Notes on the physical description of the liquid NMR system

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(Dated: March 2, 2014)

I. FREE HAMILTONIAN

The full $M = 12$ qubit system comprised 12 spin-$\frac{1}{2}$ nuclei, consisting of seven carbon nuclei and five hydrogen nuclei. We label the nuclei using $i = 1, \ldots, 12$, where $i \in C = \{1, \ldots, 7\}$ denotes a carbon nucleus and $i \in H = \{8, \ldots, 12\}$ denotes a hydrogen nucleus.

A. Lab frame

The free Hamiltonian H_f of the system in the lab frame describes the interaction of the magnetic moments of the nuclei with a constant magnetic field in the z direction (the effective magnetic field for nuclei of the same species differ due to their different local environments, the differences being called chemical shifts) and a so-called J-coupling or scalar coupling between the nuclei. The free Hamiltonian is therefore given by

$$H_f = \frac{h}{4} \sum_{i<j} J^{[ij]} \mathbf{S}^{[i]} \cdot \mathbf{S}^{[j]} + \frac{h}{2} \sum_i \nu^{[i]} \sigma_z^{[i]}, \tag{1}$$

where

$$\mathbf{S}^{[i]} = \begin{pmatrix} \sigma_x^{[i]} \\ \sigma_y^{[i]} \\ \sigma_z^{[i]} \end{pmatrix}, \tag{2}$$

with $\sigma_\mu^{[i]}$ the μ-component Pauli operator acting on the i-th nucleus.

The free Hamiltonian is fully determined by the coupling frequencies $J^{[ij]}$ and the so-called Lamor frequencies $\nu^{[i]}$.

B. Partial rotating frame

Let us move into the partial rotating frame with the rotation generated by the Hamiltonian

$$H_{\text{prot}} = \frac{h\nu_C}{2} \sum_{i \in C} \sigma_z^{[i]} + \frac{h\nu_H}{2} \sum_{i \in H} \sigma_z^{[i]}, \tag{3}$$

where ν_C and ν_H are typical Lamor frequencies for carbon and hydrogen, respectively.

The free Hamiltonian H'_f in this frame is given by

$$H'_f = e^{iH_{\mathrm{prot}}t/\hbar}H_f e^{-iH_{\mathrm{prot}}t/\hbar} - H_{\mathrm{prot}}$$
$$\approx \frac{h}{4}\sum_{i<j}J^{[ij]}\sigma_z^{[i]}\sigma_z^{[j]} + \frac{h}{4}\sum_{i<j|i,j\in C}J^{[ij]}\left[\sigma_x^{[i]}\sigma_x^{[j]} + \sigma_y^{[i]}\sigma_y^{[j]}\right] + \frac{h}{4}\sum_{i<j|i,j\in H}J^{[ij]}\left[\sigma_x^{[i]}\sigma_x^{[j]} + \sigma_y^{[i]}\sigma_y^{[j]}\right] + \frac{h}{2}\sum_i\nu^{[i]\prime}\sigma_z^{[i]},$$

(4)

where the chemical shift frequencies are $\nu^{[i]\prime} = \nu^{[i]} - \nu_C$ for $i \in C$ and $\nu^{[i]\prime} = \nu^{[i]} - \nu_H$ for $i \in H$.

To arrive at this expression we have used that the transverse (x and y) couplings between different species are quickly oscillating and average to zero. This is true if the magnitudes $|\nu_C + \nu_H|$ and $|\nu_C - \nu_H|$ of the sum and difference of the rotation frequencies are much larger than the magnitudes $|J^{[ij]}|$ of the coupling frequencies.

The values of the coupling $J^{[ij]}$ and chemical shift $\nu^{[i]\prime}$ frequencies for our system are given in Fig. 1.

	C1	C2	C3	C4	C5	C6	C7	H1	H2	H3	H4	H5
C1	30020											
C2	57.58	8779										
C3	-2.00	32.70	6245									
C4	0	0.30	0	10333								
C5	-1.25	2.62	1.11	33.16	15745							
C6	5.54	-1.66	0	-3.53	33.16	34381						
C7	1.25	37.48	0.94	29.02	-21.75	34.57	11928					
H1	0	0	2.36	166.6	4.06	5.39	8.61	3310				
H2	4.41	1.86	146.6	2.37	0	0	0	0	2468			
H3	1.81	3.71	146.6	2.37	0	0	0	0.18	-12.41	2158		
H4	-13.19	133.6	-6.97	6.23	0	5.39	3.78	-0.68	1.28	6.00	2692	
H5	7.87	-8.35	3.35	8.13	2.36	8.52	148.5	8.46	-1.06	-0.36	1.30	3649
T1	8.015	3.611	1.834	3.722	12.95	8.157	3.636	3.831	2.128	2.278	2.654	3.472
T2	1.611	0.877	1.122	0.792	1.143	1.912	0.531	0.337	N/A	N/A	0.318	0.276

