Self-assembling hybrid diamond–biological quantum devices

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Abstract

The realization of scalable arrangements of nitrogen vacancy (NV) centers in diamond remains a key challenge on the way towards efficient quantum information processing, quantum simulation and quantum sensing applications. Although technologies based on implanting NV-centers in bulk diamond crystals or hybrid device approaches have been developed, they are limited by the achievable spatial resolution and by the intricate technological complexities involved in achieving scalability. We propose and demonstrate a novel approach for creating an arrangement of NV-centers, based on the self-assembling capabilities of biological systems and their beneficial nanometer spatial resolution. Here, a self-assembled protein structure serves as a structural scaffold for surface functionalized nanodiamonds, in this way allowing for the controlled creation of...
NV-structures on the nanoscale and providing a new avenue towards bridging the bio–nano interface. One-, two- as well as three-dimensional structures are within the scope of biological structural assembling techniques. We realized experimentally the formation of regular structures by interconnecting nanodiamonds using biological protein scaffolds. Based on the achievable NV-center distances of 11 nm, we evaluate the expected dipolar coupling interaction with neighboring NV-centers as well as the expected decoherence time. Moreover, by exploiting these couplings, we provide a detailed theoretical analysis on the viability of multiqubit quantum operations, suggest the possibility of individual addressing based on the random distribution of the NV intrinsic symmetry axes and address the challenges posed by decoherence and imperfect couplings. We then demonstrate in the last part that our scheme allows for the high-fidelity creation of entanglement, cluster states and quantum simulation applications.

Keywords: nitrogen vacancy center, nanodiamonds, self-assembling

1. Introduction

Coupled solid-state spin systems as electron spins in quantum dots, phosphorous donors in silicon and color centers in diamond form promising candidates for the emerging field of quantum technologies [1]. Among these the negatively charged nitrogen-vacancy (NV −) center in diamond [2], composed of a substitutional nitrogen atom and an adjacent vacancy within the diamond lattice, the subject of this work, stands out due to its long coherence time up to milliseconds at room temperature [3]. It forms a discrete atom-like energy level structure within the diamond bandgap, with the ground state described by an electron-spin triplet (spin-1), that allows for full coherent control by means of e.g. microwave drivings and static magnetic fields [4]. Remarkably, readout and initialization through the excited state can be performed optically, benefiting from the spin-dependent fluorescence rates and an intersystem crossing, the latter of which allows for the high-fidelity state preparation by optical pumping [4]. Interaction among neighboring NV-centers can be mediated by the magnetic dipolar coupling of the electronic spins [5, 6], yet this requires distances of the order of 10 nm or below to enable coherent interaction strengths that comfortably exceed the decoherence times. However current techniques for the controlled positioning of NV-centers within bulk crystals, i.e. the creation of NV-centers by ion implantation [7], are limited to several tens of nanometers in position [8]. In contrast, the ability of biological systems for structural self-assembly [9, 10] is a powerful tool allowing for the simple and parallel creation of large ordered arrays on nanometer scales, and holding the potential for outperforming the limited resolution and structural complexity achievable by conventional lithography based on serial pattern creation. We propose to combine the self-assembly of biological systems with the guided attachment of surface functionalized nanodiamonds (NDs). The biomolecules are used as a structural scaffold to enable the formation of NV-center configurations with high spatial resolution. This can be achieved with tiled motifs such as short DNA strands [11] or membrane forming complexes including SP1 [12], LH1 [13] and TF55β [14], that allow for the creation of one and two dimensional (2D) arrays. Going beyond 2D periodic patterns, the method of DNA-origami [15, 16], based on folding a large single-stranded DNA molecule directed by staple
strands, enables the creation of more complex highly controllable structures, ranging from aperiodic arrays to real three dimensional structures. Advanced knowledge in genetic engineering now allows control over the assembly, structure and topology of biomolecular complexes as well as the attachment of nanoparticles with nanometer precision [17]. Each of these structures is suitable for hosting NDs, whose size can be controlled down to 4 nm in fabrication [18], and whose chemical attachment and site-specific binding can be directed by surface functionalization and labeling. This allows for the high precision positioning of NV-centers incorporated in such diamonds, which subsequently interact via dipolar couplings, and paves the way for a highly controllable array of interacting quantum systems.

2. Formation of SP1 ND structures

To demonstrate the feasibility of interconnecting NDs with biological structures, we present the formation of small ND complexes using an SP1 (Stable Protein 1, see figure 2(c) and appendix A) protein variant and first steps towards the formation of regular arrays of NDs on SP1 arrays. A crucial first step to enable both experiments is the genetic modification of SP1 to fuse 12 graphite-specific binding peptides to the SP1 N-terminus, which permit site specific binding of SP1 to the carbon sp2-hybridization which forms on the ND surface [19].

Site-specific binding of the SP1 is essential for small NDs (under 10 nm) to form regular structures on an SP1 array (figure 2(d)) [20]. As an important result towards the creation of ordered ND structures, we achieved the formation of numerous dimers and trimers along with larger ordered structures such as a seven ND hexagon as illustrated in figures 2(a) and (b). Here
a monolayer of genetically modified SP1 was formed by the Langmuir–Blodgett method [21] and subsequently combined with a ND solution (5 nm in diameter formed by laser ablation). Using both the SP1-template and a diluted ND solution, ordering of the NDs partially filling the SP1 template has been achieved. Such isolated structures are promising candidates for NV-coupling experiments. In particular, connected regions can be shown to form a symmetric arrangement; albeit over long distance the distortion in the SP1-lattice renders the symmetry yet imperfect. Figure 2(a) shows an image of ND structures on the SP1 monolayer and figure 2(b) is

**Figure 2.** NV center, dynamical decoupling and dipolar coupling strength. (a) Ground state electron spin triplet of the nitrogen vacancy center with zero field splitting 2.87 GHz and the degeneracy of the $|±1\rangle$ states lifted by a weak magnetic field. (b) Coherence time $T_2$ versus strength (Rabi frequency) $Ω$ of the decoupling field. Two independent noise contributions are taken into account, whose spectra are illustrated in the inset: first, nuclear spin surface noise mediated by intra-dipolar couplings (red line), which has been calculated according to appendix D following the approach developed in [22] and leads to $\tau = 2.5 \mu s$, $b = 2\pi \times 30.2$ kH$z$ and $T_2 = 13.3 \mu s$ for a fluorinated surface. Second, a high frequency (electron spin) noise with $\tau = 0.28$ ns and $b = 2\pi \times 0.25$ MHz (green dashed line), that on the MHz frequency range considered here is well approximated by a white noise with $S(ω) ≃ 2\pi \times 0.2$ kHz. This latter contribution sets an upper bound on both the coherence time $T_2$ and relaxation time $T_1$. Coherence times $T_2$ and their scaling under continuous dynamical decoupling are shown for the nuclear surface noise $T_2^{(\text{nuc})}$ (red line, right y-scale), the high frequency noise $T_2^{(\text{hf})}$ (green, dashed line) and the combined decay $T_2^{(\text{tot})} = \left[1/T_2^{(\text{nuc})} + 1/T_2^{(\text{hf})}\right]^{-1}$. Circles correspond to the 1/e decay time and squares to an exponential fit both obtained by a numerical nuclear spin noise simulation. (c) Dipolar coupling parameter $ξ$ versus the external magnetic field. Red circles denote the average and blue lines the variance arising from the random axis orientation. For large magnetic field the quantization axis is given by the external field and $ξ ≃ 1/4$. The green dashed area indicates the range that can be corrected using compensation methods. All parameters are obtained by averaging over 10$^6$ random spin orientations. Inset: Optimal magnetic field configuration for a 2D array as used for the main graph.
an enlargement of the ND hexagon. In this SP1/ND sample, the size of the measured nanoparticles is around 5 nm in diameter, therefore matching the expected ND size. Furthermore, the presence of diamonds on the sample surface has been verified by electron diffraction in the relevant areas on this sample (appendix A).

