Supplementary information for
“Efficient creation of dipolar coupled nitrogen-vacancy spin qubits in diamond”

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Abstract. In the following we give further detailed information on the used methods. We present the nitrogen-vacancy defect (NV) spin dynamics and dipolar coupling and the applied measurement protocols. We present additional detail of the characterized NV pairs. Furthermore we discuss the choices of statistical distributions and criteria for our simulations.

1. Single NV Hamiltonian
The Hamiltonian describing the relevant dynamics of a single negatively charged NV electron spin in its electronic ground state of a zero-field splitting term, a Zeeman-interaction term and hyperfine coupling terms to proximal nuclear spins:

\[ \hat{H} = \hbar \left( D \hat{S}_z^2 + \gamma \vec{B} \cdot \vec{S} + \sum_i \hat{S}_i \hat{I}_i \right) \]  

(1)

Here, \( \hbar \) is Planck’s constant, \( D = 2.87 \) GHz is the zero-field splitting imposed by the crystal confinement of the electron spin, \( \gamma = 28.03 \) GHz/T is the gyromagnetic divided by \( 2\pi \) of the electron spin, \( \vec{B} \) is the magnetic field in the location of the NV defect, \( A_i \) are hyperfine tensors representing the coupling to different nuclear spins and \( \vec{S} = (\hat{S}_x, \hat{S}_y, \hat{S}_z)^T \) and \( \vec{I}_i = (\hat{I}_{ix}, \hat{I}_{iy}, \hat{I}_{iz})^T \) are the spin operators for the electron and nuclear spins respectively.

In the experimental conditions throughout our work the zero-field splitting is the dominating term and therefore defining the quantization axis \( z \) along the NV symmetry axis, whereas all other terms can be regarded as perturbations in this basis.

External magnetic fields \( \vec{B} \) couple through the Zeeman interaction to the spin. Here static fields mostly induce a Zeeman splitting along the quantization axis \( z \), while oscillating fields can drive the spin between its eigenstates, giving rise to magnetic resonance experiments. The hyperfine coupling term accounts for the interaction with nuclear spins in the vicinity, for example the intrinsic nitrogen spin \( ^{14}\text{N} I = 1, ^{15}\text{N} I = 1/2 \) or paramagnetic carbon in the diamond lattice \( ^{13}\text{C} I = 1/2 \). For one the interaction allows to control nuclear spins via the electron spin and is therefore essential to scaling of the single NV quantum register. In return the coupling to a bath of nuclear spins also gives rise to decoherence of the electron spin as it constitutes a channel through which quantum information stored on the electron spin state can be lost to the environment.
2. Dipolar interaction Hamiltonian

In the case of two NV electron spins the Hamiltonian is expanded by a second single spin Hamiltonian and a dipolar interaction Hamiltonian:

\[ H_{\text{dip}} = \frac{\mu_0}{4\pi} \frac{h^2\gamma^2}{r^3} \left[ \hat{S}_A \cdot \hat{S}_B - 3 (\hat{S}_A \cdot \hat{r})(\hat{S}_B \cdot \hat{r}) \right], \]

with \( \mu_0 \) being the vacuum permeability, \( r \) being the distance of the spins and \( \hat{r} \) being the unit vector linking them. Here the spin operators \( \hat{S}_i = (\hat{S}_{xi}, \hat{S}_{yi}, \hat{S}_{zi})^T |_{i=AB} \) are defined in their proper coordinate frame \((x_i, y_i, z_i)\), given by the respective quantization axis, thus the operators have to be rotated into a common frame \((u, v, w)\) with rotation matrices \( R_i \)

\[ \hat{S}_i = R_i \hat{S}'_i = \begin{pmatrix} R_{xu} & R_{yu} & R_{zu} \\ R_{xv} & R_{yv} & R_{zv} \\ R_{xw} & R_{yw} & R_{zw} \end{pmatrix} \begin{pmatrix} \hat{S}'_x \\ \hat{S}'_y \\ \hat{S}'_z \end{pmatrix} |_{i=AB}. \]

