\sqrt{\text{trace} \left[ \rho^2 \right] \cdot \text{trace} \left[ \rho_{pp}^2 \right]}}.
\]  

Often only the diagonal elements of the density matrices are relevant and in such cases, the ‘diagonal correlation’ can be expressed by replacing all the operators in the above expression by their diagonal parts. In the following we describe the individual cases of two-, three- and four-qubit registers.

A. 2-qubit register

The two-qubit system, Hamiltonian parameters, and the corresponding pseudopure and the reference spectra are shown in Fig.2(a-d). As shown in Fig 1(b), the experiment involved preparing singlet using \( U_{12}^{1,2} \), followed by RF spin-lock with amplitude 2 kHz and duration 12.4 s, which are optimized for high singlet content [37]. The decay constant for singlet state was 16.2 s approximately three times the \( T_1 \) values of the two spins. The singlet is then converted into \( |01\rangle \) pseudopure state using \( U_{2}^{1,2} \). A final gradient pulse served to destroy the artifact coherences. The bar plots showing the real and imaginary parts of the theoretical and experimental density matrix are shown in Fig.2(e-h). A very high correlation of 0.995 is obtained with \( |01\rangle \) pseudopure state.

For some quantum algorithms a good starting point may be the singlet state itself, which can be extracted...
directly after the spin-lock shown in Fig. 1h. The real part of the experimental singlet density matrix shown in Fig. 2 has a correlation of 0.991. If necessary, initialization to other Bell states, starting from the singlet state, can be carried out easily:

\[
\begin{align*}
|S_0\rangle & \xrightarrow{\alpha_{1t}} |\psi^+\rangle = (|01\rangle + |10\rangle)/\sqrt{2}, \\
|S_0\rangle & \xrightarrow{\alpha_{2t}} |\phi^+\rangle = (|00\rangle + |11\rangle)/\sqrt{2}, \\
|S_0\rangle & \xrightarrow{\alpha_{2t}} |\phi^-\rangle = (|00\rangle - |11\rangle)/\sqrt{2}. 
\end{align*}
\]

The z-rotation in the above propagators can be implemented by simply chemical shift evolution for a period \(1/(2\Delta \nu)\), and the qubit selective x-rotation can be implemented by using a strongly modulated pulse. The experimental density matrices corresponding to these Bell-states have respective correlations 0.987 (Fig. 2j), 0.982 (Fig. 2k), and 0.968 (Fig. 2l).

B. 3-qubit register

The three-qubit system, Hamiltonian parameters and the corresponding pseudopure and the reference spectra are shown in Fig. 3a-d. The decay constant for singlet state of spins 1 and 2 was about 18 s, approximately three times of their \(T_1\) values. The pseudopure state was prepared using the circuit shown in Fig. 1f. Each of the two spin-locks were achieved using 6.3 s of 500 Hz WALTZ-16 modulations. The cNOT gate was implemented using a 14 segment strongly modulated RF pulse of duration approximately 60 ms and of fidelity 0.96. The bar plots showing the real and imaginary parts of the theoretical and experimental density matrix are shown in Fig. 3c-h). The correlation of the experimental density matrix with the theoretical pseudopure state is 0.952. The correlation is smaller compared to the two-qubit case, mainly due to the errors in the cNOT gate. Nevertheless, the diagonal correlation is as high as 0.983.

C. 4-qubit register

The four-qubit system, Hamiltonian parameters and the corresponding pseudopure and the reference spectra are shown in Fig. 4. The pseudopure state was prepared using the circuit shown in Fig. 1f. The singlet decay constants were about 6 s, approximately twice the \(T_1\) values of the individual spins. We were able to carry out simultaneous spin-lock of two singlet pairs and initialize a four-qubit register. The two spin-locks were achieved by 2 kHz WALTZ-16 modulations of durations 2 s and 4.5 s each. The two cNOT gates were made of 20 segments, approximately 61 ms duration and of fidelities about 0.94. The 10 segment h-gate was about 8.2 s long and of fidelity
FIG. 3: The molecular structure (a) and Hamiltonian parameters (b) of acrylonitrile dissolved in CDCl$_3$, forming a homonuclear 3-qubit register. In (b) diagonal elements are chemical shifts (in Hz) and the off-diagonal elements are the scalar coupling constants (in Hz). The $^1$H spectra correspond to the pseudopure state (c) and the equilibrium mixed state (d). The bar plots are showing the real (e,g) and imaginary (f,h) parts of theoretical (e,f) and experimental (g,h) pseudopure $|010\rangle\langle010|$ state.

