Bang-bang control of fullerene qubits using ultra-fast phase gates

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Quantum mechanics permits an entity, such as an atom, to exist in a superposition of multiple states simultaneously. Quantum information processing (QIP) harnesses this profound phenomenon to manipulate information in radically new ways [1]. A fundamental challenge in all QIP technologies is the corruption of superposition in a quantum bit (qubit) through interaction with its environment. Quantum bang-bang control provides a solution by repeatedly applying ‘kicks’ to a qubit [2, 3], thus disrupting an environmental interaction. However, the speed and precision required for the kick operations has presented an obstacle to experimental realization. Here we demonstrate a phase gate of unprecedented speed [4, 5] on a nuclear spin qubit in a fullerene molecule, and use it to bang-bang decouple the qubit from a strong environmental interaction. We can thus trap the qubit in closed cycles on the Bloch sphere, or lock it in a given state for an arbitrary period. Our procedure uses operations on a second qubit, an electron spin, in order to generate an arbitrary phase on the nuclear qubit. We anticipate the approach will be vital for QIP technologies, especially at the molecular scale where other strategies, such as electrode switching, are unfeasible.

Two well known concepts in overcoming the corruption of information stored within a qubit are decoherence free subspaces [6, 7, 8, 9], and quantum error correcting codes [10, 11, 12]. The former is the passive solution of restricting oneself to some set of states that, due to symmetries in the system, are largely immune to the dominant types of unwanted coupling. The latter is a sophisticated form of feedback control whereby the effect of unwanted coupling is detected and corrected. Between these limits there is the idea of dynamical suppression of coupling — making some rapid, low level manipulation of the system so as to actively interfere with the decoherence process. Ideas here often relate to the ‘quantum Zeno effect’ in which repeated measurement (or some related process) is capable of suppressing the natural evolution of the system [13, 14]. As the system evolves from one quantum eigenstate, |0⟩, to another, |1⟩, it passes through a superposition state α|0⟩ + β|1⟩ which, when measured, collapses to one of the two eigenstates with probabilities given by how far the system has been allowed to evolve. Therefore, if the measurements are made often, the system will have a high probability of being locked in the starting state (though, eventually, the finite probability of flipping will be realised).

In a related technique which is part of the bang-bang family of strategies [2, 3], measurement operations are replaced by the application of rapid rotations on the superposition. The original bang-bang literature proposed the use of rapid bit flips to prevent unwanted phase evolution. Our implementation is very close in spirit to that...
original paper: we perform the logical complement of the protocol, using rapid phase shifts to prevent amplitude evolution (see Fig. 1a and supplementary movie 22). In many systems, energy loss is a primary decoherence mechanism; such decoherence would be suppressed by precisely this strategy.

This technique is distinct from the projective Zeno effect in two interesting respects. In addition to locking the system in one of the two eigenstates the same sequence is capable of freezing any superposition state. Secondly, as the behaviour is always unitary, it remains deterministic even when the pulse frequency is limited. Given ideal pulses, one could trap the state in a closed cycle indefinitely.

We demonstrate this dynamic decoupling effect using a pair of coupled nuclear and electron spins in the endohedral fullerene molecule N@C60 (shown in Fig. 1b) 16. Information on the origin of the 12-level spin system in N@C60 is provided in the supplementary online material, along with other experimental details. We believe this system is the strongest candidate for a molecular qubit: the electron spin degree of freedom permits initialisation to a genuine pure state, while the protection afforded by the fullerene armour yields the longest decoherence time measured for any molecular electron spin 17 18 19. For the experiments described here, we choose four levels from the 12 present in such a way that they correspond to two qubits: an electron qubit (formed from $M_s = +3/2, -3/2$) and a nuclear qubit ($M_I = +1, 0$), as shown in Fig. 1. As the nuclear qubit has excellent natural environmental decoupling we must introduce a strong coupling by applying a resonant radio-frequency (RF) field to drive Rabi oscillations. This field is then successfully decoupled by fast phase ‘kicks’ to the system: we exploit the qubit-qubit coupling, taking the electron qubit around closed cycles so as to apply phase shifts to the nuclear qubit. Finally, we observe that by detuning the microwave pulse away from the electron spin transition frequency, this technique can be generalised to apply an arbitrary phase gate to the nuclear spin on a time scale which is much faster than normal nuclear magnetic resonance (NMR) methods.

The general pulse sequence used is shown in Fig. 2. A selective electron $\pi$-pulse on the $M_I = +1$ manifold transfers the thermal polarisation of the electron spin to the nuclear spin (this can be thought of as a controlled-NOT operation with the nucleus as control and electron as target 21). The nuclear polarisation then exhibits Rabi oscillations between the $M_I = 0$ and $M_I = +1$ levels (in Fig. 1|00⟩ and |01⟩, respectively) upon the application of a suitable RF driving field. During the Rabi oscillations, fast microwave pulses are applied on the electron spin to suppress the nuclear spin evolution. Finally, a measurement of the relevant state populations is performed using two-pulse electron spin echo detection.