The spin operator expressions in the Hamiltonian can be rewritten as

\[ \hat{S}_A \cdot \hat{S}_B = (R_A \cdot \hat{S}_A') \cdot (R_B \cdot \hat{S}_B'), \]

\[ (\hat{S}_A \cdot \hat{r})(\hat{S}_B \cdot \hat{r}) = \left( (R_A \cdot \hat{S}_A') \cdot \hat{r} \right) \left( (R_B \cdot \hat{S}_B') \cdot \hat{r} \right). \]

In general it is expected to find all possible combinations of the term

\[ a_{ij} \hat{S}_{iA} \hat{S}_{jB} \] in the expanded dot products. However, as the Zeeman term usually dominates all terms except \( i = j = z \) can be neglected:

\[ \hat{S}_{iA} \hat{S}_{jB} \ll \gamma B \quad \forall \, i, j = x, y \]

The dot product in eq. 4 then reduces to

\[ \hat{S}_A \cdot \hat{S}_B \approx \hat{S}_{ZA} \hat{S}_{ZB} (R_{zuA} + R_{zvA} R_{zwA} R_{zwB}). \]

The term in the bracket is the dot product of the \( z \) component vectors of \( R_A \) and \( R_B \), which can be expressed as

\[ \hat{S}_{ZA} \hat{S}_{ZB} \approx \hat{S}_{ZA} \hat{S}_{ZB} \cos \phi_{AB} \]

and represents the projection of the quantization axes onto each other with their angle \( \phi_{AB} \). The dot products in eq. 5 reduces accordingly to

\[ (\hat{S}_A \cdot \hat{r})(\hat{S}_B \cdot \hat{r}) \approx \hat{S}_{ZA} \hat{S}_{ZB} \cos \phi_{Ar} \cos \phi_{Br} \]

assuming the vector \( \hat{r} \) is defined in the same \((u, v, w)\) frame (without loss of generality as it can always be transformed into the same frame). With these terms the approximated Hamiltonian can then be written as

\[ H_{\text{dip}} \approx \mu_0 \frac{h^2\gamma^2}{4\pi} (\cos \phi_{AB} - 3 \cos \phi_{Ar} \cos \phi_{Br}) \hat{S}_{ZA} \hat{S}_{ZB}, \]

which is equivalent to the form shown in the main paper. Supplementary Figure 1 shows a schematic of the geometry. Note that a magnetic field dependent induced magnetic moment for initial spin state \( m_S = 0 \) is neglected, which can be assumed for operations restricted to \( m_S = \pm 1 \) or external fields close to zero, yet large enough to fulfill eq. 7. The angular constellations resulting in strongest coupling are axially aligned, parallel spins. Here all angels \( \phi_{AB} = \phi_{Ar} = \phi_{Br} = 0 \) and the angular term reduces to a factor of 2 (parallel) or -2 (antiparallel). The median angular contribution when all four crystal axes and all directions of \( \hat{r} \) have equal probability is

\[ \bar{m}_{\text{dip}} \approx 0.7 \mu_0 \frac{h^2\gamma^2}{4\pi r^3}. \]
Supplementary Figure 1 (a) Schematics showing the relevant geometry for dipolar coupling of two NV electron spins. (b) The ideal angular constellations are axially aligned parallel or anti-parallel NVs. (c) Distribution of angular contributions to the dipolar coupling strength.

3. Coherence times measurements – Electron spin echo envelope modulation

The coherence times $T_2$ of NV electron spins are measured in Electron Spin Echo Envelope Modulation (ESEEM) measurements. Supplementary Figure 2 shows the corresponding measurement sequence. Here the electron spin is prepared in a superposition state $|\Psi\rangle = \frac{1}{\sqrt{2}} (|0\rangle + e^{i\phi}|1\rangle)$ with a microwave $\pi/2$-pulse after initialization. In the subsequent evolution time $\tau$ the phase $\phi$ evolves with magnetic fields imposed by external sources, e.g. control fields and the spin bath, according to

$$\phi_1(\tau) = 2\pi \gamma \int_0^\tau dt B_z(t)$$

The spin is flipped with a microwave $\pi$-pulse and left to evolve for another time $\tau$ where the phase follows

$$\phi_2(\tau) = -2\pi \gamma \int_\tau^{2\tau} dt B_z(t)$$

Finally the total phase $\phi = \phi_1 + \phi_2$ is projected onto a population state with another $\pi/2$-pulse and read out. The intermediate $\pi$-pulse refocuses any phase evolution caused by magnetic field dynamics that do not change over the course of the measurement, effectively eliminating for example homogeneous broadening. What is left are phase evolutions caused by magnetic noise from the environment which will introduce a decay of coherence over the total evolution time $2\tau$, where the coherence time $T_2$ represents the characteristic decay length.

