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Coherent state transfer between an electron- and nuclear spin in $^{15}$N@C$_{60}$

Richard M. Brown,$^1, *$ Alexei M. Tyryshkin,$^2$ Kyriakos Porfyriakis,$^1$ Erik M. Gauger,$^1$ Brendon W. Lovett,$^1, 3$ Arzhang Ardavan,$^4$ S. A. Lyon,$^2$ G. Andrew. D. Briggs,$^1$ and John J. L. Morton$^1, 4$

$^1$Department of Materials, Oxford University, Oxford OX1 3PH, UK
$^2$Department of Electrical Engineering, Princeton University, Princeton, NJ 08544, USA
$^3$School of Engineering and Physical Sciences, Heriot Watt University, Edinburgh EH14 4AS, UK
$^4$CAESR, Clarendon Laboratory, Department of Physics, Oxford University, Oxford OX1 3PU, UK

Electron spin qubits in molecular systems offer high reproducibility and the ability to self assemble into larger architectures. However, interactions between neighbouring qubits are ‘always-on’ and although the electron spin coherence times can be several hundred microseconds, these are still much shorter than typical times for nuclear spins. Here we implement an electron-nuclear hybrid scheme which uses coherent transfer between electron and nuclear spin degrees of freedom in order to both effectively turn on/off inter-qubit coupling mediated by dipolar interactions and benefit from the long nuclear spin decoherence times ($T_{2n}$). We transfer qubit states between the electron and $^{15}$N nuclear spin in $^{15}$N@C$_{60}$ with a two-way process fidelity of 88%, using a series of tuned microwave and radiofrequency pulses and measure a nuclear spin coherence lifetime of over 100 ms.

Hybrid quantum computing schemes aim to harness the benefits of multiple quantum degrees of freedom through the coherent transfer of quantum information between them. Such transfer has previously been shown between light and atomic ensembles [1, 2], as well as electron to nuclear spin states in nitrogen vacancies [3] and $^{31}$P donors [4], and progress is being made towards coupling electron spin ensembles to superconducting qubits [5, 6]. Common motivations for state transfer between electron to nuclear spin qubits include the much longer decoherence times typically exhibited by the nuclear spin, and also the weaker dipolar interaction between nuclear spins which allows interactions between neighbouring qubits to be effectively turned off [3, 4, 7–11]. Both effects can be attributed to the relatively weak nuclear magnetic moment, typically 3 orders of magnitude smaller than an electron spin. Thus, a powerful hybrid model for quantum computing is one where the electron spin qubit (which is more readily polarised and more quickly manipulated) is used for initialisation and processing, while the nuclear spin is used as a memory. The presence of the electron spin also offers considerable advantages for the readout of a single qubit, either of the electron spin state directly [12, 13], or a quantum non-demolition measurement of the nuclear spin [14, 15].

Endohedral fullerenes (atoms held within a carbon cage) offer promise as molecular qubits due to their exceptionally long electron decoherence times [16–18] and convenient coupling to a local nuclear spin. This has led to various theoretical proposals that make of use of both the electron and nuclear spin properties of these molecules [8–11, 19]. Experimental examples of these include the use of N@C$_{60}$ to demonstrate polarisation transfer from the electron to the nuclear spin and subsequent ‘bang-bang’ decoupling [20], dynamic nuclear polarisation (DNP) [21], as well as generation of pseudo-entanglement between the electron and nuclear spin [22, 23]. The advantages of molecular spin qubits include the ability to use chemical methods to engineer precise electron dipolar interactions [24], and self assembly into larger arrays [25, 26], however this approach is limited by the ‘always-on’ nature of dipolar interactions between neighbouring spins. This is in contrast to systems such as donors in silicon, where precise qubit placement is more challenging, but where electrical gates could allow control of qubit interactions [7]. In this Letter we employ a molecular high spin system, comprising an $^{15}$N atom encapsulated within a carbon cage ($^{15}$N@C$_{60}$). We select a spin concentration such that the electron dipolar coupling is of the order of ~2 kHz. We transfer a coherent state from the electron spin degree of freedom to the nuclear spin, and show that this is able to effectively turn off the dipolar coupling between nearby qubits. We study the fidelity of the transfer process and investigate the decoherence time of the nitrogen nuclear spin at low spin concentrations.

