PHYS 87 Term Report: Exploring Singlet NMR

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1   Singlet NMR

1.1   Why Singlet NMR

Singlet state has a total spin of zero and is represented as follows:

$$|S_0>= \frac{1}{\sqrt{2}}(|\uparrow\downarrow> -|\downarrow\uparrow>) \tag{1}$$

- It has lifetime $T_s >> T_1$

- Can be used to study slow molecular processes or preserve hyperpolarized nuclear spin order, the latter is important in quantum computing

- Nuclei vs electron - wavefunction is localized, exchange coupling and singlet-triplet energy transition is a lot smaller and dominated by symmetry breaking interaction

- T_s of $^{15}N-$labeled nitrous oxide at RTP ≥ 25 min $\approx 8T_1$

- Inequivalent proton pairs in a partially deuterated sugar found to have $T_s \approx 37T_1$

In the remainder of this report, we define singlet order as the difference between population of singlet state and the mean of the triplet population.

1.2   Weak and strong coupling regimes

1.2.1   Weak coupling

Let $\hbar = 1$, we can write the Hamiltonian as:

$$H = \frac{1}{2}(\omega_1\sigma_z^1 + \omega_2\sigma_z^2 + \pi J\vec{\sigma_1}\cdot\vec{\sigma_2})$$
$$= \frac{1}{2}(\omega_1\sigma_z^1 + \omega_2\sigma_z^2 + \pi J(\sigma_x^1\sigma_x^2 + \sigma_y^1\sigma_y^2 + \sigma_z^1\sigma_z^2))$$

Note that $\sigma^+ = \sigma_x + i\sigma_y$ and $\sigma^- = \sigma_x - i\sigma_y$. We can rewrite $\sigma_x^1\sigma_x^2 + \sigma_y^1\sigma_y^2$ as the sum of two flip-flop terms:

$$\sigma_x^1\sigma_x^2 + \sigma_y^1\sigma_y^2 = \frac{1}{2}(\sigma_1^+\sigma_2^- + \sigma_1^-\sigma_2^+) \tag{2}$$

thus, the Hamiltonian can be written as:

$$H = \frac{1}{2}(\omega_1\sigma_z^1 + \omega_2\sigma_z^2 + \frac{\pi J}{2}(\sigma_1^+\sigma_2^- + \sigma_1^-\sigma_2^+) + \pi J\sigma_z^1\sigma_z^2) \tag{3}$$

Now we can look into the weak coupling regime:

- $|\omega_1 - \omega_2| >> J$

- Occurs in magnetically inequivalent spin pair e.g. ^{13}C and ^{1}H in chloroform

- $|\omega_1 - \omega_2|$ is large and there is insufficient energy for the spins to undergo flip-flop. In this case, the coupling depends only on the component of the magnetization along the external field and we can ignore the flip-flop term. The Hamiltonian is as follows:

$$H \approx \frac{1}{2}(\omega_1 \sigma_z^1 + \omega_2 \sigma_z^2 + \pi J \sigma_z^1 \sigma_z^2) \tag{4}$$

- The Zeeman states $|\uparrow\uparrow>, |\uparrow\downarrow>, |\downarrow\uparrow>, |\downarrow\downarrow>$ are therefore the eigenstates of the system, and the corresponding energy eigenvalues are $\frac{1}{2}(\omega_1 + \omega_2 + \pi J), \frac{1}{2}(\omega_1 - \omega_2 - \pi J), \frac{1}{2}(-\omega_1 + \omega_2 - \pi J), \frac{1}{2}(-\omega_1 - \omega_2 + \pi J)$

1.2.2 Strong coupling

Let $\hbar = 1$, since $\omega_1 \approx \omega_2$, we can write the Hamiltonian as:

$$H \approx \omega_1(\hat{S}_z^{\;1} + \hat{S}_z^{\;2}) + 2\pi J(\hat{\boldsymbol{S_1}} \cdot \hat{\boldsymbol{S_2}})$$

where $\hat{\boldsymbol{S_1}} = n_x \hat{S}_x^{\;1} + n_y \hat{S}_y^{\;1} + n_z \hat{S}_z^{\;1}$ and $\hat{\boldsymbol{S_2}} = n_x \hat{S}_x^{\;2} + n_y \hat{S}_y^{\;2} + n_z \hat{S}_z^{\;2}$ and $\hat{n} = (n_x, n_y, n_z)$ is a unit vector.

Note that $(\hat{\boldsymbol{S_1}} + \hat{\boldsymbol{S_2}})^2 = \hat{\boldsymbol{S_1}}^2 + \hat{\boldsymbol{S_2}}^2 + 2\hat{\boldsymbol{S_1}} \cdot \hat{\boldsymbol{S_2}}$, and $\hat{S}^2 = (\hat{\boldsymbol{S_1}} + \hat{\boldsymbol{S_2}})^2 = S(S+1)\hat{I}$. In addition, $\hat{\boldsymbol{S_1}}^2 = S_1(S_1+1)\hat{I}$ and $\hat{\boldsymbol{S_2}}^2 = S_2(S_2+1)\hat{I}$ and for spin-$\frac{1}{2}$ system, we have $\hat{\boldsymbol{S_1}}^2 = \hat{\boldsymbol{S_2}}^2 = \frac{1}{2}(\frac{1}{2}+1)\hat{I} = \frac{3}{4}\hat{I}$. With that, we can write:

$$\begin{aligned}
\hat{\boldsymbol{S_1}} \cdot \hat{\boldsymbol{S_2}} &= \frac{1}{2}(\hat{S}^2 - \frac{3}{2}\hat{I}) \\
&= \frac{1}{2}(S(S+1) - \frac{3}{2})\hat{I}
\end{aligned}$$

and the Hamiltonian can be written as:

$$H \approx \omega_1 \hat{S}_z + \pi J(S(S+1) - \frac{3}{2})\hat{I} \tag{5}$$

We can now look into the strong coupling regime:

- $|\omega_1 - \omega_2| << J$ or $\omega_1 \approx \omega_2$

- Occurs in magnetically equivalent spin pair e.g. proton-proton in H_2O

- $|\omega_1 - \omega_2|$ is small and there is enough energy for the spins to undergo flip-flop. In this case, the two states $|\uparrow\downarrow>$ and $|\downarrow\uparrow>$ are close enough in energy that a flip-flop exchange between the two energy levels can happen. As such, we cannot ignore the flip-flop term as we did in the weak coupling regime.