The interaction with the spin bath is in part coherent resulting in periodic decays and revivals of the ESEEM signal as can be seen in Supplementary Figure 2. The periodicity is caused by the Larmor precessions of the surrounding $^{13}$C nuclear spins and revivals occur every $\tau = \gamma_C \cdot |\vec{B}|$, where $\gamma_C = 10.7$ MHz/T is the gyromagnetic ratio divided by $2\pi$ of $^{13}$C nuclear spins. In the experiments magnetic fields of $|\vec{B}| = 5$ mT are used so revivals are expected to occur over the total evolution time every $2\tau = 37.4$ µs.

For the characterization of the implantation, the coherence times were only recorded on a subset of sites (sample A 77 NVs, sample B 96 NVs) with detailed ESEEM measurement. The search routine on the other hand merely measured the fluorescence contrast on the first and second revival to quickly estimate the decay.
In many cases the coherence times can be prolonged to a characteristic $T_2^\phi > T_2$ by applying additional $\pi$-pulses through-out the evolution time that decouple the NV electron spin from higher orders of magnetic field dynamics from the environment. In this work we refrained from using these dynamical decoupling sequences. First they may not necessarily be compatible with actual quantum computing gate operations and second we seek to find the bounds of feasibility rather than achieve records based on circumstantial conditions. Hence we keep our study general as possible.

4. Dipolar coupling measurements – Double electron electron resonance
In order to detect dipolar coupling a measurement sequence as shown in Supplementary Figure 3 is applied. One NV takes the role of a sensor. After initialization it is controlled with microwave pulses to perform an ESEEM sequence with a magnetic field sensitive phase $\phi$ as described in the previous section. The second NV acts as emitter. It is prepared in an eigenstate and flipped by a microwave $\pi$-pulse during the evolution of the sensor. As the dipolar coupling strength $\nu_{dip}(m_{SA}, m_{SB})$ between the two NV changes depending on the magnetic quantum numbers $m_{Si} = \hat{S}_{z i} |\Psi_i\rangle \ |i = A, B$, its contribution to the induced phase evolution of the sensor is not fully refocused. Hence the coupling strength $\nu_{dip}$ can be directly projected onto the phase evolution of the sensor by sweeping the point in time where the emitter is flipped.

In order to address both the sensor and emitter spin individually, selective microwave pulses have to be applied on the magnetic resonances. In a homogeneous magnetic field resonances of NVs with parallel axes overlap in general and can thus not be addressed individually. For this reason parallel NV are discarded from investigations.
5. Empirical model of coherence times

In order to model the coherence times of implanted NVs we rely on empirical data. We record statistics of single NV coherence times on eight nanomask implantations and ensemble coherence times of eight implantations without mask. The median coherence times are shown in Supplementary Figure 4 (a). All diamond samples used are CVD-grown single crystals with a natural abundance of paramagnetic $^{13}$C.

We apply a simple model to the data based on a few assumptions. At the highest energies and lowest fluences we expect coherence times to be limited by the $^{13}$C spin bath. Here we find the median coherence time $\tilde{T}_2$ to be on the order of 100 µs (mean $\tilde{T}_2 = 150$ µs). For the lowest energies, surface effects will dominate the decoherence processes, where median coherence times typically are limited to hundreds of ns. In between we expect a logistic growth over the energy. For the fluence we assume an exponential decrease. While there indications that there is a saturation effect for lower fluences, as well, we have not enough data to support this. In addition we expect the pair creation probabilities in the regime of lower fluences to be limited by the amount of created NVs rather than their coherence times and thus minor discrepancies between variations of the model. The empirical model can then be expressed as

$$\tilde{T}_2(E,F) = c_0 \cdot \frac{1}{2} \left(1 + \tanh \frac{E - c_1}{c_2}\right) \cdot e^{-\frac{F}{c_3}},$$

