Experimental verification of quantum heat exchange fluctuation relation

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We experimentally verify the Jarzynski and Wójcik quantum heat exchange fluctuation relation by implementing the interferometric technique in liquid-state Nuclear Magnetic Resonance setup and study the exchange heat statistics between two weakly coupled spin-1/2 quantum systems. In presence of uncorrelated initial state with individual spins prepared in local Gibbs thermal states at different temperatures, the exchange fluctuation symmetry is verified for arbitrary transient time. In contrast, when the initial preparation includes correlation, the fluctuation symmetry breaks down and further leads to an apparent spontaneous flow of heat from cold to hot. Our experimental approach is general and can be systematically extended to study heat statistics for more complex out-of-equilibrium many-body quantum systems.

Introduction.— Quantifying thermal and quantum fluctuations for mesoscopic and nanoscale systems are important both from fundamental and practical perspectives [1]. In the past two decades, considerable research have been devoted in developing a consistent theoretical framework to describe these fluctuations which have lead to the discovery of what is now collectively referred to as “fluctuation relations (FR)” [2–18]. For out-of-equilibrium systems, classical or quantum, various thermodynamic observables such as work and heat are found to follow these universal relations either in the transient [5–7] and/or in the steady state regimes [16, 17]. Apart from quantifying the probability of observing the rare events related to negative entropy production, fluctuation relations correctly describe systems residing at arbitrarily far-from-equilibrium and further serve as essential ingredient for establishing the rapidly growing field of quantum thermodynamics [19–21].

Despite impressive theoretical progress, experimental verification of these FR’s remained as a challenge in the quantum domain, primarily because of the requirement of projective measurements to construct the probability distribution function (PDF) for work/heat. In recent times, several experimental proposals have been put forward to construct such PDF [22–28]. Following projective measurement scheme, the first experimental success for the work fluctuation relation was achieved in an ion trap setup [29–32]. Later, this difficult projective measurement scheme was circumvented and an ancilla based Ramsey intereferometric approach was proposed [23] following which the work fluctuation relation was verified [24, 25]. Further successful attempts were also made recently to study similar fluctuation relation for open systems [32].

In this work, we attempt to verify the quantum version of Jarzynski and Wójcik heat “exchange fluctuation theorem ” (XFT) [7] which has not been achieved till date and this is the gap we want to fill in this work. We employ here a similar interferometric approach, as proposed for measuring work statistics, in a liquid Nuclear Magnetic Resonance (NMR) architecture to extract the full statistics of heat, flowing between two coherent quantum systems, by reading out the ancilla. We test the XFT for uncorrelated (product) initial state for arbitrary transient time and further extend our study to incorporate correlated initial states which allow an apparent spontaneous flow of heat from cold to hot.

Heat Statistics and exchange fluctuation relation in the Quantum Domain.— Here we give a brief summary of the heat statistics formalism and the corresponding Jarzynski and Wójcik XFT. We consider two quantum systems (system 1 and system 2) described by Hamiltonians $H_1$ and $H_2$ that are initially (at $t = 0^−$) decoupled and separately equilibrated at different temperatures $T_1$ and $T_2$ respectively. The composite system initially resides in an uncorrelated state $\rho_0 = \rho_1 \otimes \rho_2$ with $\rho_i = \exp[-\beta_i H_i]/Z_i, i = 1, 2$ being the Gibbs thermal state with inverse temperature $\beta_i = 1/k_B T_i$ ($k_B$ is the Boltzmann constant) and $Z_i = \text{Tr}[\exp[-\beta_i H_i]]$ is the corresponding partition function. At $t = 0$, a constant coupling between the two systems is suddenly switched on that allows finite heat exchange for a duration $t = \tau$ after which the interaction is suddenly turned off. This exchanged heat is a stochastic variable due to the inherent non-deterministic nature of quantum evolution and the randomness in the initial preparation. To quantify the associated PDF and to further connect with the XFT, we follow the two-time projective measurement scheme [12, 13, 33], one at the beginning and the other at the end of the heat exchange process. We first consider the joint PDF for energy change ($\Delta E_1$) for both the systems, given as