- From equation (5), we consider the cases when $S = 0$ and $S = 1$. Note that the energy eigenvalue can be calculated as $E = \omega_1 m_s + \pi J(S(S+1) - \frac{3}{2})$

- When $S = 0$, $m_s = 0$ and the energy eigenvalue $E = -\frac{3\pi J}{2}$. The eigenstate is the singlet state $|0,0> = \frac{1}{\sqrt{2}}(|\uparrow\downarrow> - |\downarrow\uparrow>)$

- When $S = 1$, $m_s = -1, 0, +1$ and the energy eigenvalues are $E_- = -\omega_1 + \frac{\pi J}{2}$, $E_0 = \frac{\pi J}{2}$ and $E_+ = \omega_1 + \frac{\pi J}{2}$. The eigenstates are the triplet states, and are given as $|1,-1> = |\downarrow\downarrow>$, $|1,0> = \frac{1}{\sqrt{2}}(|\uparrow\downarrow> + |\downarrow\uparrow>)$, $|1,+1> = |\uparrow\uparrow>$ respectively.

1.3 Symmetry switching

In an ensemble of weakly coupled spin pairs, the rate of all transitions are restricted to T_1 and it seems impossible to stabilize a non-equilibrium state of spin ensemble for a time longer than T_1. However, we can employ singlet and triplet states because nuclear singlet-triplet transitions break spin-exchange symmetry and are often slow (from even symmetry to odd symmetry). But two questions arise:

1. How can spin order be deposited in a state that is not an energy eigenstate?

2. How can singlet state be observed if total spin = 0?

The trick is to switch symmetry of spin interaction at stages during the experiment. When exchange symmetry is imposed, singlet-triplet transitions are quenched and lifetime of singlet state is extended. When the exchange symmetry is broken, transitions are allowed and the magnetization can be observed.Therefore, there are 3 stages to singlet NMR:

1. Break symmetry so coherent singlet-triplet transitions are allowed. Transform nuclear spin magnetization into nuclear singlet order

2. Symmetry is imposed and nuclear singlet order decays with $T_s >> T_1$

3. Because singlet is non-magnetic, observation of singlet-derived NMR requires symmetry to be broken so transitions can be restored, resulting in observable nuclear magnetization (NMR signal)

There are two classes of methods to perform singlet NMR:

1. Chemical reaction e.g. Hydrogen gas in the presence of a magnetic catalyst

2. Magnetic field - require that members of nuclear spin pair to be in inequivalent molecular sites, with different electronic environment

We will focus on the magnetic field methods, which can be accomplished using either hard pulses or adiabatic pulses.

2 Hard pulses

2.1 Hamiltonian in the rotating frame

Let $\hbar = 1$, we can write the Hamiltonian for chloroform as:

$$H = H_Z + H_{rf} + H_J$$
$$= (\frac{\omega_1}{2}\sigma_z^1 + \frac{\omega_2}{2}\sigma_z^2) + (\frac{\omega_3}{2}\cos(\omega_{rf}t)[\sigma_x^1 + \sigma_x^2]) + (\frac{\pi J}{2}\sigma_z^1\sigma_z^2)$$

where particle 1 denotes ^1H, particle 2 denotes ^{13}C, ω_1 denotes the Larmor frequency of ^1H, ω_2 denotes the Larmor frequency of ^{13}C, ω_3 is amplitude of the rf-field, ω_{rf} is the frequency of the rf-field and J is the J-coupling constant.

Under the rotating wave approximation, a particular spin is only affected by an rf-field rotating near its Larmor frequency. The hydrogen and carbon nuclear spins in a liquid chloroform sample immersed in a 9.4 T magnetic field have distinct Larmor frequencies, with $\omega_1 \approx 400$ MHz and $\omega_2 \approx 100$ MHz. This means that an rf-pulse with frequency ω_1 will not affect the dynamics of the carbon spins and ω_2 will not affect the dynamics of the hydrogen spins.

Next, we can enter the "doubly rotating" frame by choosing the unitary for the interaction frame:

$$U_I = e^{\frac{i\omega_{rf}t}{2}(\sigma_z^1 + \sigma_z^2)} \tag{6}$$

Let $\widetilde{\rho} = U_I \rho U_I^\dagger$, where $\rho = |\Psi><\Psi|$ is the density matrix and $\widetilde{\rho}$ is the density matrix in the rotating frame. We obtain the following:

$$\dot{\widetilde{\rho}} = \dot{U_I}\rho U_I^\dagger + U_I \dot{\rho} U_I^\dagger + U_I \rho \dot{U_I^\dagger} \tag{7}$$

The Liouville–von Neumann equation for time evolution of density matrix is given as $\dot{\rho} = \frac{-i}{\hbar}[H, \rho]$. Furthermore, $\dot{U_I} = \frac{i\omega_{rf}}{2}(\sigma_z^1 + \sigma_z^2)U_I$ and $\dot{U_I^\dagger} = U_I^\dagger[\frac{-i\omega_{rf}}{2}(\sigma_z^1 + \sigma_z^2)]$. We also make use of the identity $U_I[H, \rho]U_I^\dagger = [\widetilde{H}, \widetilde{\rho}]$. This results in the following simplification:

$$\dot{\widetilde{\rho}} = \frac{-i}{\hbar}[\widetilde{H}, \widetilde{\rho}] + \frac{i}{\hbar}[\frac{\hbar\omega_{rf}}{2}(\sigma_z^1 + \sigma_z^2), \widetilde{\rho}]$$
$$= \frac{-i}{\hbar}[\widetilde{H}_{eff}, \widetilde{\rho}]$$

where letting $\hbar = 1$, we have

$$\widetilde{H}_{eff} = \widetilde{H} - \frac{\omega_{rf}}{2}(\sigma_z^1 + \sigma_z^2) \tag{8}$$

To find $\widetilde{H} = U_I H U_I^\dagger$, observe first that H_Z and H_J are invariant under the unitary U_I. We then obtain the following:

$$\widetilde{H} = U_I H U_I^\dagger$$
$$= e^{\frac{i\omega_{rf}t}{2}(\sigma_z^1 + \sigma_z^2)} H e^{\frac{-i\omega_{rf}t}{2}(\sigma_z^1 + \sigma_z^2)}$$
$$= (\frac{\omega_1}{2}\sigma_z^1 + \frac{\omega_2}{2}\sigma_z^2) + (\frac{\omega_3}{2}\cos(\omega_{rf}t)[e^{\frac{i\omega_{rf}t}{2}\sigma_z^1}\sigma_x^1 e^{\frac{-i\omega_{rf}t}{2}\sigma_z^1} + e^{\frac{i\omega_{rf}t}{2}\sigma_z^2}\sigma_x^2 e^{\frac{-i\omega_{rf}t}{2}\sigma_z^2}]) + (\frac{\pi J}{2}\sigma_z^1\sigma_z^2)$$