C-13 labeled 12-qubit system
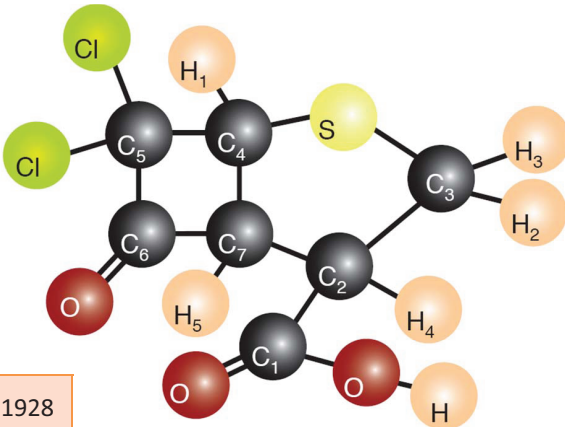
Dichloro–cyclobutanone

FIG. 1 Table giving the coupling frequencies $J^{[ij]}$, the chemical shifts $\nu^{[i]\prime}$ in Hz. The $T_1^{[i]}$ and $T_2^{[i]}$ times are given in s.

C. Full rotating frame

Let us move into the full rotating frame with the rotation generated by the Hamiltonian

$$H_{\mathrm{frot}} = \frac{h}{2}\sum_i\nu^{[i]}\sigma_z^{[i]}.$$

(5)

The free Hamiltonian H_f'' in this frame is given by

$$
\begin{aligned}
H_f'' &= \mathrm{e}^{\mathrm{i}H_{\mathrm{frot}}t/\hbar}H_f\mathrm{e}^{-\mathrm{i}H_{\mathrm{frot}}t/\hbar} - H_{\mathrm{frot}} \\
&\approx \frac{h}{4}\sum_{i<j}J^{[ij]}\sigma_z^{[i]}\sigma_z^{[j]},
\end{aligned}
\tag{6}
$$

To arrive at this expression we have used that the transverse (x and y) couplings between all spins are now quickly oscillating and average to zero. This is true if the magnitudes $|\nu^{[i]}+\nu^{[j]}|$ and $|\nu^{[i]}-\nu^{[j]}|$ of the sums and differences of the rotation frequencies are much larger than the magnitudes $|J^{[ij]}|$ of the coupling frequencies. Together these are called the weak-coupling approximations, and H_f'' is known as the weak-coupling Hamiltonian. For our system, the accuracy of the weak-coupling approximations can be verified using Fig. 1.

II. PSEUDO-PURE STATE

Using the 'cat' method, it is possible to prepare the system in the fully rotating frame in the state described by the density matrix

$$
\rho(0) \approx (1-\epsilon)\frac{\mathbb{1}_2^{\otimes M}}{2^M} + \epsilon\frac{\mathbb{1}_2}{2}\otimes(|0\rangle\langle0|)^{\otimes(M-1)},
\tag{7}
$$

where ϵ is a small positive number of the order 10^{-6}.

The first term, proportional to the identity, does not evolve under unitary evolution. It may evolve in the presence of T_1 noise. However, the effects of this evolution is the same in every experimental realisation (because the temperature and magnetic field are fixed) and this can be used to remove its effects from the analysis.

The second term corresponds to one qubit that is totally mixed but $M-1$ other qubits that are in a pure state corresponding to spin down. This term contributes to the expectation values with a weight ϵ. The fact that one qubit, which can be chosen, is totally mixed is a drawback of the 'cat' method for preparing pseudo-pure states. We choose this qubit to be the $i=7$ carbon nucleus. This is explained in more detail in the poster prepared by the experimentalists and in Nature 404 (6776), 368-370.