The $^{15}$N@C$_{60}$ system consists of an $S = 3/2$ electron spin coupled via an isotropic hyperfine interaction of 22 MHz to the $^{15}$N nuclear spin ($I = 1/2$). Under an applied magnetic field of ~0.35 T, the energy level diagram is shown in Figure 1(a)—this produces a doublet in the electron spin resonance (ESR) spectrum where each line corresponds to a state of $m_I$ [21]. To first order, the three electron $\Delta m_S = 1$ transitions in each $m_S$ subspace have the same energy and cannot be addressed individually [27]. Thus a $\pi/2$ ESR pulse (selective on one $m_I$ state) produces coherences across all three pairs of levels (with $\Delta m_S = 1$). For convenience, we will refer to an electron coherence between $m_S$ levels $+\frac{1}{2}$ : $-\frac{1}{2}$ as an inner coherence, and those between $m_S$ levels $\pm \frac{1}{2}$ : $\pm \frac{1}{2}$ as outer coherences. A qubit can be represented by the inner pair of $m_S$ levels, in the subspace of $m_I = \frac{1}{2}$ (see Figure 1(a)). The $T_{2e}$ we report here refers to this inner coherence [28].

We used dilute $^{15}$N@C$_{60}$ in a C$_{60}$ matrix ($2.5 \times 10^{15}$ spins/cm$^3$), prepared by arc discharge and ion bombard-
The effect of the dipolar interaction between the electron and nuclear spins of $^{15}\text{N}@\text{C}_{60}$ can be observed through a standard Hahn echo experiment ($\pi/2 - \tau - \theta_2 - \tau - \text{echo}$) used to measure the electron spin decoherence time ($T_{2e}$) [29].

In this experiment the $\theta_2$ pulse (which is typically $\pi$) acts to refocus effects such as magnetic field inhomogeneity as well as other interactions experienced by the spin which are constant on the timescale of $\tau$. However, if the $\theta_2$ pulse is shortened it will act to refocus only a sub-set of spins and mimic a homogeneously dilute spin sample [29–31]. Plotting $1/T_{2e}$ vs $\sin^2(\theta_2/2)$, $T_{2e}$ can be then be extended from 190 $\mu$s using the standard Hahn echo sequence to an extrapolated 300 $\mu$s in the limit $\theta_2=0$ (see Figure 1(b) and [28]). From this measurement we extract a dipolar coupling of 2.5 kHz between electron spins at the average $N@\text{C}_{60}$ separation [28], that we will show is not present between nuclear spins.

To probe the nuclear spin qubit we employ the transfer sequence shown in Figure 1 to propagate an electron coherence to a nuclear coherence. The implementation of this sequence is complicated compared to previous studies [4] by the presence of the $S = 3/2$ electron spin, such that the initial $\pi/2$ mw pulse produces both an inner coherence and unwanted outer coherences. The application of an $\pi$ pulse on the $m_S = +1/2$ transition (a controlled-NOT in quantum gate terminology) then transfers the qubit to an electron-nuclear cross coherence ($\varphi_x$). A mw $\pi$ pulse selective on $m_I = -1/2$ then completes the SWAP operation to produce a nuclear coherence ($\varphi_n$). Unwanted outer coherences generated during the sequence remain as both electron- and multiple-quantum coherences, which decay on the timescale of the electron spin decoherence time ($T_{2e}$) or faster [28]. The desired nuclear spin coherence can then be stored for many milliseconds before transfer back to the electron spin via a reverse of the sequence and readout by a conventional electron spin (Hahn) echo. The full sequence is shown in Figure 1 with the addition of carefully placed pulses to refocus the effect of inhomogeneous broadening on the spin packets in electron, nuclear and multiple quantum coherences. It is not possible to store the qubit within a nuclear coherence in the $m_S = \pm 1/2$ subspaces using this sequence, but they are considered in the supplementary material [28].

There are a number of ways to confirm that the recovered electron spin echo arises solely from a state which was stored in a nuclear spin degree of freedom. One method is to apply a time-varying phase shift to the nuclear spin (e.g., a geometric phase gate [32]) and observe a corresponding phase shift in the electron spin echo. This measurement shows no evidence of any other contribution to the electron spin echo, and is described in more detail in the supplementary material [28]. Ultimately, the success of the transfer scheme is shown by...
the ability to recover any input state with high fidelity after storage in the nuclear spin. This is achieved by exciting the full electronic and nuclear transitions, made possible by the short pulse lengths used and the narrow intrinsic sample ESR and NMR linewidths < 0.6 MHz and 15 kHz, respectively. We prepare the input states, ±X, ±Y and ±Z, by varying the phase of the initial π/2 mw pulse (±X,±Y), applying an initial π pulse (+Z) or by removing the initial pulse (−Z). Using quantum process tomography we can then extract the process matrix for the transfer scheme, χ, in the basis (I, σx, σy, σz) [33]. To accurately evaluate χ we compare the recovered states from the transfer sequence with those given by an ordinary Hahn echo (τ = τe1 + τe2). Thus, χ incorporates any losses at the storage or retrieval step, as well as during the storage period in the nuclear spin, but not any errors associated with the state generation or measurement. Figure 2 shows the measured χ, giving a fidelity of 0.88, compared to the ideal Identity process (I). We attribute this fidelity primarily due to errors in the transfer pulses—the use of composite mw pulses using the BB1 sequence improves the fidelity for +X state from 90 to 94% and we would expect further improvement with composite rf pulses (see supplementary material [28]).