Note that we can write $R_z(-\omega_{rf}t) = e^{\frac{i\omega_{rf}t}{2}\sigma_z^2}$. It can be easily shown that $R_Z(\theta)\sigma_x R_Z(\theta)^\dagger = \cos(\theta)\sigma_x + \sin(\theta)\sigma_y$. Therefore we have the following simplification:

$$\widetilde{H} = (\frac{\omega_1}{2}\sigma_z^1 + \frac{\omega_2}{2}\sigma_z^2) + (\frac{\omega_3}{2}\cos(\omega_{rf}t)[R_z(-\omega_{rf}t)\sigma_x^1 R_z(-\omega_{rf}t)^\dagger + R_z(-\omega_{rf}t)\sigma_x^2 R_z(-\omega_{rf}t)^\dagger]) + (\frac{\pi J}{2}\sigma_z^1\sigma_z^2)$$
$$= (\frac{\omega_1}{2}\sigma_z^1 + \frac{\omega_2}{2}\sigma_z^2) + (\frac{\omega_3}{2}[(\sigma_x^1 + \sigma_x^2)\cos^2(\omega_{rf}t) - (\sigma_y^1 + \sigma_y^2)\cos(\omega_{rf}t)\sin(\omega_{rf}t)]) + (\frac{\pi J}{2}\sigma_z^1\sigma_z^2)$$
$$= (\frac{\omega_1}{2}\sigma_z^1 + \frac{\omega_2}{2}\sigma_z^2) + (\frac{\omega_3}{2}[(\sigma_x^1 + \sigma_x^2)(\frac{\cos(2\omega rft)+1}{2}) - (\sigma_y^1 + \sigma_y^2)\frac{\sin(2\omega rft)}{2}]) + (\frac{\pi J}{2}\sigma_z^1\sigma_z^2)$$
$$\approx (\frac{\omega_1}{2}\sigma_z^1 + \frac{\omega_2}{2}\sigma_z^2) + (\frac{\omega_3}{4}[\sigma_x^1 + \sigma_x^2]) + (\frac{\pi J}{2}\sigma_z^1\sigma_z^2)$$

where in the last step, we made use of the rotating wave approximation and ignore the terms that oscillate at twice ω_{rf}. Combining the above result with equation (8), we now obtain

$$\widetilde{H}_{eff} = \frac{1}{2}\Delta\omega_1\sigma_z^1 + \frac{1}{2}\Delta\omega_2\sigma_z^2 + (\frac{\omega_3}{4}[\sigma_x^1 + \sigma_x^2]) + (\frac{\pi J}{2}\sigma_z^1\sigma_z^2) \tag{9}$$

where $\Delta\omega_1 = \omega_1 - \omega_{rf}$ and $\Delta\omega_2 = \omega_1 - \omega_{rf}$.

2.2 Quantum gates

Hard pulses can be used to transform an equilibrium state to a singlet state. As a proof of concept, we show how $|\downarrow\downarrow>$ can be transformed into $|S_0> = \frac{1}{\sqrt{2}}(|\uparrow\downarrow> - |\downarrow\uparrow>)$ using a Hadamard gate and a CNOT gate, both which can be implemented via unitary rotations.

Figure 1 shows how to create an entangled bell state using a Hadamard gate and a CNOT gate. The Hadamard gate and CNOT gate are represented by the matrix in equation (10) and (11).
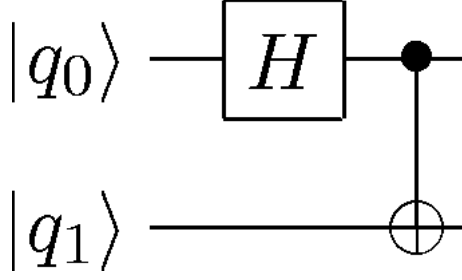
Figure 1: Creating a maximally entangled Bell state using Hadamard gate and CNOT gate

$$HADAMARD = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & 1 \\ 1 & -1 \end{bmatrix} \tag{10}$$

$$CNOT = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{bmatrix} \tag{11}$$

We define a rotational unitary $R_i(\theta)$ as below:

$$R_i(\theta) = e^{-i\theta I_i} \tag{12}$$

For a two spin system, we extend the definition to:

$$R_{i,j}(\theta) = e^{-i\theta I_i \otimes I_j} \tag{13}$$

where $i, j \in \{x, y, z, 1\}$, $I_x = \frac{1}{2}\sigma_x$, $I_y = \frac{1}{2}\sigma_y$ and $I_z = \frac{1}{2}\sigma_z$ are Pauli matrices normalized to have trace 1 and $I = I_1$ is the identity matrix. A helpful visual representation of $R_i(\theta)$ for a single qubit is a rotation about the $i-axis$ in the Bloch's sphere, where we represent $|\psi> = e^{i\gamma}(\cos(\frac{\theta}{2})| \uparrow> + e^{i\phi}\sin(\frac{\theta}{2})| \downarrow>)$. The $e^{i\gamma}$ coefficient can be ignored, since it corresponds to global phase, which can not be physically observed.

We can implement a θ rotation about the i axis using both the state representation and the density matrix representation as given below

$$|\widetilde{\Psi}> = R_i(\theta)|\Psi> \tag{14}$$

$$\widetilde{\rho} = R_i(\theta)\rho R_i(\theta)^{\dagger} \tag{15}$$

Note that the Hadamard gate (with a global phase difference) can be implemented as a sequence of unitary: $R_y(-\frac{\pi}{4})R_x(\pi)R_y(\frac{\pi}{4})$.

A CNOT gate can be implemented using a series of gates: a Hadamard gate, followed by a controlled phase shift by π, and a second Hadamard gate. A controlled phase shift can also be implemented using rotational matrices: $R_{z,z}(-\pi)R_{1,z}(\frac{\pi}{2})R_{z,1}(\frac{\pi}{2})$. Listing 1 shows the generation of a singlet state using the idea outlined above using the state representation. The next section will demonstrate the same concept using the density matrix representation, and from a thermal equilibrium state.