III. FREE HAMILTONIAN FOR THE PSEUDO-PURE STATE

The task is then to describe how the $M-1$ qubit pure state evolves. To do this, we consider the second term of Eq. (7) and expand it

$$
\rho(0) = \frac{\mathbb{1}_2}{2}\otimes(|0\rangle\langle0|)^{\otimes(M-1)}
\tag{8}
$$

$$
= \frac{1}{2}|0\rangle\langle0|\otimes(|0\rangle\langle0|)^{\otimes(M-1)} + \frac{1}{2}|1\rangle\langle1|\otimes(|0\rangle\langle0|)^{\otimes(M-1)}.
\tag{9}
$$

We see initially has the form

$$
\rho(0) = \frac{1}{2}\sum_{s=0}^{1}|s\rangle\langle s|\otimes\rho_s(0),
\tag{10}
$$

where $\rho_s(0) = (|0\rangle\langle0|)^{\otimes(M-1)}$ is the density matrix for the the $M-1$ qubit system. Provided our Hamiltonian conserves the z component of the spin of the reference qubit $\sigma_z^{[7]}$ (as is the case for the free Hamiltonian in the fully rotating frame above), it is possible to write it in the form

$$
H''(t) = \sum_{s=0}^{1}|s\rangle\langle s|\otimes H_s''(t),
\tag{11}
$$

where $H_s''(t)$ is a Hamiltonian for the $M-1$ qubit system. The Hamiltonian therefore acts on each of the subspaces (corresponding to spin up/down of the reference qubit) of the full Hilbert space separately and does not mix the two subspaces. Therefore the density matrix will stay within the ansatz

$$
\rho(t) = \frac{1}{2}\sum_{s=0}^{1}|s\rangle\langle s|\otimes\rho_s(t),
\tag{12}
$$

where the $M-1$ qubit density matrices for each subsystem evolves according to

$$i\hbar\frac{\mathrm{d}\rho_s(t)}{\mathrm{d}t} = [H_s''(t), \rho_s(t)]. \tag{13}$$

The experiment therefore realises two unitary evolutions, each according to the $M-1$ qubit Hamiltonian $H_{f,s}'' = \langle s \,|\, H''(t) \,|\, s \rangle$. The part of this corresponding to the free Hamiltonian will be

$$H_{f,s}'' = \langle s \,|\, H_f''(t) \,|\, s \rangle \tag{14}$$

$$= \frac{h}{4} \sum_{i<j|i\neq 7} J^{[ij]} \sigma_z^{[i]} \sigma_z^{[j]} + \frac{h(2s-1)}{4} \sum_{i\neq 7} J^{[i7]} \sigma_z^{[i]}, \tag{15}$$

obtained from the M qubit Hamiltonian $H''(t)$.

The results of measurements on the $M-1$ qubits will thus be an even mixture of the results from the two different unitary evolutions.

Note that the above statements do not change in the presence of T_2 noise, since this also does not mix the two subspaces. However, T_1 noise will flip the reference qubit on average every ≈ 3.6 s therefore we will have to make sure our evolution time is much smaller than this.

There are a few things to note. The Hamiltonian of Eq. (15) is invariant under the flipping of all $M-1$ spins $\sigma_z^{[i]} \mapsto -\sigma_z^{[i]}$ and the flipping of the control qubit $s \mapsto 1-s$. The same will be true for the initial state, control Hamiltonian, and T_1 and T_2 noise contributions to the Linbladian. Therefore, the populations of configuration states due to the the two different states of the reference qubit will be exactly the same up to the flipping of all $M-1$ spins. So 100% successful ground state preparation will appear as 50% of the population in the ground state of $H_{f,0}''$ and 50% of the population in the ground state of $H_{f,1}''$, the two ground states being related by a bit flip.

IV. CARBONS ONLY

By applying additional pulses, it is possible to decouple the carbon nuclei from the hydrogen nuclei such that the carbon nuclei are effectively isolated and governed by the $M=7$ qubit free Hamiltonian

$$H_f''(t) = \frac{h}{4} \sum_{i<j|i,j\in C} J^{[ij]} \sigma_z^{[i]} \sigma_z^{[j]}. \tag{16}$$

In more detail, this decoupling is achieved by performing gates on the hydrogen nuclei such that their spins oscillate rapidly. The interaction with the carbon will be averaged out to zero.

V. CONTROL HAMILTONIAN

A. Lab frame

In addition we apply a time-dependent magnetic field along the x axis proportional to $\sum_{i\neq 7} \cos(2\pi\nu^{[i]}t)/\mu^{[i]}$ such that we obtain a control Hamiltonian of the form

$$H_c(t) = -2hf(t) \sum_{ij|i\neq 7} \cos(2\pi\nu^{[i]}t)\frac{\mu^{[j]}}{\mu^{[i]}}\frac{\sigma_x^{[j]}}{2}, \tag{17}$$

where $\mu^{[i]}$ is the magnetic moment of the i-th spin. This is a sum of terms that each oscillates quickly according to angular frequency $\omega^{[i]}$, but also has a much slower time-dependence determined by the control frequency $f(t)$. Note that we do not pulse at the frequency corresponding to the reference qubit, as if it is coupled to the other qubits we do not wish to evolve it.