$$p_\tau(\Delta E_1, \Delta E_2) = \sum_{m,n} \left(\prod_{i=1}^{2} \delta(\Delta E_i - (\epsilon^i_m - \epsilon^i_n))\right) p^0_{m|n} p^0_{n}$$

where $p^0_{n} = \prod_{i=1}^{2} e^{-\beta_i \epsilon^i_n}/Z_i$ is the probability to find the system in the common eigenstate $|n\rangle$ with energy eigenvalue $\epsilon^i_n$ after the first projective measurement. The second projective measurement at $t = \tau$ collapses the system into another common eigenstate $|m\rangle$ with probabili-
the Fourier transformation of the heat PDF $p$ is positive. In this work, our primary quantity of interest is $p_{\text{in}}^{m}$ of heat flowing into the system 1 and is considered to be positive. Here $Q$ denotes the unitary propagator evolving with the composite Hamiltonian $\mathcal{H}$. Now using the principle of micro reversibility of quantum dynamics for autonomous system, $p_{\text{in}}^{m} = p_{\text{in}}^{T}$ and with the given uncorrelated Gibbs initial condition one receives

$$
p_{\tau}(\Delta E_{1}, \Delta E_{2}) = e^{\beta_{1} \Delta E_{1} + \beta_{2} \Delta E_{2}} p_{\tau}(-\Delta E_{1}, -\Delta E_{2}). \quad (2)
$$

In the limit, when the two systems are weakly coupled, $\Delta E_{1}$ and $\Delta E_{2}$ can be interpreted as heat and by defining $\Delta E_{1} \approx -\Delta E_{2} = Q$, one receives the Jarzynski and Wójcik XFT, given as [12, 34]

$$
p_{\tau}(Q) = \exp \left[ (\beta_{1} - \beta_{2})Q \right] p_{\tau}(-Q). \quad (3)
$$

Note that, as per our convention, $Q$ is the net amount of heat flowing into the system 1 and is considered to be positive. In this work, our primary quantity of interest is the corresponding characteristic function (CF), given by the Fourier transformation of the heat PDF $p_{\tau}(Q)$ [34],

$$
\chi_{\tau}(u) = \int dQ e^{-iuQ} p_{\tau}(Q),
$$

$$
= \text{Tr} \left[ U(\tau, 0)(e^{-iH_{1}} \otimes 1_{2})U(\tau, 0)(e^{iH_{1}} \otimes 1_{2})\rho_{0} \right]. \quad (4)
$$

Here $u$ is the parameter conjugate to $Q$. In terms of the CF the XFT in Eq. 3 translates to $\chi_{\tau}(u) = \chi_{\tau}( -u - i(\beta_{1} - \beta_{2}))$ [35–38]. In what follows, we implement experimentally the ancilla-assisted interferometric scheme in liquid NMR architecture to measure the above CF and extract the corresponding heat PDF [26–28] to analyze the heat exchange process and to verify XFT. Note that, a crucial advantage in the ancilla based technique is to be able to investigate CF for arbitrary initial preparation that includes quantum correlations and quantum coherences of the composite system (see supplementary material). The CF obtained following projective measurement scheme fails to capture signatures that arise from such correlated initial states.

**Experimental Setup and Interferometric Technique.**—
In our experiments, we use liquid-state NMR spectroscopy of three $^{19}$F nuclei (F$_{1}$, F$_{2}$ and F$_{3}$) in 1,1,2-Trifluoro-2-iodoethane (TFIE) (Fig-1), dissolved in Acetone. All our experiments are performed in 500 MHz BRUKER NMR spectrometer at an ambient temperature. We identify F$_{1}$ as qubit 1, F$_{2}$ as qubit 2 and F$_{3}$ as the ancillary qubit. The molecules in the sample are all identical and sufficiently isolated [39–41] and all the dynamics and heat exchange processes are completed in time scales such that environmental effects can be neglected. In our NMR setup, the longitudinal and transverse relaxation time constants are greater than 6.30 s and 0.80 s, respectively. The internal Hamiltonian ($H_{\text{int}}$) of the three spin system in the rotating frame of the Radio frequency (RF) pulses can be written as (see supplementary material)