Listing 1: Simple simulation of creating singlet state (using the state representation) to illustrate how quantum gates work

```
1  psi = [0; 0; 0; 1]; % |00>
2
3  % Constants
4  sigx = [0 1; 1 0]/2;                          % Pauli Matricies
5  sigy = [0 -1i; 1i 0]/2;
6  sigz = [1 0; 0 -1]/2;
```

```
7  cnot = [1 0 0 0; 0 1 0 0; 0 0 0 1; 0 0 1 0];        % CNOT gate
8  Had = 1/sqrt(2) * [1 1; 1 -1];                      % Hadamard Gate
9
10 % Time evolution unitary operator
11 U =@(theta,sigma1, sigma2) expm(-1i*theta*kron(sigma1,sigma2));
12 Uevolve =@(H,t) expm(-1i*H*t);
13
14 % To create singlet state, first qubit through a hadamard gate, then through cnot gate
15
16 % Proof of concept
17 psi_1 = kron(Had,I)*psi
18 psi_2 = cnot*psi_1
19
20 % Using nmr pulses
21 % Hadamard 45 Iy -> 180 Ix -> 45I-y
22 HadNmr = U(-pi/4,sigy,I)*U(pi,sigx,I)*U(pi/4,sigy,I);
23 HadNmr = HadNmr*expm(1i*pi/2*eye(4)) %global phase
24
25 % Controlled phase shift by pi 90 Iz -> 90 Sz -> -90 2 IzSz
26 PiNmr = U(-pi,sigz,sigz)*U(pi/2,I,sigz)*U(pi/2,sigz,I);
27 PiNmr = PiNmr*expm(1i*pi/4*eye(4)) % global phase
28
29 %Cnot
30 HadNmr2 = U(-pi/4,I,sigy)*U(pi,I,sigx)*U(pi/4,I,sigy);
31 HadNmr2 = HadNmr2*expm(1i*pi/2*eye(4)) %global phase
32 CnotNmr = HadNmr2*PiNmr*HadNmr2
33
34 psi = HadNmr*psi
35 psi = CnotNmr*psi
```

2.3 Creating singlet state from thermal state

The complexities with the NMR initial state stem from the Boltzmann distribution, which give rise to a mixed state. There are only two states in the single qubit case so we can just factored out the population of the second state into an identity term and keep track of the ratio of the spin up and down states. In the two-qubit case, there are four possible states so extracting an identity still leaves us in an inconvenient mixture of three states. In order to create a singlet state (a pure state), it will be convenient if we can start from a pure $|00>$ or pseudopure state.

We will now examine the thermal equilibrium density operator, which is given below:

$$\rho_0 = \frac{e^{-\beta H}}{Z} \tag{16}$$

where $\beta = \frac{1}{K_B T}$, K_B is the Boltzmann constant and Z is the partition function defined as $Z = Tr(e^{-\beta H})$. In the high temperature limit, we can consider the first two terms of the Taylor series expansion since $|\beta H| << 1$, so

$$\begin{aligned}
\rho_0 &\approx \frac{1}{Z}[I - \beta H] \\
&\approx \frac{1}{Z}[I + \frac{1}{2K_B T}(\omega_1 \sigma_z^1 + \omega_2 \sigma_z^2 + \pi J \sigma_z^1 \sigma_z^2)] \\
&\approx \frac{1}{Z}[I + \frac{1}{2K_B T}(\omega_1 \sigma_z^1 + \omega_2 \sigma_z^2)] \\
&= \frac{I}{4} + \epsilon_1 \sigma_z^1 + \epsilon_2 \sigma_z^2
\end{aligned}$$

where we made use of the weakly coupled Hamiltonian in the second step, ignore the J-coupling term in the third step (since $J << \omega_1, \omega_2$), and condense the coefficients into the ϵ terms in the final step.

We also note that ϵ_1 which corresponds to ^1H is roughly four times ϵ_2 which corresponds to ^{13}C i.e. $\epsilon_1 \approx 4\epsilon_2$, so letting $\epsilon = \epsilon_2$, we have the below simplification

$$\rho_0 = \frac{I}{4} + 4\epsilon\sigma_z^1 + \epsilon\sigma_z^2 \tag{17}$$

We can use the procedure outlined in Figure 2 to generate the pseudopure state. Note that we can ignore the identity matrix because it does not evolve. Furthermore, in the first step, we apply $R_x(1.318)$ because $\cos(1.318) = \frac{1}{4}$, we have the following evolution:

$$4\epsilon\sigma_z^1 + \epsilon\sigma_z^2 \rightarrow 4\cos(1.318)\epsilon\sigma_z^1 - 4\sin(1.318)\epsilon\sigma_y^1 + \epsilon\sigma_z^2$$
$$\rightarrow \epsilon\sigma_z^1 - \sqrt{15}\epsilon\sigma_y^1 + \epsilon\sigma_z^2$$

The gradient pulse is a B field whose magnitude depends on spatial location, which causes each spin in the system to experience a different field. The different spins in the sample will rotate at different frequencies, which results in the x-y component of the magnetization to decay quickly. This effectively kills off the off-diagonal terms of the density matrix.
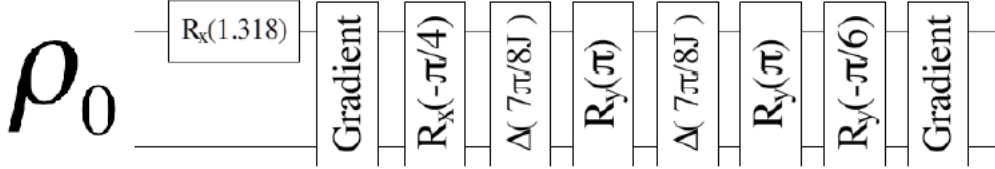

Figure 2: Creation of pseudopure state

The gradient crushes the σ_y^1 component, resulting in $\rho = \epsilon\sigma_z^1 + \epsilon\sigma_z^2$. The $\frac{\pi}{4}$ rotation about the x-axis result in $\rho = \frac{\epsilon}{\sqrt{2}}(\sigma_y^1 + \sigma_z^1 + \sigma_y^2 + \sigma_z^2)$. The next 4 blocks corresponds to $-\frac{\pi}{4}$ under the J coupling term $\sigma_z \otimes \sigma_z$. The evolution is broken down in half by π rotations to counteract the precession under the constant magnetic field in the $\hat{z}$ direction. The final gradient pulses kills the remaining off-diagonal terms, resulting in the following pseudopure state:

$$\rho = \frac{\epsilon\sqrt{3}}{16}\begin{bmatrix} 3 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix} \tag{18}$$

The Hadamard gate can be implemented as a series of unitary rotation, while the CNOT gate can be implemented as a series of unitary rotation together with time evolution under the weakly coupled Hamiltonian. The code to create the singlet state in the density matrix representation, starting from the thermal equilibrium state, is given in Listing 2.