The nuclear decoherence time (T2n) can be found by varying the time the qubit is held within the nuclear spin state (2τn). The resulting exponential decay in echo intensity gives T2n as long as 135±10 ms (at 10 K). At this temperature, T2n is 160 µs and thus the nuclear memory has almost three orders of magnitude improvement in the decoherence time. Nuclear dipolar coupling can be assessed through the effect on T2n of an ‘instantaneous diffusion’ experiment, similar to that applied to the electron spin. Reducing the length of the nuclear refocusing pulse (0.2 ≤ sin2(θrf/2) ≤ 1.0, see Figure 1(b)) results in no appreciable change in T2n at 20 K. Hence, coherent transfer reduces the inter-qubit coupling term from the electron-electron dipolar constant to the nuclear-nuclear dipolar interaction which we show to be weak as expected, ≪ 25 Hz [36].

The temperature dependence of the fundamental spin relaxation parameters in the system are shown in Figure 3. The electron relaxation time, T1e (measured by a standard inversion recovery sequence (π − τ − π/2 − T − π − T − echo [29]) is shown to increase exponentially with decreasing temperature. This follows an Arrhenius dependence, consistent with a two-phonon process resonant with an excited vibrational mode [17, 34] and can reach several seconds at low temperatures. Electron spin flips (whose timescale is characterised by T1e) ultimately act to limit the nuclear coherence time. In the temperature range, 50–80 K, we find that T2n follows T1e with the experimentally determined relationship, T2n ∼ 0.6 T1e. Below 50 K, a secondary mechanism is evident that limits the nuclear decoherence time to ∼130 ms. We analytically model relaxation in the system by applying the Lindblad equation, with the relevant raising and lowering operators, to a given initial state (e.g. a pure nuclear coherence, for T2n or inverted electron state, for T1e):

\[
\dot{\rho} = -\gamma_a (\rho S^+ S^- + S^- S^+ - \rho - 2S^± S^\mp) - i[\mathcal{H}, \rho]
\]

where γa represents both γ1, the electron spin relaxation rate between the ms levels ±3/2 ↔ ±1/2 and γ2, the relaxation rate between ms levels ±1/2 ↔ −1/2. The raising and
lowering operators are given by $S^+$ and $S^-$. Applying relaxation in the high temperature limit and assuming no direct nuclear relaxation, the relevant density matrix elements show a nuclear dephasing rate, $\Gamma_n = (3\gamma_1 + 4\gamma_2)$. Similarly, taking Eq. 1 and solving a series of coupled linear equations the electron polarisation is expressed in terms of two parts:

$$P(t) = \alpha e^{-\lambda_+ t} + \beta e^{-\lambda_- t}$$  \hspace{1cm} (2)

where $\alpha$ and $\beta$ are prefactors which are a function of $\gamma_1$ and $\gamma_2$, and the eigenvalues $\lambda_\pm$ are given by:

$$\lambda_\pm = \Gamma_n \pm \sqrt{(3\gamma_1)^2 + (4\gamma_2)^2}$$  \hspace{1cm} (3)

It can be shown that the slower decaying component, $\lambda_- = \Gamma_e \sim 0.3 \Gamma_n (T_{2n} \sim 0.3 T_{1e})$, when $3\gamma_1 = 4\gamma_2$. To reconcile this ratio with the experimentally obtained $T_{2n} \sim 0.6 T_{1e}$ additional relaxation processes can be included in the model, for instance, if $\gamma_1$ is given by $m_S = \pm \frac{1}{2} \leftrightarrow m_S = \mp \frac{1}{2}$ then when $\gamma_1 = \gamma_2 \geq 2$ a theoretical $T_{2n}$ of up to $2/3 T_{1e}$, can be found.

In conclusion, we have reported the coherent transfer of qubit states between electron- and nuclear spin degrees of freedom, in a high spin system. The quantum process tomography of the two-way transfer shows a fidelity of 88%, while we measure a nuclear decoherence time of up to 130 ms, almost three orders of magnitude longer than the electron spin coherence time. Thus, the $^{15}$N nuclear spin can be employed as both a quantum memory and to effectively turn off inter-qubit coupling. This is a crucial element in the realisation of fullerenic hybrid QIP schemes that exploit the nuclear and electron spin [8–11, 19], especially given recent work in producing larger fullerene architectures [24]. Alternatively, the coupling between spin ensembles and cavities could be exploited [5, 6], along with the storage of multiple microwave excitations [35], to produce a robust multimode nuclear memory.

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* Electronic address: richard.brown@materials.ox.ac.uk

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We extract only an estimated upper bound for the nuclear-nuclear dipolar coupling due to the limit of $T_2n$. The dipolar coupling is expected to be $\sim 10^6$ weaker between nuclear spins compared to electron spins and thus of order milliHz.