$$
H_{\text{int}} = \sum_{i=1}^{3} \frac{\omega_{i}}{2} \sigma_{i}^{z} + \sum_{i<j=1}^{3} \frac{J_{ij}}{4} \sigma_{i}^{z} \sigma_{j}^{z}, \quad (5)
$$

where $\omega_{i}$ is the off-set frequency of $i$-th nuclei and $J_{ij}$ being the scalar coupling between $i$-th and $j$-th nuclei as explained in Fig-1. F$_{1}$ and F$_{2}$ exchange heat by interacting under a constant coupling Hamiltonian. The composite Hamiltonian for F$_{1}$ and F$_{2}$ is

$$
\mathcal{H} = H_{1} + H_{2} + 2\pi J (\sigma_{1}^{z} \otimes \sigma_{2}^{y} - \sigma_{1}^{y} \otimes \sigma_{2}^{z}), \quad (6)
$$

where $H_{1} = -\frac{\omega_{0}}{2} \sigma_{1}^{z} \otimes 1_{2}$, and $H_{2} = 1_{1} \otimes \frac{\omega_{0}}{2} \sigma_{2}^{z}$. $\sigma^{i}(i = x, y, z)$ is the $i$-th component of Pauli spin-$1/2$ operator. In our experiments, for both F$_{1}$ and F$_{2}$ we set $\omega_{0} = 2\pi$ kHz and $J = 1$ Hz as the engineered coupling.
strength between them which is much smaller than \( \omega_0 \), ensuring the weak-coupling limit between the qubits. We are interested in extracting the statistics of heat flowing between the qubits \( F_1 \) and \( F_2 \) by measuring CF \( \chi_T(u) \) in Eq. 4. For the first set of experiments with uncorrelated (product) initial states, we prepare the ancillary qubit (\( F_3 \)) in a Pseudo-Pure State (PPS) \( |0\rangle |0\rangle \) by using a spatial averaging technique [42] and the other two \( ^{19}\text{F} \) nuclei (\( F_1 \) and \( F_2 \)) are prepared in pseudo-equilibrium state \( \rho_1 \otimes \rho_2 \), where \( \rho_i = \exp\left[-\beta_i H_i/|Z_i| \right] \) is the Gibbs thermal state with spin temperatures \( T_i = 1/\beta_i \). In all our experiments \( F_2 \) is always initialized at infinite spin temperature, \( T_2 = \infty \). This is achieved by applying a \( \pi/2 \) pulse on \( F_2 \), which equalizes the qubit populations, followed by a Pulsed Field Gradient (PFG), that destroys coherence and produces a maximally mixed state. \( F_1 \), on the other hand, is initialized to various finite spin temperatures by applying pulses from 0 to \( \pi/2 \) followed by a PFG.

Following this initialization, we incorporate an interferometric protocol [24, 25], shown in Fig. 2, that maps the \( \chi_T(u) \) onto the ancillary qubit \( F_3 \). The gates used for this protocol are prepared by utilizing the internal Hamiltonian \( H_{int} \) (Eq. 5) and the RF pulses. The corresponding experimental pulse sequences are given in the supplementary material. At the end of this protocol, the desired CF \( \chi_T(u) \) can be received by reading out \( \left\{ \sigma_y^+ + i\sigma_y \right\} \) component of the ancilla (see supplementary material), the inverse Fourier transform of which then hands over the PDF \( p_u(Q) \). We measure \( \chi_T(u) \) by allowing maximum heat exchange between \( F_1 \) and \( F_2 \) which corresponds to a time duration \( \tau = 0.5 \) s for the given coupling strength.