We have statistically evaluated the SP1 ND sample of figure 2(a): this contains a total of 268 NDs, which corresponds to a dilute 13% filling of the SP1 lattice. Counting connected clusters characterized by the typical SP1 distance $11 \pm 1$ nm reveals that 33% of these NDs appear in the form of localized clusters that reflect the underlying SP1 template symmetry and distances. In particular, 27 can be found in pairs, six as triplets, two in a combination of four and a single octet, each representing non-overlapping clusters.

To further verify the crucial role of the underlying lattice for the structure formation, we have evaluated the probability of finding at least one seven ND hexagon, as depicted in figure 2(b) and part of the counted octet structure, and for a symmetric arrangement of four, respectively, based on the same number of NDs but in the absence of a SP1-lattice. Assuming the particles to be statistically independent with an equal probability in space, allowing for arbitrary rotations and a spatial uncertainty of $\pm 1$ nm, the probability of a seven ND cluster follows as $p_{\text{free}}^{(7)} \approx 10^{-10}$. Opposed to that, on a SP1-lattice structure and under the assumption that each ND randomly sticks to the center of a SP1-ring, the probability is given by $p_{\text{latt}}^{(7)} \approx 10^{-3}$. For the four ND combination $p_{\text{free}}^{(4)} \approx 10^{-3}$ and $p_{\text{latt}}^{(4)} \approx 0.44$. Here we have neglected the influence of filling effects, well justified in the low-density limit. The fact that the probabilities in the presence of a supporting lattice structure $p_{\text{latt}}^{(7)}$ and $p_{\text{latt}}^{(4)}$ are orders of magnitude larger than the ones for an undirected arrangement $p_{\text{free}}^{(7)}$ and $p_{\text{free}}^{(4)}$, respectively, provides further evidence for the successful ND-SP1 attachment.

Moreover, two references were used to ensure that the SP1 template is essential for achieving a uniform spacing between adjacent NDs. The first sample has been prepared without the SP1 template and contained only adsorbed NDs, in which case only irregular ND aggregates and no individual NDs were observed in the transmission electron microscope (TEM) measurements, supported by the absence of a pattern in the fast Fourier transform (FFT) image of the sample. This shows that in the absence of SP1 the NDs are attached randomly to the surface. In this sample no ordered pattern was observed. The second sample is with the SP1 template but without the NDs in which case we did not find any nano-particles on the sample.

In a different approach, small ND structures were also achieved using larger (average diameter 30 nm created by grinding) NDs. The ND clusters were formed by mixing solutions of NDs and SP1 under ambient conditions. The average number of NDs in such a complex can be controlled by the concentration ratio of SP1 to NDs. Mixing a 1 mg ml$^{-1}$ ND solution with a 1 mg ml$^{-1}$ SP1 solution at a ratio of 1 : 1 mainly leads to the formation of dimers and trimers and for even higher concentrations of SP1 large diamond clusters can be observed (figure 2(e)). As the NDs are larger than the SP1, the exact structure of the clusters is controlled by the ND shape as several SP1s will bind the NDs across a surface. To verify that the creation of the clusters is due to the binding with SP1 rather than electrostatic forces we have also followed the same procedure in the absence of SP1. In this case no ND clusters are observed.
3. Decoherence and dynamical decoupling

A key challenge for quantum computation and simulation with self-assembled arrays of NDs is that the currently achieved relatively short NV coherence times of a few microseconds in NDs [18, 23, 24] have to be compared to the typical coupling strength of several kHz between NV-centers in adjacent NDs [6, 25].

Several sources of noise influence the coherence time of NV-centers in NDs: the internal bath of impurity spins as P1 centers of nitrogen donors and C-13 carbon spins [24, 26, 27], surface spins and high frequency surface related noise components. The underlying mechanism of this latter contribution remains a subject of debate ranging from dangling bonds and dynamical strain to phonon induced electronic surface noise [24, 28–30].

In current experiments with NDs, coherence times are predominantly limited by the quasi-static internal spin noise, comparable in magnitude to bulk experiments with similar impurity concentrations [18, 23]. Upon combination with dynamical decoupling schemes [26, 31, 32], coherence times up to $T_2 \approx 67 \mu$s [23] have been reported for NDs. These rather poor coherence times, in particular in view of reported coherence times reaching milliseconds in bulk diamond [3, 24, 27], are a result of the typically low sample purity (type Ib diamond), that ensures a sufficient yield of NV-centers in NDs [23]. Motional averaging renders the impact of surface noise on the $T_2$-time small in such a regime compared to the low frequency internal bath of impurity spins.

However going towards isotopically pure (type IIa) diamonds, whose NV yield might be enhanced by nitrogen implantation and in addition exploiting the fact that low frequency noise can be efficiently decoupled, coherence times of milliseconds as observed in bulk sample experiments [3, 24, 27] can be expected from the internal noise source alone. In such a regime, which we will focus on in our analysis, surface noise will form the dominant source of decoherence. High frequency surface noise, hard to decouple due to its nanosecond correlation time, will provide an upper limit to the achievable coherence times.

Insight into the surface noise contribution, in particular as far as the high frequency part is concerned, can be inferred from recent $T_1$-relaxation time measurements. Note that the $T_1$-time imposes an upper bound for the achievable coherence time $T_2$ [22] (see appendix B.4). Those studies have revealed a significant reduction of $T_1$ with decreasing ND size [24, 33] or increasing NV-center proximity to the surface in bulk sample experiments [28, 30], as well as its sensitivity to different surface coatings [33, 34]. That way, reductions of the relaxation time $T_1$ by several orders of magnitude down to a few microseconds have been identified in nanoparticles opposed to typical bulk times of several miliseconds [28, 33]. However, also promising relaxation times of up to $T_1 = 1.2$ ms in $\sim 20$ nm [23] NDs and $T_1 \sim 9$ ms [28] for NV-centers as close as 5 nm to the surface have been reported recently. Such a noise, capable of affecting the population decay, requires significant spectral noise contributions at the NV-center zero-field splitting transition frequency, i.e. will be characterized by correlation times on the nanosecond scale [28]. Apart from $T_1$-relaxation, decay time measurements on continuously driven spin-lock configurations [28] on NV-centers $\leq 5$ nm from the surface suggest decoupled surface limited $T_2$ coherence times of up to 1–3 ms.