IV. CONCLUSIONS

We have demonstrated that robust initialization of NMR quantum registers are possible via long-lived singlet states. It is hard to initialize proton-based NMR registers using traditional methods. As a result many popular NMR registers were based on carbon spins or a combination of protons and carbons which permitted initialization by traditional methods. The proposed method of using long-lived singlet states enables us to initialize larger registers even though the long range interactions are weak. Molecules are of interest where in the inter pair dipolar couplings are sufficiently weak to keep the singlet states long-lived, while the covalant bond mediated scalar interactions among the nearest neighbor spins are sufficiently strong. Since para hydrogens naturally exist in singlet states, the method can be applied directly to the initialization of registers based on parahydrogens. While the register initialization is the first application of long-lived singlet states for QIP, more applications, like for example enhancing the memory of registers, may be realized in future. Similar techniques may be used for multi-qubit initialization in non-NMR systems exhibiting long-lived singlet states.
Acknowledgments

Authors gratefully acknowledge discussions with Prof. Anil Kumar and with Prof. G. S. Agarwal. The use of 500 MHz NMR spectrometer at NMR Research Center, IISER-Pune is also acknowledged.

[1] M. A. Nielsen and I. L. Chuang, Quantum Computation and Quantum Information, Cambridge University Press (2002).
[2] T. D. Ladd, F. Jelezko, R. Laflamme, Y. Nakamura, C. Monroe, and J. L. O'Brien, Nature 464, 45 (2010).
[3] C. Ramanathan, N. Boulant, Z. Chen and D. G. Cory, Quant. Info. Proc. 3, 15-44 (2004).
[4] D. Suter and T. S. Mahesh, J. Chem. Phys. 128, 052206 (2008).
[5] D. P. DiVincenzo, Fortschr. Phys. 48, 771 (2000).
[6] M. Goldman, Spin Temperature and Nuclear Magnetic Resonance in Solids, Oxford University Press (1970).
[7] A. Abragam, Principles of Nuclear Magnetism, Oxford University Press (1961).
[8] M. H. Levitt, Spin Dynamics, J. Wiley and Sons Ltd., Chichester (2002).
[9] M. S. Anwar, J. A. Jones, D. Blazina, S. B. Duckett, H. A. Carteret, Phys. Rev. A 70, 032324 (2004).
[10] G. W. Morley, J. van Tol, A. Ardavan, K. Porfyrakis, J. Zhang, and G. A. D. Briggs Phys. Rev. Lett. 98, 220501 (2007).
[11] D. G. Cory, A. F. Fahmy, and T. F. Havel, Proc. Natl. Acad. Sci. USA 94, 1634 (1997).
[12] N. Gershenfeld and I. L. Chuang, Science, 275, 350 (1997).
[13] C. Negrevergne, T. S. Mahesh, C. A. Ryan, M. Ditty, F. Cyr-Racine, W. Power, N. Boulant, T. Havel, D. G. Cory, and R. Laflamme1, Phys. Rev. Lett. 96, 170501 (2006).
[14] D. G. Cory, M. D. Price, and T. F. Havel, Phys. D 120, 82 (1998).
[15] K. Dorai, Arvind, and A. Kumar, Phys. Rev. A 61, 042306 (2000).
[16] E. Knill, I. L. Chuang, and R. Laflamme, Phys. Rev. A 57, 3348 (1998).
[17] T. S. Mahesh and A. Kumar, Phys. Rev. A 64, 012307 (2001).
[18] E. Knill, R. Laflamme, R. Martinez, and C. H. Tseng, Nature 404, 368 (2000).