**Experimental results and discussions.—** We first display in Fig. 3(a-b) the experimental and theoretical results for the real and imaginary components of the CF \( \chi_T(u) \), for a particular spin temperature \( T_1 = 63.9 \) nK. As mentioned earlier, the spin temperature of \( F_2 \) is always set to infinity [43]. We take a set of measurements in one complete period of \( u \in [0, \pi/2 \omega] \) (red dots in Fig. 3(a-b)) and further take advantage of the periodicity \( \chi_T(u) = \chi_T(u + 3\pi/2 \omega) \) to cascade (orange dots in Fig. 3(a-b)) the obtained data for subsequent periods. We phenomenologically add a small constant damping factor to \( \chi_T(u) \) with decay constant 10 Hz in both theoretical and experimental data. The inverse Fourier transform of the obtained CF produces the desired PDF \( p_u(Q) \) which shows three distinct peaks at \( Q = \pm 1 \) kHz and \( Q = 0 \) Hz. The corresponding peak amplitudes reflect the probability of heat flowing from one qubit to another. The location of the peaks can be understood from the energy eigenvalues of the composite Hamiltonian \( H \) (Eq. 6). The \( \pm 1 \) kHz peak corresponds to the transition between the zero energy states and the highest-lowest energy states. The corresponding probabilities can be analytically found and are proportional to \( 1/2 \sin^2(2J\tau) \times 1/(\exp(\tau \beta \omega_0) + 1) \). The peak at \( Q = 0 \) represents no heat exchange process between the qubits and in this particular scenario, it’s peak amplitude is independent of the spin temperatures and is proportional to \( 1/2 (1 + \cos^2(2J\tau)) \). Note that, as per our convention, positive value of \( Q \) corresponds to heat flowing from \( F_2 \) to \( F_1 \) and vice versa. Fig. 3(c) therefore confirms that on an average heat flows from hot qubit \( F_2 \) to cold qubit \( F_1 \) and thereby validates the second law of thermodynamics at the level of ensemble average. In contrast, at the microscopic realm, a finite probability corresponding to heat flowing from cold to hold exists which contributes to negative entropy production. With reduction in temperature \( T_1 \) the peak value at \( Q = -1 \) kHz reduces and disappears completely for \( T_1 = 0 \) (Fig. 3(d)).

In contrast, as the temperature of \( F_1 \) increases (Fig. 4(a-c)) the probability of back-flow of heat from \( F_1 \) to \( F_2 \) increases, and the peak value at \( Q = -1 \) kHz increases which becomes exactly equal to the peak value at \( Q = 1 \) kHz at \( T_1 = \infty \). We next plot the ratio \( \ln \left[ p_{+}(Q)/p_{-}(Q) \right] \) against \( Q \) for four sets of temperature to confirm the Jarzynski and Wojcik XFT. Note that, as the coupling Hamiltonian in Eq. 6 is a constant one, \( p_{-}(Q) \) is obtained simply by flipping the forward PDF \( p_{+}(Q) \). Fig. 4(d) shows very good agreement between the theoretical and the experimentally obtained results with the expected slope equal to \( \Delta \beta = \beta_1 - \beta_2, \beta_1 = 1/k_BT_1 \). In Fig. 4(e) we tabulate the values of these slopes.

**Effect of initially correlated states.—** We next direct our attention towards correlated initial state. As mentioned earlier, the ancilla based techniques offers to capture the effect of arbitrary initial correlation present in the composite system. Note that, in presence of such
initial correlations the inverse FT of \( \chi_\tau(u) \) may not correspond to the actual PDF of heat \([44, 45]\) (see supplementary material). However, it produces the correction definition for the first cumulant, the average heat \( \langle Q \rangle = \text{Tr} \left[ H_1 (\rho_1(t) - \rho_1(0)) \right] \), where \( \rho_1(\tau) \) being the reduced density matrix of \( F_1 \) at time \( \tau \). In our experiment, we choose a particular uncorrelated state and introduce a finite amount of correlation, affecting only the off-diagonal elements of the composite density matrix elements, in the initial preparation, as shown in Fig. 5(a-b), and measure \( \chi_\tau(u) \) to extract the corresponding \( p_\tau(Q) \). Fig. 5(c)-(d) compare the distributions obtained for the correlated case with the corresponding uncorrelated one. As seen, the presence of finite correlation leads to a crucial change in the statistics and provide evidence of reversal of heat flow. This further imply the breakdown of the standard Jarzynski-Wójcik XFT. Similar effect has recently been observed for a two qubit system by measuring the qubit states following quantum state tomography \([46]\).