As a result of the sensitivity to different types of surface coating [33, 34], significant improvements of the coherence times can be expected by surface termination and functionalization, even though a complete elimination of the high frequency noise component seems to be beyond the scope of such techniques [28]. Replacing electronic spins associated
with the sp2-hybridization by less detrimental terminating elements allows for a significant T2-time elongation, as can be seen in our analysis of electronic surface spin noise in appendix D.

In the following, the decoherence properties of NDs are modeled as the combination of two independent noise sources with well-separated timescales. For this task we assume a fluorine termination of the ND surface, leading to a dense nuclear spin-1/2 bath with a nearest neighbor distance of 2.5 Å [35]. Besides replacing electronic surface spins associated with the carbon sp2-hybridization by less detrimental nuclear spins and in addition providing a well-defined spin bath model, fluorine coating is amongst the terminating elements leading to the lowest (high frequency) surface noise amplitudes [28]. Moreover it has been shown to stabilize the negative charge state of the NV-center [36]. This nuclear spin bath will provide the low frequency noise component that can be significantly suppressed by the application of decoupling schemes. On the other hand we have added a high frequency noise that, on the frequency scale considered here, will act essentially as white noise and provides an upper bound on the maximally achievable decoupled T2-coherence time in accordance with T1-time studies. Other internal spin noise sources will be neglected assuming a low impurity density compared to the dense surface nuclear spin bath and will be efficiently decoupled along with this latter noise source, thus not significantly affecting the presented results. For the noise decoupling we will assume a continuous resonant driving of the relevant qubit transition [6, 31, 32, 37], such that in a frame rotating with the resonant microwave frequency and after a reduction to the driven two level system the Hamiltonian can be expressed as

$$H = \frac{\tilde{b}(t)}{2} \hat{\sigma} + \frac{\Omega}{2} \sigma_z \quad \text{with} \quad \langle b_j(t)b_j(0) \rangle = b_j^2 e^{-\frac{t}{\tau}}.$$ (1)

Here the noise is modeled by the magnetic field frequency shift $\tilde{b}(t)$ with a root mean square amplitude of the jth component $b_j$ and a correlation time $\tau$. The decoupling field Rabi frequency is denoted by $\Omega$ and $\sigma_j$ operators refer to the Pauli spin-1/2 operators. The corresponding noise spectrum follows as

$$S_j(\omega) = \int_{-\infty}^{\infty} \langle b_j(t)b_j(0) \rangle e^{i\omega t} \, dt = \frac{2 b_j^2 \tau}{1 + \omega^2 \tau^2}$$ (2)

and is illustrated for both noise sources in figure 1(b). Here the fluorine terminated nuclear spin surface noise has been calculated for a spherical diamond with radius $r = 5$ nm based on the mean-field approach developed in [22] and outlined in more detail in appendix D. We thus expect a noise correlation time of $\tau_{\text{nucl}} = 2.5 \mu s$ and a mean square root amplitude $b_j^{\text{nucl}} = 2\pi \times 30.2$ kHz ($\tau \propto 1/(n^{3/2})$ and $b_j^2 \propto n^2 r$ with $n$ the surface spin density and $r$ the ND radius), that could be further improved by spin bath polarization and decoupling schemes [35, 38]. For the high frequency noise component we have chosen $\tau_{\text{hf}} = 0.28$ ns as identified in [28] and $b_j^{\text{hf}} = 2\pi \times 0.25$ MHz corresponding to single electronic impurities, which can be approximated by a white noise spectrum $S(\omega) \approx 2\pi \times 0.2$ kHz on the MHz frequency range under consideration. The total coherence time $T_2^{(\text{tot})}$ out of the two independent noise sources then follows as

$$T_2^{(\text{tot})} = \left[ \frac{1}{T_2^{(\text{nucl})}} + \frac{1}{T_2^{(\text{hf})}} \right]^{-1}$$ (3)

with $T_2^{(\text{nucl})}$ the nuclear spin bath related and $T_2^{(\text{hf})}$ the high frequency white noise part as illustrated in figure 1(b).
For the nuclear spin noise, assuming the relevant Markovian limit $t \gg \tau$ and $\Omega t > 1$, the decoherence decay rate $R(t)$ is determined by the noise spectrum $S(\omega)$ evaluated at the decoupling frequency, i.e. $R(t) = (1/2)S_\tau(\Omega)$. The more general formalism will be discussed in detail in appendix B [39]. This allows one to define an effective $T_2^{\text{nucl}}$-time of the system resulting in

$$T_2^{\text{nucl}}(\Omega) = \frac{1 + \Omega^2 \tau_{\text{nucl}}^2}{b^2 \tau_{\text{nucl}}^2} = T_2^{\text{nucl}}(\Omega = 0) \left( 1 + \Omega^2 \tau_{\text{nucl}}^2 \right)$$

for the Lorentzian noise spectrum under consideration. As shown in figure 1(b), this noise source can be efficiently decoupled with continuous driving fields with MHz Rabi frequency amplitudes reaching a coherence time of $T_2^{\text{nucl}} = 2.5 \text{ ms}$ for $\Omega = 1 \text{ MHz}$.

On the other hand the high frequency noise component is to a good approximation insensitive to decoupling fields in the considered frequency range, providing an upper limit $T_2^{\text{hf}} \approx 1.4 \text{ ms}$ to the maximally achievable coherence time. This follows out of [28, 33, 40] (see appendix B.4)

$$\left( T_2^{\text{hf}} \right)^{-1} = \frac{1}{2} S_\tau^{\text{hf}}(\Omega) + \frac{3}{4} S_y^{\text{hf}}(\omega_0) \approx \frac{1}{2} S_\tau^{\text{hf}}(\Omega) \approx \frac{1}{2} S_y(0) = \left( \frac{h_y^{\text{hf}}}{b} \right)^2 \tau^{\text{hf}} = (1.4 \text{ ms})^{-1}$$

with $\omega_0$ the energy level difference of the uncoupled system. Here we have used that the noise is uncorrelated on the relevant timescale together with $S_\tau(\omega) \gg S_\tau^{\text{hf}}(\omega_0)$ and the white noise character $S_\tau^{\text{hf}}(\omega) \approx S_y(0)$.

In experiments it is possible to achieve much higher decoupling fields up to $\Omega \approx 300 \text{ MHz}$ such that even a small number of electron spins can be decoupled (for a discussion of electron spin noise see appendix D). Importantly, decoherence due to intensity fluctuations of the decoupling field can be suppressed by using a concatenated decoupling scheme as proposed in [32].