Listing 2: Simulation of creating singlet state in the density matrix representation, starting from the thermal equilibrium state

```
1  % Hamiltonian for heteronuclear states
2  H = w1*kron(sigz,I) + w2*kron(I,sigz) + 2*pi*J*kron(sigz,sigz);
3
4  % Initial state of density matrix
5  epsilon = .5; % pseudopure ratio
6  rho_initial = 1/4*(eye(4) + 4*epsilon*kron(sigz,I) + epsilon*kron(I,sigz))
7
8  % Time evolution unitary operator
9  U =@(theta,sigma1, sigma2) expm(-1i*theta*kron(sigma1,sigma2));
10 Uevolve =@(H,t) expm(-1i*H*t);
11
```

```matlab
12  % NMR pulse sequence for generating pseudopure state, starting from thermal equilibrium state
13
14  % Creating pseudopure states
15
16  % Rx(1.318) apply to H
17  rho = U(1.318,sigx,I)*rho_initial*U(1.318,sigx,I)';
18
19  % apply gradient
20  for i = 1:length(rho)
21      for j = 1:length(rho)
22          if i ~= j
23              rho(i,j) = 0;
24          end
25      end
26  end
27
28  % Rx(-pi/4) apply to both H and C
29  rho = U(-pi/4,sigx,I)*U(-pi/4,I,sigx)*rho*U(-pi/4,I,sigx)'*U(-pi/4,sigx,I)';
30
31  % evolve with J-coupling for 7pi/(8J)
32  rho = Uevolve(H, 7*pi/(8*J))*rho*Uevolve(H, 7*pi/(8*J))';
33
34  % Ry(pi) apply to both H and C
35  rho = U(pi,sigy,I)*U(pi,I,sigy)*rho*U(pi,I,sigy)'*U(pi,sigy,I)';
36
37  % evolve with J-coupling for 7pi/(8J)
38  rho = Uevolve(H, 7*pi/(8*J))*rho*Uevolve(H, 7*pi/(8*J))';
39
40  % Ry(pi) apply to both H and C
41  rho = U(pi,sigy,I)*U(pi,I,sigy)*rho*U(pi,I,sigy)'*U(pi,sigy,I)';
42
43  % Ry(-pi/6) apply to both H and C
44  rho = U(-pi/6,sigy,I)*U(-pi/6,I,sigy)*rho*U(-pi/6,I,sigy)'*U(-pi/6,sigy,I)';
45
46  % apply gradient
47  for i = 1:length(rho)
48      for j = 1:length(rho)
49          if i ~= j
50              rho(i,j) = 0;
51          end
52      end
53  end
54
55  rho_PS = rho - 0.2117*eye(4)
56
57  % apply Hadamard gate
58  rho = U(-pi/4,sigy,I)*U(pi,sigx,I)*U(pi/4,sigy,I)*rho*U(pi/4,sigy,I)'*U(pi,sigx,I)'*U(-pi/4,
       sigy,I)';
59
60  rho_had = rho - 0.2117*eye(4)
61
62  % apply CNOT gate
63  rho = U(pi/2,I,sigy)*rho*U(pi/2,I,sigy)';
64
65  rho = Uevolve(H, 1/(4*J))*rho*Uevolve(H, 1/(4*J))';
66
67  rho = U(pi,sigx,I)*U(pi,I,sigx)*rho*U(pi,I,sigx)'*U(pi,sigx,I)';
68
69  rho = Uevolve(H, 1/(4*J))*rho*Uevolve(H, 1/(4*J))';
70
71  rho = U(pi,sigx,I)*U(pi,I,sigx)*rho*U(pi,I,sigx)'*U(pi,sigx,I)';
```

```
72
73  rho = U(pi/2,I,sigx)*rho*U(pi/2,I,sigx)'
74
75  % Final bell state created
76  rho_singlet = rho - 0.2117*eye(4)
```

3 Adiabatic pulses

3.1 Illustration with Landau-Zener TLS

We will first illustrate the theory of adiabaticity using a simple two-level system (TLS) in the context of a Landau-Zener experiment. Adiabatic quantum operations is based on the Adiabatic theorem, which states that a quantum system initially prepared in an eigenstate of a Hamiltonian will remain in an instantaneous eigenstate of that Hamiltonian as it evolves with time, provided that the evolution in time is sufficiently slow and the gap between the eigenstate and the rest of the energy spectrum is sufficiently large.

To illustrate the Adiabatic theorem, we created a simulation of the Landau-Zener experiment for a two level system. A constant magnetic field is applied in the $\hat{x}$ direction, while a time-varying linear sweep is applied in the $\hat{z}$. The Hamiltonian is simple and is given as below:

$$H(t) = -\Delta\sigma_x - \epsilon(t)\sigma_z \tag{19}$$

Δ is the magnitude of the constant magnetic field applied in the $\hat{x}$ direction, while $\epsilon(t) = \epsilon_{max}(\frac{2t}{\tau} - 1)$, where τ is the time period of the experiment and ϵ_{max} is the magnitude of the maximum field of the linear sweep. We then perform the Schrodinger's time evolution of the state, which is given as