**Summary.**— We experimentally verify the quantum version of the transient heat XFT by implementing an interferometric approach in a three qubit liquid NMR architecture. The experimental results show perfect agreement with the fluctuation symmetry when the composite system is prepared in the uncorrelated Gibbs thermal states with different temperatures. Inclusion of finite amount of correlation in the initial state leads to a breakdown of the fluctuation symmetry and further reverses the direction of the heat flow against the temperature bias, thereby providing additional knob for controlling heat flow. Future work will direct towards implementing a quantum state tomography technique to monitor the qubit states to further analyze and test the recently established relation between the heat exchange and Rényi divergences \([47]\).

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| Temperature \( T_i \) (nK) | Theory \( \Delta \beta_i \times 10^{-1} \) | Experiment \( \Delta \beta_i \times 10^{-1} \) | % Error |
|-------------------------------|-----------------------------|-----------------------------|---------|
| 22.53                         | 20.21                       | 21.57                       | 6.72    |
| 29.84                         | 15.25                       | 15.57                       | 2.03    |
| 63.9                          | 7.12                        | 7.01                        | 1.68    |

FIG. 4. (Color online) (a)-(c): PDF of heat exchange for different spin temperatures of \( F_1 \) (a) \( T_1 = 22.53 \text{ nK} \), (b) \( T_1 = 29.84 \text{ nK} \), (c) \( T_1 = \infty \). Solid (blue) lines and the dots correspond to theoretical and experimental results, respectively. (d): Verification of Jarzynski and Wójcik heat XFT plots for \( \ln [p_\tau(Q)/p_\tau(-Q)] \) as a function of \( Q \) for four different temperatures of \( F_1 \). (e): Table containing theoretical and experimentally obtained values for the slope \( \Delta \beta = \beta_1 - \beta_2, \beta_i = 1/k_B T_i \) from (d). All other parameters are the same as in Fig. (3)

FIG. 5. (Color online) Absolute values for the density matrix elements for the composite system \( F_1 \) and \( F_2 \) for (a) uncorrelated and (b) correlated initial state. (c)-(d): Comparison between the corresponding heat exchange PDF’s. Solid (blue) lines and dots represent theoretical and experimental results, respectively. Here the spin temperatures for \( F_1 \) and \( F_2 \) are \( T_1 = -161.1 \text{ nK} \) and \( T_2 = 197.8 \text{ nK} \), respectively

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In the final step, the controlled gate $V$. The modified density matrix is given as, 

$$\rho = \text{Tr}_{1,2}[\rho_{F}] = \frac{1}{2} \left[ \text{Tr}[U \rho_{in} U^\dagger], \frac{1}{Z} \right].$$

The off-diagonal components of this density matrix are simply related to the expectation values of the $\sigma_x$ and $\sigma_y$ components for the ancilla. We can therefore write,

$$\langle \sigma_x \rangle + i \langle \sigma_y \rangle = \text{Tr}[U \rho_{in} U^\dagger],$$

$$\text{Tr}[\rho_{in}],$$

$$\text{Tr}[(e^{i u H_1} \otimes 1_2) U^\dagger (e^{-i u H_1} \otimes 1_2) U \rho_{in}],$$

$$\text{Tr}[U (e^{-i u H_1} \otimes 1_2) U \rho_{in} (e^{i u H_1} \otimes 1_2)].$$

SUPPLEMENTARY MATERIAL:

Interferometric Technique to obtain the characteristic function for heat

In this section, we summarize the interferometric technique [1–3] to obtain the CF for heat as given in Eq. (4) of the main text. We follow the circuit in Fig. (6). We begin with the initial state of the three qubit system $|0\rangle_1|0\rangle_2|\rho_{in}\rangle$ where $\rho_{in}$ is an arbitrary initial state for the two qubits ($F_1, F_2$) that exchange heat and $|0\rangle_1|0\rangle_2$ is the state for the ancillary qubit. Therefore, the global density operator in the ancillary basis is given as,

$$\rho_A = \begin{bmatrix} \rho_{in} & 0 \\ 0 & 0 \end{bmatrix}.$$

In the next step we apply the Hadamard gate, $H$, on the ancillary qubit. As a result, the density matrix modifies to

$$\rho_B = H \rho_{in} H^\dagger = \frac{1}{2} \begin{bmatrix} \rho_{in} & \rho_{in} \\ \rho_{in}^\dagger & \rho_{in}^\dagger \end{bmatrix}.$$