4. Engineering of interactions, spin gates and quantum simulation

4.1. Dipolar coupling and decoupled gates

Dipolar interactions between electron spins of two adjacent NV-centers provide a possibility for implementing gate operations [5, 6]. Combined with the continuous driving of the decoupling field, the total effective Hamiltonian in a frame rotating with the microwave frequency of the driving field can be written as (see appendix C)

$$H' \approx \sum_i \frac{b_i(t)}{2} \sigma^i_\zeta + \sum_i \frac{\Omega_i}{2} \sigma^i_\chi + \sum_{i>j} \frac{J_{ij}}{2} \sigma^i_\zeta \sigma^j_\zeta.$$  

Herein the first two parts describe the dephasing noise and decoupling for the individual NV-centers as introduced in the previous section, respectively. The last part accounts for the dipolar coupling with $J_{ij} = 2 \xi_{ij} \mu_{ij}$, where $\xi_{ij}$ depends on the external magnetic field strength $|\vec{B}|$ and its orientation with respect to both the NV symmetry axes and the vector $\vec{r}_{ij}$ connecting NV-center $i$ and $j$. In the limit of high magnetic fields $\xi_{ij} = 1/4(1 - 3 \cos^2 \theta_{ij})$, where $\theta_{ij} = \angle(\vec{r}_{ij}, \vec{B})$ and $\mu_{ij} = \mu_0 \gamma_{el} \hbar / (4\pi r_{ij}^3)$ with the latter being $\mu_{ij} = 52 \text{ KHz}$ for an NV-center distance $r_{ij} = 10 \text{ nm}$. $\mu_0$ and $\gamma_{el}$ denote the magnetic permeability and the electron gyromagnetic ratio, respectively. It is important to note that the configuration of NDs leads to a random relative orientation of the
NV symmetry axes in space, the latter forming a ‘natural’ quantization axis along the N–V direction by the associated crystal-field splitting of the ground state triplet \(D \sim 2.87 \text{ GHz}\) (see figure 1(a)). This leads to two important consequences: first, a uniform quantization axis has to be defined by a sufficiently strong external magnetic field to guarantee a uniform dipolar coupling, as illustrated in figure 1(c) together with its optimal 2D-orientation. As shown in the figure, this can be achieved applying a magnetic field \(B \gtrsim 0.5 \text{ T}\) \((\gamma_\text{e} B/(2 \pi) \gtrsim 14 \text{ GHz})\), in which case the magnetic energy shift dominates over the crystal-field splitting \((\gamma_e B \gg D)\). Second, the crystal-field splitting is responsible for an orientation dependent transition frequency in that regime, depending on the angle between the symmetry axis and the external field \(\theta_i\) and scaling as \(\alpha D \cos 2\theta_i\). As a consequence, the transition frequencies of individual NV-centers differ by typical values of several 100 MHz, thus providing the possibility for individual microwave addressing for the values of \(\Omega\) obtained from figure 1 and at the same time maintaining a uniform dipolar coupling interaction. Moreover these inhomogeneous energy splittings justify the omission of dipolar flip-flop interaction terms in (6), that would not be energy conserving in our setup. As a remark, spin-mixing in the ground state triplet by magnetic fields not aligned with the symmetry axis, reduces both the contrast of optical spin readout and the spin initialization efficiency by optical cycling [41]. This might be overcome by projective readout techniques [42] and spin initialization at low magnetic fields followed by an adiabatic increase of the field amplitude.

Combining the dipolar interaction with decoupling suppresses the environmental coupling, i.e. decoherence, but also part of the gate interaction, a general problem in the application of decoupling sequences. We will consider that effect for two distinct decoupling configurations: \(M_1\), corresponding to a homogeneous decoupling field \(\Omega_i = \Omega\), and \(M_2\) corresponding to \(\Omega_i = -\Omega_j\) for \(i \in \text{neighb}(j)\). These will turn out to provide crucial gate interactions and in addition their combination allows one to restore the original form of the dipolar coupling as will be discussed in section 4.2. The effective interaction in the presence of decoupling is best seen by transforming the original Hamiltonian

\[
H_{M_k} = H_{M_k}^0 + H_{\text{dip}},
\]

wherein \(H_{\text{dip}}\) denotes the dipolar part and \(H_{M_k}^0\) the continuously driven system in the decoupling configuration \(M_k\), to an interaction picture with respect to the driving, which in the relevant limit \(\Omega \gg J_{ij}\) results in

\[
H_{I,M_k} = e^{+iH_{M_k}^0 t} H_{\text{dip}} e^{-iH_{M_k}^0 t} \approx \frac{1}{2} \sum_{(i,j)} J_{ij} S_{\text{dip}}^{ij}.
\]

Here the Hamiltonian has been restricted to nearest neighbor interactions, i.e. \((i, j)\) sums over neighboring NV-centers, and the effective interactions take the form

\[
S_{M_1}^{ij} = s^+_i s^+_j + \text{h.c.}
\]

\[
S_{M_2}^{ij} = s^+_i s^+_j + \text{h.c.},
\]

taking into account that the off-resonant contributions are suppressed as the decoupling field and dipolar coupling are well-separated in frequency. \(s^+_\pm = 1 + \langle \pm | 1 \rangle\) and \(s^-_\pm = 1 - \langle \pm | 0 \rangle\) are the ladder operators in the \(\sigma_z\)-eigenbasis \(| \pm \rangle = 1/\sqrt{2} (| 1 \rangle \pm | 0 \rangle)\), related to the ladder operators \(\sigma_z\) in the standard \(\sigma_z\)-eigenbasis by \(s^+_\pm = U \sigma_z U^\dagger\) with \(U = \exp (-i\pi/4\sigma_z)\). These basic interactions are illustrated in the inset of figure 3(a) for a two qubit interaction.
The two qubit setting is shown in figures 3(a–b), illustrating the fidelity and time evolution to create a maximally entangled state by a $\pi/2$ and $5\pi/2$ two qubit rotation in the $\mathcal{M}_1$ manifold leading to a maximally entangled state. Here we have assumed an initial state $|++\rangle$ with the final fidelity referring to the perfect evolution out of (8). The numerical simulations have been performed in the rotating frame (6) with the noise processes simulated as described in D.2. Inset: Energy levels and dipolar coupling for the different decoupling configurations $\mathcal{M}_1$ and $\mathcal{M}_2$. (b) State population versus time for zero decoupling (dashed) and $\Omega = 1.5$ MHz (solid). The former case leads to a maximally mixed state. (c) Fidelity versus systematic error $\epsilon$, quantifying the relative deviation of the actual dipolar coupling $J'$ from the anticipated dipolar coupling strength $J$, i.e. $J' = J(1 + \epsilon)$, for a $\pi/2$ rotation with (red) and without (blue) applying the error compensation sequence for a decoupling field $\Omega = 1.5$ MHz (continuous) and $\Omega = 0.7$ MHz (dashed). The noise parameters are given in figure 1 and $J = J_{12} = 26$ kHz corresponding to the configuration in figure 1(c) for $\eta_2 = 10$ nm.

Figure 3. Two qubit gates. (a) Fidelity versus decoupling field strength for a two qubit gate interaction and a $\pi/2$ and $5\pi/2$ rotation in the $\mathcal{M}_1$ manifold leading to a maximally entangled state. Here we have assumed an initial state $|++\rangle$ with the final fidelity referring to the perfect evolution out of (8). The numerical simulations have been performed in the rotating frame (6) with the noise processes simulated as described in D.2. Inset: Energy levels and dipolar coupling for the different decoupling configurations $\mathcal{M}_1$ and $\mathcal{M}_2$. (b) State population versus time for zero decoupling (dashed) and $\Omega = 1.5$ MHz (solid). The former case leads to a maximally mixed state. (c) Fidelity versus systematic error $\epsilon$, quantifying the relative deviation of the actual dipolar coupling $J'$ from the anticipated dipolar coupling strength $J$, i.e. $J' = J(1 + \epsilon)$, for a $\pi/2$ rotation with (red) and without (blue) applying the error compensation sequence for a decoupling field $\Omega = 1.5$ MHz (continuous) and $\Omega = 0.7$ MHz (dashed). The noise parameters are given in figure 1 and $J = J_{12} = 26$ kHz corresponding to the configuration in figure 1(c) for $\eta_2 = 10$ nm.