$$|\psi(t_0 + \Delta t) >= e^{\frac{-iH\Delta t}{\hbar}}|\psi(t_0) > \tag{20}$$
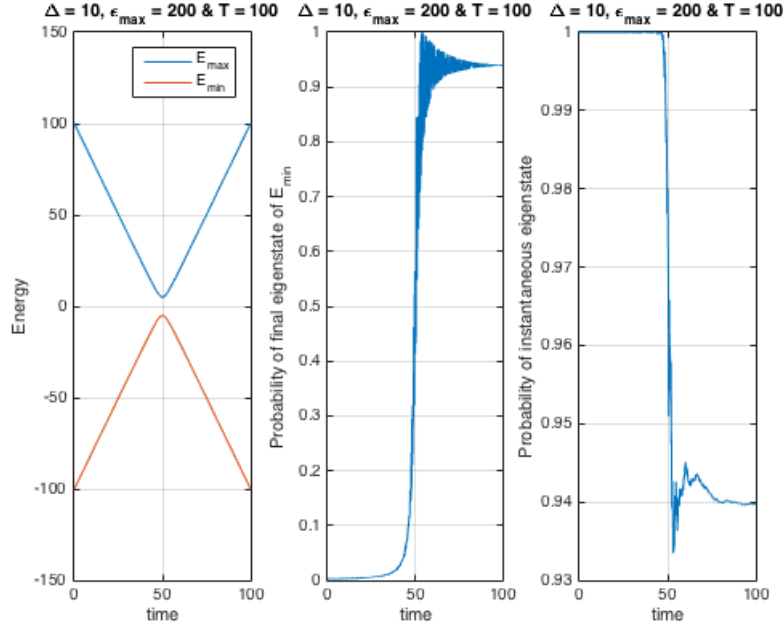
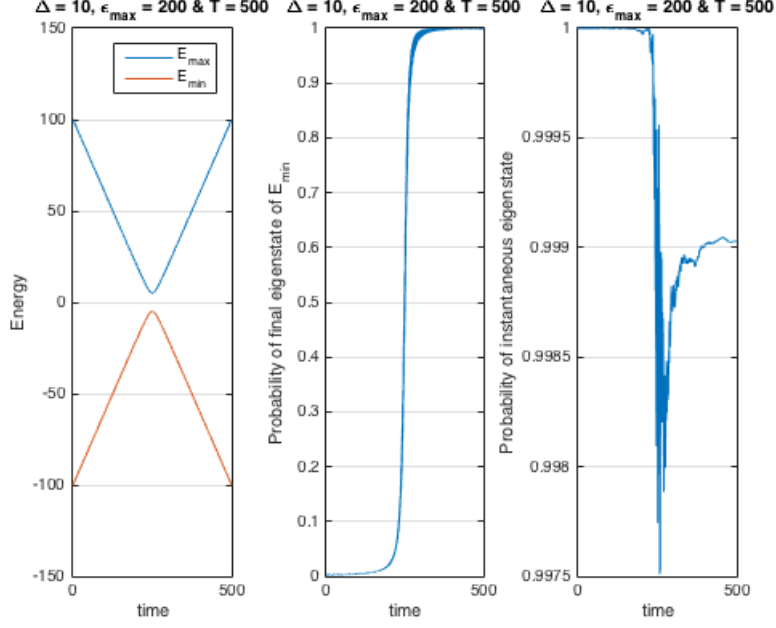

Figure 3: Adiabatic transition in Landau-Zener TLS

Figure 4: Adiabatic transition in Landau-Zener TLS

Figure 3 and 4 demonstrates the Adiabatic theorem, where Figure 3 shows a transition in a regime that is less adiabatic compared to Figure 4. Note that τ is increased by 5 times, resulting in the transition in Figure 4 to be significantly more adiabatic than the transition in Figure 3. Another way to increase the adiabaticity of the system will be to increse Δ, or to decrease ϵ_{max}.

3.2 Characterizing adiabaticity of a system

In this section, we will talk about how to characterize the adiabaticity of a system. In particular, we will discuss Berry's superadiabatic formalism.

We will first derive the general form of a Hamiltonian in an interaction frame. Suppose V implements the unitary for the interaction frame that we are interested in. Note that $\widetilde{\rho} = V^\dagger \rho V$. We make the following derivation:

$$\dot{\widetilde{\rho}} = \dot{V}^\dagger \rho V + V^\dagger \dot{\rho} V + V^\dagger \rho \dot{V}$$

$$= \dot{V}^\dagger V V^\dagger \rho V + V^\dagger(\frac{-i}{\hbar}[H, \rho])V + V^\dagger \rho V V^\dagger \dot{V}$$

$$= \dot{V}^\dagger V \widetilde{\rho} - \frac{i}{\hbar}[\widetilde{H}, \widetilde{\rho}] + \widetilde{\rho} V^\dagger \dot{V}$$

$$= (-V^\dagger \dot{V})\widetilde{\rho} - \widetilde{\rho}(-V^\dagger \dot{V}) - \frac{i}{\hbar}[\widetilde{H}, \widetilde{\rho}]$$

$$= \frac{-i}{\hbar}[\widetilde{H} - i\hbar V^\dagger \dot{V}, \widetilde{\rho}]$$

where we made use of the completeness relation and the von Neumann equation in the second step, the identity $V^\dagger[H, \rho]V = [\widetilde{H}, \widetilde{\rho}]$ in the third step, and $V^\dagger V = I \rightarrow \dot{V}^\dagger V + V^\dagger \dot{V} = 0 \rightarrow \dot{V}^\dagger V = -V^\dagger \dot{V}$ in the third step. We can thus represent $H_{eff} = D + C$, where $D = V^\dagger H V$ and $C = -i\hbar V^\dagger \dot{V}$.

We now consider a time-dependent Hamiltonian $H_0(t)$ with instantaneous eigenbasis $|\lambda_0(t) >$ at time t. We can transform the Hamiltonian into an interaction frame under the unitary operator $V_1 = \sum_\lambda |\lambda_0(t) >< \lambda_0(0)|$ which instantaneously diagonalizes the Hamiltonian, yielding the form $H_1(t) =$

$D_1(t) + C_1(t)$, where $D_1(t) = V_1^\dagger H_0(t) V$ is diagonal and $C_1(t) = -i\hbar V_1^\dagger \dot{V}_1$ is the inertial term accounting for the time dependence of the Hamiltonian. A transition is considered adiabatic if $||D_1|| >> ||C_1||$ or $Q_1 >> 1$, where the adiabatic Q factor is defined as:

$$Q_1 = \min_t \frac{||D_1(t)||}{||C_1(t)||} \tag{21}$$

We can apply the same process iteratively to yield a new interaction frame. By diagonalizing the Hamiltonian H_i, we can obtain $V_{i+1} = \sum_\lambda |\lambda_{i+1}(t) >< \lambda_{i+1}(0)|$ and find $H_{i+1} = D_{i+1} + C_{i+1}$, where $D_{i+1}(t) = V_{i+1}^\dagger H_i(t) V_{i+1}$ and $C_{i+1}(t) = -i\hbar V_{i+1}^\dagger \dot{V}_{i+1}$. The adiabatic Q factor in the interaction frame $i+1$ can then be represented as:

$$Q_{i+1} = \min_t \frac{||D_1(t)||}{||C_1(t)||} \tag{22}$$

Deschamps et al shows that a system is considered adiabatic as long as it is adiabatic in one of the interaction frames. Therefore, we can define the superadiabatic Q factor as:

$$Q_s = \max_i Q_i \tag{23}$$

and the system is adiabatic if $Q_s >> 1$.

Another way to characterize the adiabaticity of the system is the angle between the Bloch vector $|\psi_{state}(t) >$ which tracks the actual state of the system under Schrodinger's time evolution, and the instantaneous eigenstate of the Hamiltonian denoted by $|\psi_{instant}(t) >$. The cosine of the angle is given below:

$$\cos \alpha(t) = < \psi_{state}(t)|\psi_{instant}(t) > \tag{24}$$

since the states are normalized and $\sqrt{< \psi_{instant}(t)|\psi_{instant}(t) >< \psi_{state}(t)|\psi_{state}(t) >} = 1$. Therefore, the system as adiabatic as $\alpha(t)$ approaches zero or as $< \psi_{state}(t)|\psi_{instant}(t) >$ approaches 1.