[19] M. Carraovetta, O. G. Johannessen, M. H. Levitt, Phys. Rev. Lett. 92, 153003 (2004).
[20] M. Carraovetta and M. H. Levitt, J. Am. Chem. Soc. 126, 6228 (2004).
[21] D. A. Lidar and K. B. Whaley, Irreversible Quantum Dynamics”, F. Benatti and R. Floreanini (Eds.), Springer Lecture Notes in Physics vol. 622, Berlin (2003); Also available at arXiv:quant-ph/0301032.
[22] M. Carraovetta and M. H. Levitt, J. Chem. Phys. 122, 214505 (2005).
[23] G. Pileio and M. H. Levitt, J. Chem. Phys. 130 (2009) 214501.
[24] K. Gopalakrishnan and G. Bodenhausen, J. Magn. Reson. 182, 254 (2006).
[25] R. Sarkar, P. R. Vasos, and G. Bodenhausen, J. Am. Chem. Soc. 129, 328 (2007).
[26] G. Pileio, M. Carraovetta, E. Hughes, and M. H. Levitt, J. Am. Chem. Soc. 130, 12582 (2008).
[27] S. Cavadini, J. Dittmer, S. Antonijevic and G. Bodenhausen, J. Am. Chem. Soc. 127, 15744 (2005).
[28] G. Pileio, M. Carraovetta and M. H. Levitt, Phys. Rev. Lett. 103, 083002 (2009).
[29] A. K. Grant and E. Vinogradov, J. Magn. Reson. 193, 177 (2008).
[30] T. Jonischkeit, U. Bommerich, J. stadler, K. Woelk, H. G. Niessen, and J. Bargon, J. Chem. Phys. 124, 201109 (2006).
[31] E. Y. Chekmenev, J. Hovener, V. A. Norton, K. Harris, L. S. Batchelder, P. Bhattacharya, B. D. Ross, and D. P. Weitkamp, J. Am. Chem. Soc. 130, 4212 (2008).
[32] P. R. Vasos, A. Comment, R. Sarkar, P. Ahuja, S. Jannin, J. P. Anserment, J. A. Konter, P. Hautle, B. van den Brandt, and G. Bodenhausen, Proc. Nat. Aca. Sci. 106, 18469 (2009).
[33] 17 R. W. Adams, J. A. Aguilar, K. D. Atkinson, M. J. Cowley, P. I. P. Elliott, S. B. Duckett, G. G. R. Green, I. G. Khazal, J. Lopez-Serrano, and D. C. Williamson, Science 323, 1708 (2009).
[34] W. S. Warren, E. Jenista, J. Stadler, K. Woelk, H. G. Niessen, and J. Bargon, J. Chem. Phys. 124, 201109 (2006).
[35] E. Y. Chekmenev, J. Hovener, V. A. Norton, K. Harris, L. S. Batchelder, P. Bhattacharya, B. D. Ross, and D. P. Weitkamp, J. Am. Chem. Soc. 130, 4212 (2008).
[36] P. R. Vasos, A. Comment, R. Sarkar, P. Ahuja, S. Jannin, J. P. Anserment, J. A. Konter, P. Hautle, B. van den Brandt, and G. Bodenhausen, Proc. Nat. Aca. Sci. 106, 18469 (2009).
[37] 17 R. W. Adams, J. A. Aguilar, K. D. Atkinson, M. J. Cowley, P. I. P. Elliott, S. B. Duckett, G. G. R. Green, I. G. Khazal, J. Lopez-Serrano, and D. C. Williamson, Science 323, 1708 (2009).
[38] W. S. Warren, E. Jenista, J. Stadler, K. Woelk, H. G. Niessen, and J. Bargon, J. Chem. Phys. 124, 201109 (2006).
[39] E. Y. Chekmenev, J. Hovener, V. A. Norton, K. Harris, L. S. Batchelder, P. Bhattacharya, B. D. Ross, and D. P. Weitkamp, J. Am. Chem. Soc. 130, 4212 (2008).
[40] P. R. Vasos, A. Comment, R. Sarkar, P. Ahuja, S. Jannin, J. P. Anserment, J. A. Konter, P. Hautle, B. van den Brandt, and G. Bodenhausen, Proc. Nat. Aca. Sci. 106, 18469 (2009).
[41] 17 R. W. Adams, J. A. Aguilar, K. D. Atkinson, M. J. Cowley, P. I. P. Elliott, S. B. Duckett, G. G. R. Green, I. G. Khazal, J. Lopez-Serrano, and D. C. Williamson, Science 323, 1708 (2009).
[42] W. S. Warren, E. Jenista, J. Stadler, K. Woelk, H. G. Niessen, and J. Bargon, J. Chem. Phys. 124, 201109 (2006).