The two qubit setting is shown in figures 3(a–b), illustrating the fidelity and time evolution to create a maximally entangled state by a $\pi/2$ and $5\pi/2$ two qubit rotation in the $\mathcal{M}_1$-coupling manifold, respectively. Note that the required time for the latter case exceeds $T_2(\Omega = 0)$ by more than a factor of three, therefore impressively demonstrating the decoupling that allows for a 95% final state fidelity with a decoupling field of $\Omega = 1.5$ MHz.

4.2. Restoring the original Ising-type dipolar coupling form

In contrast to these simple two qubit examples, recovering the full dipolar Ising-type interaction form, that is the $\sigma_z \otimes \sigma_z$-type coupling appearing in (6), marks a crucial step towards the realization of a universal set of quantum gates. Its importance is reflected in a wide range of applications such as the creation of cluster states for quantum computation or in quantum simulations, both discussed in the upcoming sections 4.3 and 4.4.

The Ising-type interaction, originally altered and partially suppressed by the decoupling field, cannot be recovered by any local operation out of the reduced decoupled manifold interactions $H_{I,\mathcal{M}_1}$. However the decoupled dipolar interaction contributions $H_{I,\mathcal{M}_2}$ and $H_{I,\mathcal{M}_3}$,
corresponding to the two different decoupling field settings, can be added in time in order to recover the full dipolar interaction form based on the observation

\[ H_{zz} = H_{I,M_1} + H_{I,M_2} = \sum_{(i,j)} (J_{i,j}/2) \sigma_i^j \sigma_z^j \text{.} \quad (10) \]

In the Trotter \((11a)\) or Suzuki–Trotter \((11b)\) formalism this can be performed by

\[
\exp(-i H_{zz} t) = \left[ R_{M_1} \left( t/(2n) \right) R_{M_2} \left( t/n \right) \right]^n + \mathcal{O}\left( \left( J_{ij}/n \right)^2 \right) \quad (11a) \\
\exp(-i H_{zz} t) = \left[ R_{M_1} \left( t/(2n) \right) R_{M_3} \left( t/(2n) \right) \right]^n + \mathcal{O}\left( \left( J_{ij}/n \right)^3 \right) \quad (11b)
\]

with \( R_{M_i} (t) = \exp(-i H_{I,M_i} t) \). The switching frequency between the two types of interactions \( M_1 \) and \( M_2 \), or equivalently the maximal magnitudes of the addition sequence time intervals \( t/n \) that still provide sufficiently low errors, depend crucially on the Hamiltonian timescales. For the addition of the effective (interaction frame) Hamiltonians \( H_{I,M_k} \) as following out of \((10)\), this timescale is determined by the rather small \((\text{kHz})\) dipolar coupling frequency. In contrast, a time addition directly based on \((7)\) as could be obtained by the two purely global \( \pi \)-phase shifted decoupling configurations \( M_1 \) and \( M_3 \), the latter defined by \( \Omega_i \equiv -\Omega \), would have to be based on the much higher \((\text{MHz})\) magnitudes of the decoupling field Rabi frequency \( \Omega \). Even though this would recover the pure dipolar coupling, at the same time the decoupling field sign inversion on a timescale \( \tau \lesssim 1/\Omega \) would effectively average out the decoupling effect. Therefore this is not a viable approach and we will focus on the implementation \((10)\) instead. As the effective Hamiltonians \( H_{M_1} \) and \( H_{M_2} \) are the result of distinct, non-commuting interaction frames \( [H_{M_1}^0, H_{M_2}^0] \neq 0 \), each pulse has to be carefully adjusted for their implementation and will be discussed in the following.

Recalling the interaction picture definition, its time evolution can be created by the evolution sequence

\[
R_{M_i} (t) \equiv e^{-i H_{I,M_i} t} = e^{i H_{M_i}^0 t} e^{-i H_{M_i}^0 t} \equiv E_{M_i} (t) U_{M_i} (t) \quad (12)
\]

with \( U_{M_i} (t) = \exp(-i H_{M_i} t) \) and \( E_{M_i} (t) = \exp(i H_{M_i}^0 t) \). Three options can be exploited in order to create \((12)\).

1. Directly implementing the pulse sequence by applying fast local microwave pulses in order to implement \( E_{M_i} (t) \). Such local manipulations are feasible as they can be implemented on much faster timescales as opposed to the rather slow \((\text{kHz})\) dipolar coupling dynamics.

2. Adjusting the total time by making use of the vastly different timescales of the decoupling field \( \Omega \) and the dipolar interaction \( J_{ij} \) both appearing in the Hamiltonian \( H_{M_i} \). That is, on short timescales \( \Delta t \ll J_{ij}^{-1} \), the dipolar part characterized by kHz frequencies can be neglected compared to the MHz evolution of the decoupling field, such that \((12)\) can be implemented to a good approximation by a simple time adjustment. This is based on two observations, namely that \( \exp( i \Omega /2 \sigma_i t) = \exp(- i \Omega /2 \sigma_i t') \) with the ‘short’ time \( t' = (2 \pi - \text{mod} \left[ \Omega t, 2 \pi \right]) / \Omega \) determined by the fast decoupling field frequency scale,and that on such a timescale \( E_{M_i} (t') \approx U_{M_i} (t') \). Therefore \((12)\) can be implemented by the time adjustment \( R_{M_i} (t) \approx U_{M_i} (t + t') \), applicable as long as the decoupling field is sufficiently strong \( \Omega \gg J_{ij} \).
Implementing echo pulses in order to remove the $E_{M_k}$ contribution, which changes the interaction picture evolution from the normal one according to (12). The application of local $\pi$-pulses $S_{\pi} = \exp\left( -i(\pi/2) \sum \sigma_i^z \right)$ either in the $z$ or $y$-direction ($k = z, y$), allows for the implementation of (12) by

$$R_{M_k}(t) = S_{\pi}^\dagger U_{M_k}(t/2) S_{\pi} U_{M_k}(t/2). \quad (13)$$

This follows out of the invariance of $H_{I,M_k}$ under such an echo pulse sequence, $S_{\pi}^\dagger H_{M_k}^0 S_{\pi} = -H_{M_k}^0$ and the commutation of both parts $[H_{I,M_k}, H_{M_k}^0] = 0$. Originating in the non-commutativity of $H_{I,M_k}$ and $H_{M_k}^0$ for $k \neq k'$ this echo pulse sequence has to be applied to each $M_k$ interaction separately and cannot be implemented globally on the total evolution sequence.

Based on the two qubit interaction (10) and the ability for local addressing and manipulations as a result of quantization axis dependent magnetic field level shifts, all other types of one and two qubit interactions can be implemented. This again benefits from the different timescales between the two-qubit dipolar interaction and the local microwave addressing. Therefore, local operations can be treated as instantaneous pulses with respect to the two qubit evolution timescale, which besides local operations allows one to change the interaction type to e.g. $\sigma_i^+ \sigma_j^+ = U_{c_{ij}} \sigma_i^z \sigma_j^z U_{c_{ij}}^\dagger$ with $U_{c_{ij}} = \exp\left( i \pi/4 (\sigma_i^+ + \sigma_j^+) \right)$. More complicated Hamiltonians can be implemented based on time additions (11a, 11b) as will be illustrated for a Heisenberg-chain Hamiltonian in section 4.4.