(14)

where the coefficient $c_i$ are determined in a fit to the data. We find a saturation value $c_0 = 104$ µs, a logistic inflection point $c_1 = 14.8$ keV, a curvature parameter $c_2 = 16.3$ keV and a decay constant $c_3 = 1.2 \cdot 10^{12}$ cm$^{-2}$. The resulting median coherence times curve is show in Supplementary Figure 4 (b).
Supplementary Figure 4 (a) Empirical median coherence times of NVs implanted at different energies and fluences. The data was collected on and eight nanomask implantations (measured on single NV, green) and eight implantations without mask (measured on ensembles, blue). (b) Fitted median coherence times.

6. Coherence times distributions

For the simulations we typically use exponential distributions of coherence times. This shape of distribution is commonly found in NVs implanted with high fluences, for example in the data recorded for the coherence times model or as seen Figure 3 (d) in the main text. The shape of coherence times distributions may, however, be an important factor in the design of NV structures, as high probabilities for short coherences will impact the success rates of the strong coupling condition. For the simulation of the scaling we therefore also investigate gamma distributions of higher orders that would particularly reflect the avoidance of short coherence times. Gamma distributions with different shape factors $k$ are shown in Supplementary Figure 5. In the simulations we chose the shape of $k = 3$ as $k = 2$ distributions have steep onset at low values and therefore do not correspond to our requirements.

Supplementary Figure 5 Comparison of statistical coherence time distributions for equal median coherence time of 100 µs. Exponential distributions (green) are typically observed in high fluence implantations and have a high probabilities for short coherence times. Gamma distributions of shape $k = 2$ (blue) and 3 (red) are suitable to model avoidance of short coherence times.
7. Detailed $T_2$ and $\nu_{\text{dip}}$ of identified coupled sites

The measurements of coherence times (ESEEM) and dipolar couplings (DEER) of identified sites with coupling NV spins are shown in Supplementary Figure 6 and a list of the derived values is shown in Supplementary Table 1.

**Supplementary Table 1** – List of sites with identified dipolar coupling and list NV characteristics.

| sample | site | $T_2$ of NV$_A$ (µs) | $T_2$ of NV$_B$ (µs) | Limiting $1/T_2$ (kHz) | $\nu_{\text{dip}}$ (kHz) | strong |
|--------|------|-----------------------|-----------------------|-------------------------|-------------------------|--------|
| A      | 1    | 120                   | 30                    | 33                      | 3900                    | yes    |
| A      | 2    | 80                    | 50                    | 20                      | 99                      | yes    |
| A      | 3    | 400                   | 250                   | 4                       | 55                      | yes    |
| B      | 1    | 60                    | 2                     | 500                     | 48                      | no     |
| B      | 2    | 90                    | 50                    | 20                      | 50                      | yes    |
| B      | 3    | 120                   | 80                    | 13                      | 18                      | yes    |
| B      | 4    | 310                   | 150                   | 7                       | 8                       | yes    |
| B      | 5    | 90                    | 2                     | 500                     | 10                      | No     |
| B      | 6    | 120                   | 80                    | 13                      | 5                       | No     |

**Supplementary Figure 6** ESEEM of NV A (a), NV B (b) with Gaussian envelope fits to derive $T_2$ and DEER (c) measurements with sinusoidal fits to derive $\nu_{\text{dip}}$ in sites with identified dipolar coupling.

8. Criteria for Coupled Networks

We consider a site with any amount of NV defects a coupled network size $n$ when a connected graph of the order $n$, where NV defects represent nodes and couplings fulfilling the strong coupling condition represent edges, can be found. This implies that the NVs do not have to be ordered in any fashion and that not every possible connection has to be strongly coupled. Furthermore a complete graph, where all possible pairs of nodes are connected, is equally considered a network as a linear graph or chain.
Supplementary Figure 7 shows all possible graphs for orders two through five that are considered a network of the respective size.

*Supplementary Figure 7* All possible graphs with two through five nodes that are considered a coupling network of the respective size. The nodes (circles) represent NV defects and the edges (lines) represent couplings between two NV that fulfil the strong coupling condition.