It is possible to apply a phase gate to a qubit by rotating one of the basis states around a complete cycle through an auxiliary level (Fig. 1c). This can be simply seen by evaluating the operator for a complete one-resonance rotation applied to a $S=1/2$ particle:

$$U_{2\pi} = e^{-i\sigma_z \pi} = \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix},$$

where $\sigma_z$ is the Pauli spin matrix. Therefore, when this rotation is selectively performed on the |01⟩ - |11⟩ transition, state |01⟩ will acquire a $-\pi$ phase with respect to |00⟩ (i.e. a $\pi$ phase shift). Although the electron spin used in this case is $S = 3/2$, the Bloch vector for higher spin systems (in high-symmetry environments, such as our spherical fullerene) behaves identically to the $S = 1/2$ case 21 22.

Fig. 3a shows the effect of applying a $\pi$ phase shift during the nuclear Rabi oscillations — the evolution is reversed each time a microwave pulse is applied, as illustrated on the nuclear Bloch sphere in Fig. 3b. It is not necessary to apply perfect $\pi$ phase shifts in order to lock the spin. In Fig. 3c, smaller phase shifts are implemented. After the first pulse, the nuclear spin evolves around a lesser circle on the Bloch sphere. A second (identical) phase shift brings the nuclear spin back onto a great circle, with an overall $\pi$ phase shift (illustrated in Fig. 3d). This kind of error cancellation is analogous to the 90°, 180°, 90°, type of pulse correction NMR 23 24. By increasing the repetition rate of the phase shift pulses, the nuclear spin evolution can be locked in one particular state (Fig. 3e), and released as desired (Fig. 3f).

Any microwave pulse of finite duration which is resonant with the primary |01⟩-|11⟩ transition also performs a detuned excitation of the |00⟩-|10⟩ transition (illustrated in Fig. 4a). The difference between these two transition frequencies is fixed in our system by the hyperfine coupling constant $a = 15.8$ MHz, but the effective detuning can be controlled through the microwave pulse power (B1). In the limit of strong selectivity (weak pulses) only the resonant transition is significantly excited, and a complete cycle (|01⟩-|11⟩-|01⟩) generates a $\pi$ phase shift in the nuclear qubit. Faster (non-selective) pulses are possible, provided that B1 is chosen such that both electron transitions undergo an integer number of complete cycles, thus ensuring the system returns to the subspace {|00⟩, |01⟩} after the microwave pulse. This permits the implementation of phase shifts which differ from $\pi$, as
FIG. 3: The natural evolution between two nuclear spin states of the nitrogen atom can be disrupted by the application of decoupling pulses. Unperturbed Rabi Oscillations are shown in black, while those under the influence of decoupling pulses are shown in red. The decay observed is an artifact of the inhomogeneity in the RF driving field, and is not a true decoherence phenomenon. (a, b) Microwave pulses are applied on the electron spin at regular intervals (indicated by arrows), inverting the phase of one of the nuclear spin states and reversing the evolution of the nuclear spin qubit. (c, d) When we implement a phase shift less than $\pi$, an odd-even behaviour is observed, corresponding to greater and lesser paths on the Bloch sphere. (e) Increasing the repetition rate of the microwave pulses locks the system in a particular state. (f) The qubit can be locked and released at any point.

shown in Figs. 3c and 3d. The phase acquired by each cycle has a geometric interpretation: it is equal to half of the solid angle subtended by the path of an eigenstate around the Bloch sphere (see Fig. 1b). The differences in the two phases obtained defines the phase shift on the nuclear qubit.

A straightforward extension of this idea is to drive both the electron spin transitions ($|00\rangle$-$|10\rangle$ and $|01\rangle$-$|11\rangle$), with equal and opposite detuning (i.e. at a frequency half-way between their resonances). Here, the condition of both transitions going through an integer number of complete cycles can be satisfied for any value of B1. The populations of both transitions evolve in the same way, whilst the phase acquired is opposite, as illustrated in FIG. 4. Arbitrary nuclear phase gates are implemented by driving two electron spin transitions simultaneously (see Fig. 1b). (Left) The path of the electron magnetisation vector driven by a microwave field. (Right) The corresponding z-magnetisation. (a) One transition is driven resonantly, and one strongly detuned. On each cycle, the phase accumulated is proportional to the area enclosed by the path. Both transitions must undergo an integer number of complete cycles to ensure the populations remain unchanged. (b) With both transitions detuned by equal and opposite amounts, the population evolution for each is the same, whilst the phase accumulated is of opposite sign. Hence, the relative phase shift can be tuned by controlling the microwave pulse power.