It is also worth noting that we have limited the previous discussion to next neighbor interactions in the dipolar coupling, and only in that case the form of Hamiltonians (10) and (8) is strictly valid. For short rotation angles and linear arrangements this forms a good approximation as can be seen in the upcoming simulations for the cluster state (figure 4(a)) and Heisenberg simulations (figure 5). However for higher dimensional arrangements and long time evolutions, higher-order couplings have to be removed by combining the time addition sequences with local pulses, which will be discussed in more detail in appendix E.3 and is performed in the 2D cluster state simulation depicted in figure 4(b).

### 4.3. Cluster state creation

An interesting application of the concepts developed in the preceding sections is the creation of cluster states. These highly entangled states, defined as the unique eigenstates of the multi-body generators $K^{(i)} = \sigma_i^z \otimes (_{i,j}) \sigma_j^z$ via the eigenvalue equation $K^{(i)} \left| \phi_C \right> = \left| \phi_C \right> \forall i$, allow one to perform any quantum computation operation by purely local measurements on individual qubits [43]. It has been shown [43] that the product of two-body phase gates $S$ applied to a specific initial product state allows for the creation of such an eigenstate, namely $| \phi_C \rangle = S \left| ++\cdots+ \right>$. The connection to the Ising Hamiltonian (10) that can be realized in the ND system proposed follows if we note that $S \approx \exp\left( -i \pi/4 \sum_{i,j} \sigma_i^z \sigma_j^z \right)$ up to local operations, the latter being implementable by fast microwave pulses on the electron spin manifold. Thus, the availability of the interaction creating the cluster resource state, combined with local addressing and the well-separated timescales of the microwave and dipolar interaction, makes the assembled ND system a promising candidate for cluster state computation implementations. Numerical simulations of the creation of one- and two-dimensional cluster states for different numbers of qubits and decoupling field strengths are shown in figure 4. For the one-dimensional case, qubit number
dependent fidelities between 80% and 90% and even above can be achieved, close to the noise-free limit imposed by non-next nearest neighbor couplings and errors. As expected, the fidelity decreases with the number of qubits involved, which both makes the state overlap to the perfect reference state more prone to deviations and increases the impact of errors. These fidelities could be further improved by removing non-nearest neighbor interactions upon integration of local pulses into the addition sequence as outlined in appendix E.3 and by decreasing the timesteps in the addition sequence, i.e. increasing $n$ in (11b). For the numerical simulations of the linear arrangement, a modest complexity of $n = 2$ has been chosen. Note however, that the timesteps $(t/n)$ in the addition sequence have to be sufficiently large, that is $\Omega (t/n) \gg 1$, in order for the effective Hamiltonian form (8) to be valid, i.e. significantly increasing $n$ requires one to increase the Rabi frequency $\Omega$ as well.

Figure 4(b) illustrates the fidelity for the creation of a 2D four qubit cluster state. As in that case, cross-diagonal non-nearest neighbor couplings are significant ($\sim 0.35$ of the nearest neighbor interaction), so they have been removed by a more involved addition sequence as illustrated in the lower part of figure 4(b). Herein the lowest level (i) assumes the creation of
(10) as described in section 4.2. Including the off-diagonal contributions this results in

$$H^{2D}_{zz} = \sum_{(i,j)} \frac{1}{\sqrt{2}} \sum_{<i,j>} 2 S_{M_i}^z$$

with $S_{M_i}$ as defined in (9a) and $(i,j)$ summing over nearest neighbors whereas $<i,j>$ accounts for off-diagonal couplings. By using that $U_i S_{M_i}^z U_i^\dagger = -S_{M_i}^z$ and $U_i \sigma_i^x \sigma_j^z U_i^\dagger = -\sigma_i^z \sigma_j^x$ for $U_i = \exp (-i\pi/2\sigma_i^x)$, a local application of $U_i$ pulses on selected (red marked) qubits allows one to remove cross diagonal couplings by the time-addition step (i) in figure 4(b). As this also removes part of the desired nearest neighbor Ising-type coupling, a second time addition (ii) serves to fix that issue. As a remark, such a combination of the addition sequence with local unitary operations can also serve to adjust and weight individual coupling components $J_{ij}$. The fidelity for the cluster state creation approaches 80% for such a sequence and a comparison to the noise-free case reveals that this is clearly limited by the coherence time. Note that the low fidelity for $\Omega \lesssim 0.2$ MHz in the noise-free (dashed) simulation arises from the effect that the effective Hamiltonian description (8) is only valid for sufficiently large Rabi frequencies, whereas the fidelity saturation value for $\Omega \gtrsim 0.5$ MHz reveals the error that can be ascribed to the time-addition implementation.

Figure 5. Heisenberg XXZ-chain with five qubits and $\delta = 1.5$. (a) The Hilbert–Schmidt norm distance for a Heisenberg chain time evolution of $t = \pi/(2J)$ (solid lines) is plotted versus the decoupling field Rabi frequency $\Omega$ and various repetitions $n_{cy}$ of the time addition sequence shown in (b). Dashed lines correspond to the fidelity of the pure $\sigma_i^x \otimes \sigma_j^y$ contribution, marked by the blue box in (b). Orange and lime-green lines are reference values that represent the noise-free and the noise-free case in the absence of non next-neighbor interactions, respectively. The numerical simulation is based on (6), the noise parameters of section 3 implemented as in D.2, local pulses ($U_i$) and the change of decoupling configurations have been assumed to happen instantaneously. The numerical simulation is based on (6), the noise parameters of section 3 implemented as in D.2, local pulses ($U_i$) and the change of decoupling configurations have been assumed to happen instantaneously. (b) Illustration of the addition sequence leading to the Heisenberg chain Hamiltonian based on the initial decoupled dipolar interactions $M_1$ and $M_2$. In the simulation (a) both additions have been performed by (11b) with $n = 1$. (Hilbert–Schmidt norm distance: $\text{tr} [(U' - U)^\dagger (U' - U)]$ with $U$ the perfect and $U'$ the imperfect realization.)
4.4. Heisenberg chain simulation

As a second application of the concepts developed in section 4.2, we have illustrated the possibility of simulating a Heisenberg-chain Hamiltonian of the form

\[ H = -\frac{1}{2} \sum_{j=1}^{N} J_{\mu} \sigma_{\mu} \sigma_{\mu+1} \]

with \( \mu = \{x, y, z\} \) and \( J_x = J_z = J, J_y = \delta J \) in figure 5. This task essentially requires three steps as depicted in figure 5(b): creating the \( \sigma_x \) contribution out of the basic decoupled interaction following the concept outlined in section 4.2, and mapping \( \sigma_z - \sigma_x \) by the unitary local pulse operation \( U_{\pi} \exp(-i \sum_j \pi/4 \sigma_y) \). Second, creating the \( S_{M_i} \sigma_y \) contribution, which directly corresponds to an effective decoupled interaction (8) and is therefore obtained in a trivial way. In a last step both contributions are added based on the Trotterization approach (11b) taking the weighting factor \( \delta \) into account. The accuracy of such a procedure is illustrated in figure 5(a) for a \( \theta = \pi/2 \) evolution. Significant improvements can be obtained by increasing the decoupling Rabi frequency. A comparison to noise-free simulations, revealing the effect of Trotterization and non-nearest neighbor errors, shows that the final fidelity is decoherence limited.