Note that the normalization for $f(t)$ is chosen such that it equals the frequency of the Bloch sphere rotation driven by the corresponding term in the final Hamiltonian.

B. Full rotating frame

In the full rotating frame the control Hamiltonian becomes

$$H_c''(t) = e^{iH_{\text{frot}}t/\hbar} H_c(t) e^{-iH_{\text{frot}}t/\hbar} \tag{18}$$

$$\approx -hf(t) \sum_{i \neq 7} \frac{\sigma_x^{[i]}}{2}. \tag{19}$$

Here we have made several approximations. The first assumption is that $f(t)$ is effectively constant over the time-scales over which the system evolves. In particular it should have very small Fourier coefficients corresponding to frequencies of the order $\nu^{[i]}$ or $|\nu^{[i]} - \nu^{[j]}|$. This assumption may not be strictly valid if we decrease $f(t)$ very quickly, as we will, but the errors shouldn't affect the principle of the adiabatic process and will only occur at the beginning of the process when it is most robust. The second assumption is that $|\nu^{[i]} + \nu^{[j]}| \gg f(t)$, so that we can ignore quickly rotating terms. This is the rotating wave approximation and is very accurate. The third assumption is that $|\nu^{[i]} - \nu^{[j]}| \gg f(t)$, which ensures that each oscillating term in the control Hamiltonian is on resonance with and drives only a single spin. Unfortunately for the large values of $f(t)$ we will use, this approximation will not be obeyed. The side effect will be additional slightly faster rotations around an axis in the xz-plane at the beginning of our adiabatic evolution. If this is a problem, it should be possible for us to simulate this effect.

VI. NOISE

As a first approach, we choose to model T_1 and T_2 noise as occurring independently for each qubit. Preliminary measurements by the experimentalists suggest that this noise model is a good one for our system. Weak noise of this type is described by a Lindbladian term in the master equation

$$\frac{\mathrm{d}}{\mathrm{d}t}\rho_s(t) = \frac{1}{i\hbar}[H_s''(t), \rho_s(t)] + \mathcal{L}\rho(t), \tag{20}$$

where the Lindbladian superoperator has the form

$$\mathcal{L}\rho = \sum_i \sum_{\mu=x,y,z} \gamma_\mu^{[i]} \left[\sigma_\mu^{[i]}\rho\sigma_\mu^{[i]\dagger} - \tfrac{1}{2}\left\{\sigma_\mu^{[i]\dagger}\sigma_\mu^{[i]}, \rho\right\}\right] = \sum_i \sum_{\mu=x,y,z} \gamma_\mu^{[i]} \left[\sigma_\mu^{[i]}\rho\sigma_\mu^{[i]\dagger} - \rho\right]. \tag{21}$$

We choose $\gamma_\mu^{[i]}$ such that in the presence of no coherent term ($H_s''(t) = 0$) the expectation values of the spin components decay as

$$\frac{\mathrm{d}}{\mathrm{d}t}\begin{pmatrix} \text{tr}(\sigma_x^{[i]}\rho(t)) \\ \text{tr}(\sigma_y^{[i]}\rho(t)) \\ \text{tr}(\sigma_z^{[i]}\rho(t)) \end{pmatrix} = -\begin{pmatrix} \text{tr}(\sigma_x^{[i]}\rho(t))/T_2^{[i]} \\ \text{tr}(\sigma_y^{[i]}\rho(t))/T_2^{[i]} \\ \text{tr}(\sigma_z^{[i]}\rho(t))/T_1^{[i]} \end{pmatrix}. \tag{22}$$

The values of the $T_1^{[i]}$ and $T_2^{[i]}$ times are given in Fig. 1. This is achieved by setting

$$\gamma_x^{[i]} = \frac{h}{4T_1^{[i]}}, \tag{23}$$

$$\gamma_y^{[i]} = \frac{h}{4T_1^{[i]}}, \tag{24}$$

$$\gamma_z^{[i]} = \frac{2h}{4T_2^{[i]}} - \frac{h}{4T_1^{[i]}}. \tag{25}$$

Note that we have assumed zero magnetisation in thermal equilibrium. A magnetisation could be considered if desired.