Figure 5 shows an adiabatic transition in the Landau-Zener experiment with the $\cos^2 \alpha(t)$ and the Q_i terms variation with time. It can be seen that Q_i increases as we enter a new interaction frame initially, but then it decreases after due to numerical error which causes instability.
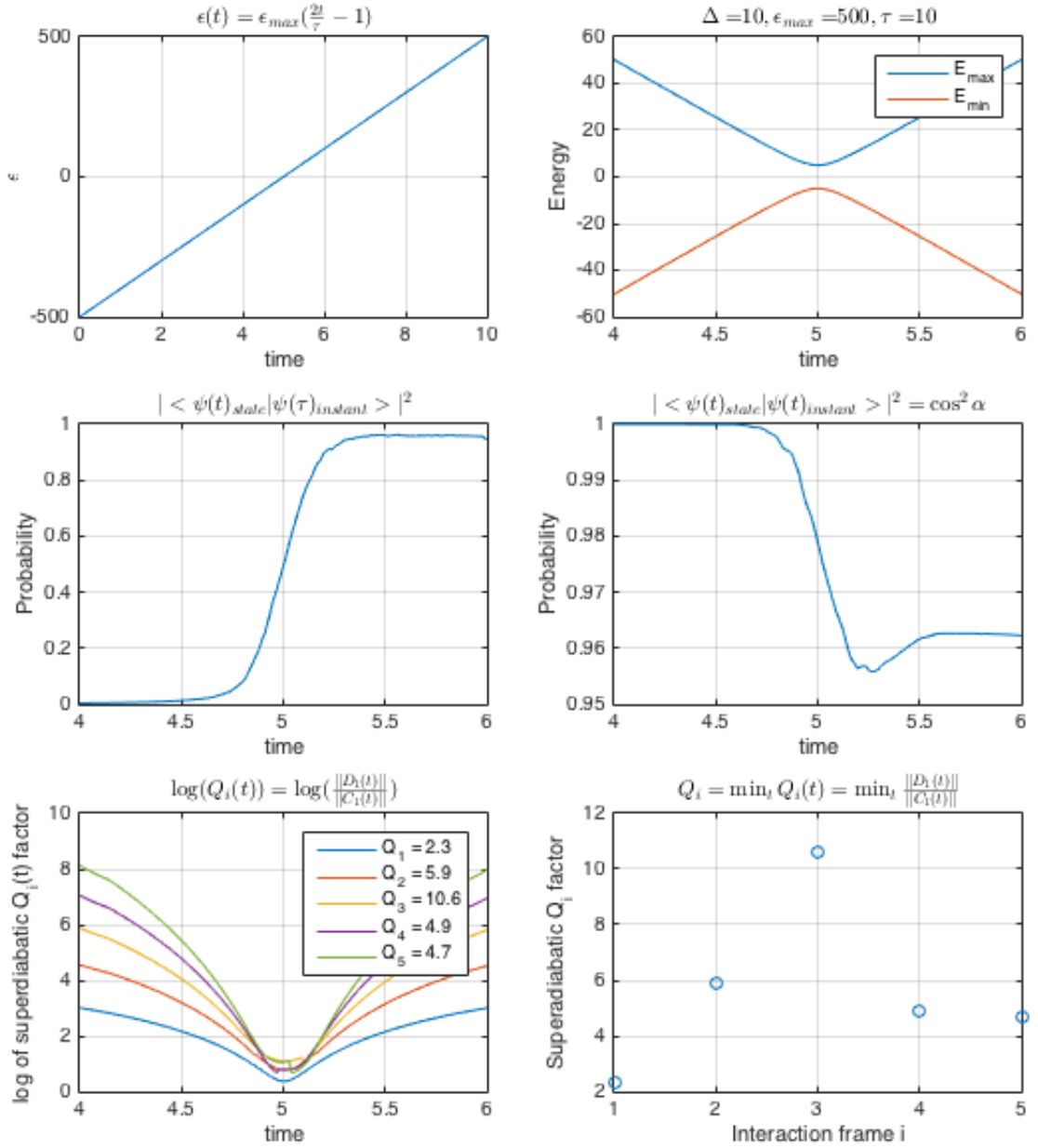
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Figure 5: Adiabatic transition in Landau-Zener TLS

The code for finding the adiabaticity of the TLS in the Landau-Zener experiment is given in Listing 3 below.