4.5. Compensation of systematic errors

Distance variations between adjacent vacancy centers and different orientations of the symmetry axes make it hard in practice to guarantee a uniform coupling. Therefore the coupling coefficient \( J_{ij} \) appearing in \( H_{M_1} \) (8) and \( H_{M_2} \) (10) may be replaced by \( J(1 + \epsilon_{ij}) \) with \( \epsilon_{ij} \) describing the systematic error from the optimal case. However, extending the concepts provided in [44] allows one to construct compensation sequences as will be discussed in detail in appendix E, provided that the error \( \epsilon_{ij} \lesssim 0.5 \) and that non-nearest neighbor couplings can be efficiently suppressed, as discussed in appendix E.3. We analyzed the compensation method for the two qubit case in figure 3(c) and applied it to a four qubit cluster state in figure E1. Due to the significantly increased time, that is eight and sixteen times the original gate operation, respectively, the region of benefit increases with the decoupling field strength provided that it exceeds a threshold magnitude. As expected the two qubit gate compensation is more efficient providing good results already for a 1.5 MHz decoupling field in contrast to the multiqubit counterpart that relies on a more general sequence less efficient in time.

5. Summary

In summary, we proposed a new method to create scalable arrangements of NV-centers in diamond by exploiting the ability of biological systems for self-assembly along with the precise positioning of surface functionalized NDs in such structures. We experimentally realized and verified the creation of ordered ND structures on a protein scaffold, namely on a SP1 monolayer, as well as the SP1-assisted formation of ND clusters in solution. Based on the achievable NV distances on the nanometer scale we proposed and analyzed theoretically the implementation of single and multiqubit gates and demonstrated their application for the creation of cluster states, thereby addressing the typical problems as the limited coherence time and heterogeneous dipolar coupling strengths. Moderate decoupling fields around 1 MHz, well within reach of current experimental setups, allow for efficient decoupling from surface spin noise. Along with significant dipolar couplings of several tens of kHz and the viability of individual addressing, gate fidelities above 90% can be expected even for multiple qubits and
imperfect couplings. We believe that the combination of NDs with biological systems provides a promising approach towards scalability, overcoming the limitations of current attempts and offering a high level of control in the structure formation.

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Appendix A. SP1 protein complex and experimental details

One remarkable aspect of biomolecules is their ability to recognize a wide range of substances with a high degree of specificity. This feature of biomolecules has been extensively explored and a variety of artificial peptide aptamers, which specifically recognize various inorganic materials, have been created by selecting binders from random arrays of amino acids displayed on phages or bacteria (combinatorial biological method) [45–49]. SP1 is a thermally stable protein, originally isolated from poplar trees [50], which self-assembles to an 11 nm ring-shape dodecamer (12-mer). The protein is exceptionally stable under extreme conditions, being resistant to proteolysis, high temperatures, organic solvents and high levels of ionic detergent [51, 52].

The SP1 multivalency allows the display of 12 binding sites on each protein complex in its N-termini, resulting in a stable and strong binding agent. Various known peptide aptamers were fused to SP1 in the past. The peptide aptamers were fused to the N-termini of the SP1 via genetic engineering methods. A library of SP1 variant was constructed, consisting of tailored SP1 proteins with specific binding capabilities. These included gold, silicon dioxide, titanium dioxide, nickel, and copper.

A12 amino-acid carbon nano tube (CNT) binding peptide was identified and isolated by Kase et al, using the M13 phage display library [46]. This peptide was genetically fused in-frame to SP1 N-Termini. The gene construct was then transformed into BL-21 Escherichia coli cells for further expression and purification of the protein. The new fusion protein consisted of 12 CNT binding sites, six on each side of the ring. This enabled the creation of SP1 variants which tightly bind to CNTs to form a stable SP1/CNT complex [19]. In this work we used the same SP1 variant to attach and order the ND structures. The carbon sp2-hybridization formed on the surface of the NDs was used to link the NDs. In the case of passivated NDs, the strong connection of the binding group to sp2-hybridization should exchange the passivating groups.

Formation of small ordered nanoparticle areas on a SP1 monolayer is performed using the Langmuir–Blodgett method [21]. In this method a trough is filled with a subphase solution that
contains the SP1 proteins and by adding glucose to the subphase solution the SP1 floats to the solution–air interface. Then, by slowly reducing the interface surface area, the SP1 are forced to compress to a point where they become a monolayer. The SP1 monolayer is transferred to a substrate and washed with distilled water to remove excess salts from the subphase solution. In figure A1 (a) an AFM scan of a SP1 layer on a silicon chip with a scratched area is shown. By measuring the height difference between the silicon chip’s surface (scratched area) and the rest, we verified the existence of a monolayer of height 2 nm, which corresponds to the height of the SP1 protein on a Si surface [53]. In a second stage the substrate with the SP1 array is inserted into a beaker with nanoparticle solution on an orbital shaker, and afterwards it is washed and dried. In addition to NDs, experiments with gold particles (5 nm nanoparticles from Sigma

Figure A1. (a) AFM scan and line profile (inset) of a dense monolayer of CNT binding SP1 with a scratched area. (b) Small ordered area of 5 nm gold nanoparticles on a SP1 monolayer formed by the Langmuir–Blodgett method. The periodicity is observed to be 11 nm, equal to the diameter of the SP1. Alongside the nanoparticles we still have salt particles (the bigger particles), which damage the order and periodicity of the array. The samples were scanned by scanning electron microscopy (Extra High Resolution Scanning Electron Microscopy MagellanTM 400L).

Figure A2. Electron diffraction image and TEM image of the area where the image was taken.
Aldrich) have been performed. In that case small ordered areas have been achieved (see figure A1(b)); while long range order is missing. As for NDs (5 nm produced by laser ablation from Ray Techniques Ltd) the excess salts were sufficiently removed by cleaning.

In order to confirm that the particles (shown in figure 2) are indeed NDs, electron diffraction measurements have been performed on the sample in the relevant areas. The measurements were taken by the TEM Tecnai T12 G2 Spirit. The measured diffraction (1, 1, 1) lattice parameter results in 2.08 Å and the (2, 2, 0) lattice parameter is 1.26 Å. This agrees well with the corresponding diamond lattice parameters known from the literature and given by 2.04 Å for (1, 1, 1) and 1.25 Å for (2, 2, 0) [54] (see figure A2).

2D-FFT was performed on the area surrounding the seven ND hexagon image. As a result of disorder the Fourier analysis was performed on a small domain size of the sample. There is no long range order due to dislocations of the SP1 lattice. We chose an area with 16 NDs surrounding the hexagon. To reduce noise and the influence of the irregular ND shapes, we took only the center coordinates of each measured ND (figure A3(a)). The FFT shows a hexagonal lattice structure with periodicity of $\pm 0.090 \pm 0.005 \text{ nm}^{-1}$, which results in a periodicity of $\pm 11.1 \pm 0.6 \text{ nm}$ in the image space (figure A3(b)). As a reference, 2D-FFT was also performed on a partially filled rotated hexagonal lattice with a fixed period of 11 nm (figure A3(c)). The location of particles in the reference image was chosen to be the closest to the particles in the real image. The resulting Fourier transform image (figure A3(d)) is similar to the experimental image (figure A3(b)).