This operation is followed by application of a controlled gate $V = \exp[-i u H_1] \otimes 1_2$ on the qubit $F_1$. The corresponding change in the density matrix is given as,

$$\rho_C = \frac{1}{2} \begin{bmatrix} \rho_{in} & \rho_{in} V^\dagger \\ V \rho_{in} & V^\dagger \rho_{in} V^\dagger \end{bmatrix}.$$

The next step includes the unitary propagator $U$ corresponding to the composite Hamiltonian $H$, Eq. (6) of the main text, along with a $\sigma_z$ rotation on the ancillary qubit. The modified density matrix is given as

$$\rho_D = \frac{1}{2} \begin{bmatrix} U \rho_{in} U^\dagger & U \rho_{in} U^\dagger \\ U^\dagger \rho_{in} U^\dagger & U^\dagger \rho_{in} U^\dagger \end{bmatrix}.$$

In the final step, the controlled gate $V_1$ is applied once again on the qubit $F_1$. The final global density matrix is given by,

$$\rho_E = \frac{1}{2} \begin{bmatrix} U \rho_{in} U^\dagger & U \rho_{in} U^\dagger V^\dagger \\ U^\dagger \rho_{in} U^\dagger & U^\dagger \rho_{in} U^\dagger V^\dagger \end{bmatrix}.$$

Now, tracing out the qubits $F_1$ and $F_2$, we receive the reduced density matrix for the ancilla $F_3$ as,

$$\rho = \text{Tr}_{1,2}[\rho_{F}] = \frac{1}{2} \left[ \text{Tr}[U \rho_{in} U^\dagger], \frac{1}{Z} \right].$$

Note that, the above final expression Eq. (7) is not yet the CF of heat as obtained in Eq. (4) following the two-time measurement protocol. It is only when the initial state $\rho_{in}$ for $F_1$ and $F_2$ is given by an uncorrelated (product) Gibbs state, i.e., $\rho_{in} = \rho_0 \otimes \rho_0$ where $\rho_0 = \exp[-\beta_1 H_1]/Z_1 \otimes \exp[-\beta_2 H_2]/Z_2$, which imply $|\rho_0, H_1 \otimes 1_2 = 0\rangle$, the above expression reduces to

$$\langle \sigma_x \rangle + i \langle \sigma_y \rangle = \text{Tr}[U (e^{-i u H_1} \otimes 1_2) U \rho_0],$$

which is exactly the CF $\chi_T(u)$ in Eq. (4).

It is important to note that, for arbitrary initial condition the PDF of Eq. (7) may not correspond to the correct PDF of heat as it is not always positive definite. However it’s first moment produces the correct definition for the average heat $\langle Q \rangle = \text{Tr}_1 \left[ H_1 (\rho_{in} (t) - \rho_{in}) \right]$.

Pulse sequence for Interferometric Circuit

![FIG. 6. (Color online) Circuit diagram for the interferometric technique to measure the CF of heat $\chi_T(u)$. $\rho_i, (i = A, B, C, D, E)$ represents the intermediate states of the global system ($F_1, F_2, F_3$) after gate operations.](image-url)
qubit pulse obtained by using GRAPE optimization technique. The three qubit liquid NMR system is found in the thermal equilibrium state at the room temperature, the deviation density matrix of which can be written as $(\sigma_i^z + \sigma_j^z + \sigma_k^z)/2$. To get the initial state of $|000\rangle \otimes \rho_1 \otimes \rho_2$, where $\rho_i = \exp \left[-\beta_i H_i\right]/Z_i$ with $Z_i$ being the respective partition function, we follow a similar pulse sequence as given in [4]. After initialization, Hadamard gate is implemented using GRAPE with a duration of 600 $\mu$s and fidelity of 99.9%. The control operation $V$ can be split into $z$ and $x$ rotations and a free evolution under the $\sigma_i^z\sigma_j^z$ coupling, written as,