Fig. 4b. The relative phase accumulated (which defines the phase gate applied) is determined only by B1, allowing an arbitrary phase gate to be applied on the nuclear spin (see also [26]). The duration of this gate ($\sim$100 ns) is orders of magnitude shorter than typical NMR phase gates, and about $10^5$ times shorter than existing geometric phase gates in NMR [4].

We have demonstrated an ultra-fast fast phase gate on a nuclear spin qubit, by driving a coupled electron qubit around a closed cycle. The gate speed can exceed even the nuclear precession frequency, which is only possible through exploiting the transition selection rules in the system. Through repeated application of this fast phase gate we have bang-bang decoupled a nuclear spin qubit from a permanent driving field.

The experiments described here were performed on isolated N@C_{60} molecules in solution, in which the natural noise is low. The magnitude of interactions in a fullerene-based processor will be at most that experienced by close-packed N@C_{60} arrays, where the nuclear spin dipole in-
teraction is of the order 100 Hz, or approximately 40 times weaker than the RF driving field we apply here. Paramagnetic impurities within such structures could increase the natural noise further, however, the speed of the decoupling gates demonstrated in our experiment show that interactions as strong as 100 kHz can be suppressed.

This scheme has a broad applicability: the minimum complexity required of a quantum system is three levels (the two qubit levels and one auxiliary level) coupled by a suitably rapid allowed transition. However, as we demonstrate here, the approach also works with more than three levels and multiple allowed transitions among those levels. Indeed, a very natural implementation will be any system with a coupled electron and nuclear spin, giving (in the $S = 1/2$ case) four levels on two different energy scales. For example, two very different qubits systems also suited to our approach are phosphorous impurities in silicon, and N-V centers in diamond. Both of these have been identified by the QIP community as promising qubits. Generally, our demonstration highlights the potential benefits of physical ‘qubit’ systems beyond the simple 2-level structure.

In addition to suppressing unwanted coupling to an environment, this effect is explicitly required in certain quantum computing schemes (for example, to control the interaction between neighbouring qubits in perpetually coupled spin-chains \cite{27}). Given the great difficulties associated with tailoring interactions in quantum systems, it is likely that decoupling strategies of this kind will form a quintessential element in any real quantum computer.

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II. MATERIALS AND METHODS

The molecular species used in this work is N@C$_{60}$ (also known as $i$-NC$_{60}$), consisting of an isolated nitrogen atom in the $^4S_{3/2}$ electronic state incarcerated by a C$_{60}$ fullerene cage. Our production and subsequent purification of N@C$_{60}$ is described elsewhere [28]. High-purity N@C$_{60}$ powder was dissolved in CS$_2$ to a final concentration of $10^{15}$ cm$^{-3}$, freeze-pumped to remove oxygen, and finally sealed in a quartz tube. Samples were 0.7 cm long, and contained approximately $5 \cdot 10^{13}$ N@C$_{60}$ molecules. Pulsed Electron Paramagnetic Resonance (EPR) measurements were made at 190 K using an X-band Bruker Elexsys580e spectrometer, equipped with a nitrogen-flow cryostat.

N@C$_{60}$ has electron spin $S = 3/2$ coupled to the $^{14}$N nuclear spin $I = 1$. The EPR spectrum consists of three lines centered at electron g-factor $g = 2.003$ and split by a $^{14}$N isotropic hyperfine interaction $a = 0.56$ mT in CS$_2$ [10]. The electron-nucleus double resonance (ENDOR) spectrum consists of four principle lines associated with the four $M_S$ states, each of which is further split into two by the second-order hyperfine interaction [19], enabling selective excitation of (for example) the $M_I=0$ to $M_I=\pm1$ transition. In these experiments we applied two simultaneous RF fields (22.598 and 24.782 MHz) to coherently drive both the $|00\rangle$ - $|01\rangle$ and $|10\rangle$ - $|11\rangle$ transitions. This is done solely to improve sensitivity, and as all microwave pulses do not exchange populations between these two subspaces, they can be treated independently.

The electron spin transition $M_S = +3/2$ to $M_S = -3/2$ is driven via the intermediate levels $M_S = \pm1/2$, however upon a complete $\pi$ or $2\pi$ rotation, no population remains in the intermediate levels. This can be straightforwardly seen by evaluating the rotation operators for high-spin systems.

In the majority of data presented here, microwave pulse power was chosen so the second off-resonance transition was also excited, such that driving the system around one complete cycle generated an approximate $\pi/2$ phase shift. Thus, a $\pi$ phase shift was implemented by twice driving the system through a complete cycle.