Listing 3: Landau-Zener experiment for a two level system

```
1  % Constants
2  I = eye(2);                        % 2x2 Identity
3  sigz = 0.5*[1 0; 0 -1];            % Pauli Matricies
4  sigx = 0.5*[0 1; 1 0];
5  sigy = 0.5*[0 -1i; 1i 0];
6  N = 5;                             % Number of superadiabatic frames
```

```matlab
 7
 8  % Pre-defined variables
 9  delta = 10;                          % maximum field along x direction
10  epsmax = 500;                        % maximum field along z direction
11  T = 10;                              % time period
12  tstep = 0.01;                        % time step
13
14  % Functions
15  eps = @(t) (2*t/T - 1)*epsmax;       % linear field along z direction
16  H = @(t) -delta.*sigx - eps(t).*sigz;  % Hamiltonian
17  U = @(t) expm(-1i.*H(t).*t);         % time evolution unitary operator
18
19  % Simulation
20  time = 0:tstep:T;
21  psi = zeros(2, length(time));        % state vector
22  emax = zeros(1, length(time));       % upper energy eigenvalue
23  emin = zeros(1, length(time));       % lower energy eigenvalue
24  psimin = zeros(2, length(time));     % instantaneous Hamiltonian (lower energy eigenstate)
25  psimax = zeros(2, length(time));     % instantaneous Hamiltonian (upper energy eigenstate)
26  probInst = zeros(1, length(time));   % Probability of state vector being in the instantaneous
         Hamiltonian eigenstate
27
28  for j = 1:length(time)
29      t = time(j);
30
31      % Diagonalization of Hamiltonian
32      [eigV, eigH]= eig(H(t));
33      emax(j) = max([eigH(1,1), eigH(2,2)]);
34      emin(j) = min([eigH(1,1), eigH(2,2)]);
35
36      if emin(j) == eigH(1,1)
37          psimin(:,j) = eigV(:,1);
38          psimax(:,j) = eigV(:,2);
39      else
40          psimin(:,j) = eigV(:,2);
41          psimax(:,j) = eigV(:,1);
42      end
43
44      % Schrodinger's time evolution of state
45      if j == 1
46          psi(:,1) = psimin(:,1);
47      else
48          psi(:,j) = U(t)*psi(:,j-1);
49      end
50
51      % Probability of state vector being in the instantaneous Hamiltonian eigenstate
52      probInst(j) = abs(psi(:,j)'*psimin(:,j)).^2;
53
54  end
55
56  % Probability of being in the final Hamiltonian eigenstate
57  prob = abs(psi' * psimin(:,length(psimin)))'.^2;
58
59  % Angle between instananeous Hamiltonian and state vector
60  alpha = acos(sqrt(probInst));
61
62
63  % Adiabatic Qi factor
64  Qi = zeros(N,length(time));
65  Vi = zeros(2,2,length(time));
66  Di = zeros(2,2,length(time));
```

```
67  Ci = zeros(2,2,length(time));
68  nUp = psimin;
69  nDown = psimax;
70
71  for n = 1:N
72      nUp0 = nUp(:,1);
73      nDown0 = nDown(:,1);
74      Vi(:,:,1) = nUp0*nUp0' + nDown0*nDown0';
75      for j = 2:length(time)
76          t = time(j);
77          if n == 1
78              Hi = H(t);
79          else
80              Hi = Di(:,:,j) + Ci(:,:,j);
81          end
82          Vi(:,:,j) = nUp(:,j)*nUp0' + nDown(:,j)*nDown0';
83          Di(:,:,j) = Vi(:,:,j)'*Hi*Vi(:,:,j);
84          Vidiff = (Vi(:,:,j) - Vi(:,:,j-1))/tstep;
85          Ci(:,:,j) = -1i*Vi(:,:,j)'*Vidiff;
86          Qi(n,j) = norm(Di(:,:,j),'fro')/norm(Ci(:,:,j),'fro');
87
88          % Diagonalization of Hamiltonian
89          Hi = Di(:,:,j) + Ci(:,:,j);
90          [eigV, eigH]= eig(Hi);
91          if eigH(1,1) < eigH(2,2)
92              nDown(:,j) = eigV(:,1);
93              nUp(:,j) = eigV(:,2);
94          else
95              nDown(:,j) = eigV(:,2);
96              nUp(:,j) = eigV(:,1);
97          end
98      end
99  end
```

We also attempt to create an inversion pulse, with $H = -\omega_1(t)\sigma_x - \Delta\omega(t)\sigma_z$, with $\omega_1(t)$ and $\Delta\omega(t)$ for the first half of the pulse (i.e. $t \leq \tau/2$) defined as below:

$$\omega_1(t) = \omega_1^{max}\tanh[2\epsilon t/\tau] \tag{25}$$

and

$$\Delta\omega(t) = A\frac{\tan[\kappa(1 - 2t/\tau)]}{\tan\kappa} \tag{26}$$

where ω_1^{max} corresponds to the maximum RF field strength, and ϵ, κ and A are parameters that can be optimized. For the second half of the pulse (i.e. $t > \tau/2$), $\omega_1(t) = \omega_1(\tau - t)$ and $\Delta\omega(t) = -\Delta\omega(\tau - t)$.

Figure 6 below shows the adiabatic Q factors and the angle α between the Bloch vector and the instantaneous eigen vectors as they vary with time, for the same Landau-Zener experiment performed with an inversion pulse.
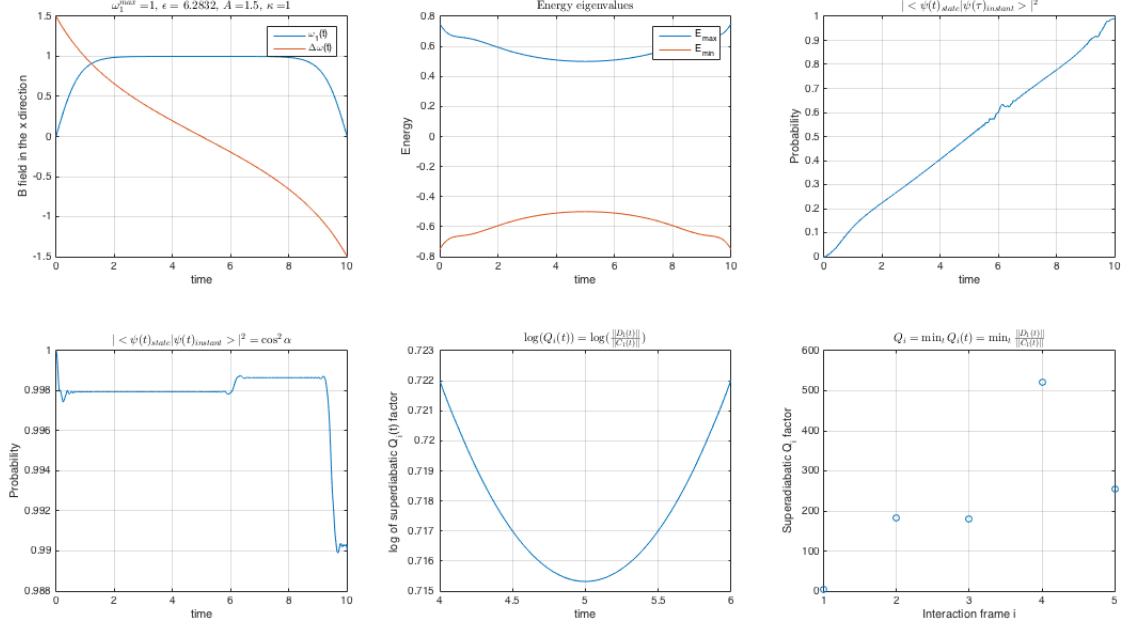
Figure 6: Inversion pulse

3.3 Adiabatic pulses for singlet state

We can adiabatically transform the high-field energy eigenstates $\{|\uparrow\uparrow>, |\uparrow\downarrow>, |\downarrow\uparrow>, |\downarrow\downarrow>\}$ into low field energy eigenstates $\{|S_0>, |T_+>, |T_0>, |T_->\}$. The precise correspondence depends on the sign of γ and J. If the signs of γ is the same as J, $|\uparrow\downarrow>$ corresponds to $|S_0>$ in the adiabatic transformation. If the signs are different, then $|\downarrow\uparrow>$ corresponds to $|S_0>$ in the adiabatic transformation.

To implement adiabatic pulses for generation of singlet state, we need to extend the single qubit model we used above to a two qubit system, and consider again the thermal equilibrium state.