$$V = \exp \left[-i H_1 \otimes 1_2\right] = U_{1z}^{12} U_z U_{zz} U_{zz} U_x,$$ (9)

where $U_{zz} = \exp \left[i \phi (\sigma_i^z + \sigma_j^z)\right]$, $U_z = \exp \left[-i \phi (\sigma_i^z \sigma_j^z)\right]$ and $U_x = \exp \left[-i \phi (\sigma_i^z + \sigma_j^z)\right]$. $\phi$ is the angle of rotation and is expressed as $2\pi \omega_0 u$. $U_{zz}^{12}$ and $U_x$ are realized by using GRAPE, with total maximum duration being 720 $\mu$s and 660 $\mu$s respectively, with all fidelity being above 99.9%. $U_{zz}$, on the other hand, can be implemented by free evolution under the internal Hamiltonian of the molecule Eq. 12. The interaction operator $H$ was again prepared using GRAPE, with total time of 7.5 ms and fidelity well over 99%.

**Internal Hamiltonian of liquid NMR system**

In this section, we explain the internal Hamiltonian of the liquid NMR system given in Eq. 5 of the main text. The NMR sample consists of $10^{15}$ molecules of 1,1,2-Trifluoro-2-iodoethane (TFIE) dissolved in suitable solvents, Acetone in our case and placed in an external magnetic field directed along $z$, $B = B_0 \hat{z}$. This results to a Zeeman splitting term $\gamma_i B \sigma_i$, where $\gamma_i$ is the gyromagnetic ratio of the $i^{th}$ nuclei. Another Zeaman-like term, $\gamma_i \sum_{\mu,\nu} B_{\mu} d_{\mu\nu}^i \sigma_i^\mu$, arises because of the modifications of the electronic cloud surrounding the nucleus, where $d_{\mu\nu}^i$ is called the Chemical Shift Tensor. The spins in the molecule can interact via a scalar $J$-coupling, mediated by electronic cloud through bonds and dipolar-dipolar interaction, through space. As mentioned earlier, our liquid sample is enough diluted that inter-molecular interactions can be neglected. Thus the Hamiltonian of the system takes the form

$$H = \sum_i \gamma_i B_0 (\sigma_i^z + \sum_{\nu} d_{zz}^i \sigma_i^\nu) + \sum_{i<j} J_{ij} \sigma_i^z \sigma_j^z + H_{\text{dipole}}.$$ (10)

Being prepared in the liquid state, the molecules in the sample undergo rapid rotations. The rotational motion averages out the dipole-dipole interaction and the electron mediated spin-spin scalar coupling is averaged to its isotropic value. The Hamiltonian thus reduces to,

$$H = \sum_{\mu,i=1}^N \gamma_i B_0 (\delta_{z\mu} + \vec{d}_{z\mu}) \sigma_i^\mu + \sum_{i<j=1}^N J_{ij} \sigma_i \sigma_j.$$ (11)

where $J$ is the trace of $J_{\mu\nu}$ tensor and $\vec{d}$ is a motionally averaged value of the chemical shift $d$ tensor. $N$ refers to number of nuclei in a molecule. We recognize $\omega_i = \gamma_i B_0 (1 + \vec{d}_{zz})$ as the Larmor frequency of the $i^{th}$ nuclei in the system corresponds to the large external magnetic field $B_0$. For fluorine ($\gamma_i \sim 2.5 \times 10^8 \text{s}^{-1} \text{T}^{-1}$) this is of the order of 470MHz at $B_0 = 11.74\text{T}$. Further using secular approximation [5], the Hamiltonian simplifies to

$$H = \sum_{i=1}^N \omega_i \sigma_i^z + \sum_{i<j=1}^N J_{ij} \sigma_i^z \sigma_j^z.$$ (12)