The formation of the larger (average ND size 30 nm created by grinding) ND complexes, as shown in figure 2(e) of the main text, was achieved by mixing 50 μL of 1 mg ml$^{-1}$ of the SP1 solution with 50 μL of 1 mg ml$^{-1}$ of the 30 nm NDs solution. To the mixture we added 900 μL of distilled water. 10 μL of the final solution was applied on a silicon chip and scanned by scanning electron microscopy (Extra High Resolution Scanning Electron Microscopy MagellanTM 400L).

**Figure A3.** (a) ND image built from the coordinates of the NDs in the inset. (b) 2D-FFT of (a): the inset is a cross section over 5 points, giving an average peak distance of $\pm 0.090 \pm 0.005 \text{ nm}^{-1}$, which results in a periodicity of $\pm 11.1 \pm 0.6 \text{ nm}$. (c) Reference of a partially filled hexagonal lattice with a fixed period of 11 nm. (d) 2D-FFT of (c).

**Appendix B. Dynamical decoupling and the filter-spectrum overlap approach**

The effect of dynamical decoupling or more precisely the decoherence decay rate of a decoupled system can be described in terms of a filter function overlap, representing the effect
of the decoupling field, with the noise spectrum [39, 55, 56] (see figure B1). This allows for a very illustrative analysis and description of the working principles of dynamical decoupling methods. The only restriction in the perturbative derivation below arises from the assumption of the weak coupling limit that requires the coherence time $T_2$ to be large compared to the noise correlation time $\tau$, which is generally fulfilled for the parameters considered here. Moreover, the expressions are exact in any limit for the free induction decay and pulsed decoupling schemes provided that the noise is Gaussian as can be easily checked by comparing the final expressions with those derived in a non-perturbative way in e.g. [22]. A summary of the formulas will be given in section appendix B.3. Finally, the uncorrelated limit and the relation of the coherence time to the $T_1$-relaxation time will be addressed in appendix B.4.

### B.1. Decoherence decay rate

Consider a two level system evolving under the Hamiltonian (in the rotating frame)

$$H = \hbar \frac{b(t)}{2} \sigma_z + \frac{\Omega(t)}{2} \sigma_x$$

with $b(t)$ a random, zero-mean fluctuating detuning describing the effect of pure dephasing and originating from the environmental coupling and $\Omega(t)$ the classical control decoupling field. We will assume that the system is initially ($t_0 = 0$) prepared in the state

$$|\psi_\phi\rangle = \frac{1}{\sqrt{2}} \left( |e\rangle + e^{i\phi} |g\rangle \right),$$

then, after a time $t$ the probability for still finding the system in that initial state is given by

$$\langle \psi_\phi | \rho | \psi_\phi \rangle = \frac{1}{2} \left( 1 + \cos^2\phi \ e^{-\text{R}_1(t)t} + \sin^2\phi \ e^{-1/2(\text{R}_1(t)+\text{R}_2(t))t} \right),$$

describing purely the effect of decoherence and not taking the coherent evolution into account (see figure B2). The decay rates appearing in appendix B.3 can be expressed as
∫ω = −∞∞ R t tπ SF() 1 2 1 2 () () d (B.4)

with S(ω) = ∫−∞∞ exp (−iωτ)(b(t)b(t + τ))dτ the noise spectrum and F_k(ω) a decoupling field dependent filter function (see figure B1). Exact expressions can be found in appendix B.3.

In the limit of \( t \gg \tau \) and \( \Omega t > 1 \) and for a constant \( \Omega \), \( R_y(t) \approx 1/2 S(\Omega) \) and \( R_x(t) \approx 0 \) (more precise \( R_y(t) \approx R_x(t) \)). The coherence decay in time (B.3) takes the form

\[
\langle \psi^\rho | \rho | \psi^\rho \rangle = \frac{1}{2} \left( 1 + \cos^2 \phi e^{-R_y t} + \sin^2 \phi e^{-1/2 R_x t} \right) \quad \text{with} \quad R_y = \frac{1}{2} S(\Omega). \tag{B.5}
\]

This has a clear interpretation in that the first part (the \( \sigma_x \) eigenstate decay) is related to a population decay whereas the second part (the \( \sigma_y \) eigenstate decay) corresponds to a decay of the corresponding coherences, a process that happens in the Markovian limit \( t \gg \tau \)—also characterized by a time independent decay rate—with half of the population decay rate. In the non-Markovian limit the decay rate of the coherence contributions is increased by an additional factor \( R_y(t) \). Note also that for the case of free induction decay, i.e. \( \Omega = 0 \), \( R_y(t) = R_x(t) \) and thus both decay contributions are equal as expected by the isotropy of the system.

### B.2. Decay rate derivation

Following the description in [39, 55] we will derive the general decoherence decay formula (B.3). It is advantageous to evaluate the decoherence behavior in the \( \sigma_z \) eigenbasis \( \{ \pm \} \) in which the effect of the decoupling field can be interpreted as creating an energy gap suppressing flipping processes by the (off-resonant) detuning fluctuations. Using the Nakajima–Zwanzig projection operator approach [57] allows one to obtain a master equation for the system interacting with a noise bath up to second order in the coupling constant for the evolution under (B.1)[39]

\[
\frac{d \rho}{dt} = -\frac{i}{\hbar^2} \int_0^t dt' \phi(t - t') [S(t'), S(t')\rho(t')] + \text{h. c.} \tag{B.6}
\]

with \( \phi(t - t') = \langle b(t)b(t') \rangle_0 \) and \( \sigma_z = \exp \left( i \int_0^t \Omega(t')/2 dt' \sigma_z \right) \) \( \sigma_z \) the \( \sigma_z \) operator in the interaction.
picture with respect to the decoupling field. It turns out that coherences and populations are decoupled in the differential equation expressed in the $\sigma_z$-basis states leading to $(\rho_{ij} = \langle \phi | \rho | \phi \rangle)$.

$$\frac{d}{dt} \left( \rho_{++} - \rho_{--} \right) = -\frac{1}{2} \gamma_1(t) \left( \begin{array}{cc} 1 & -1 \\ -1 & 1 \end{array} \right) \left( \rho_{++} - \rho_{--} \right),$$  \hspace{1cm} (B.7)

wherein (see definitions in section appendix B.3, $U = \exp \left( i \int_0^t \Omega(t) \, dt \right)$, $R$ denotes the real part)

$$\gamma_1(t) = \int_0^t dt' \phi(t - t') R \left[ U(t) U^\dagger(t') \right], \quad R_x(t) = \frac{1}{t} \int_0^t dt' \gamma_1(t') dt'$$  \hspace{1cm} (B.8)

leading to the solutions

$$\rho_{++}(t) = \frac{1}{2} \left[ (2 \rho_{++}^0 - 1) e^{-R_x(t)t} + 1 \right], \quad \rho_{--}(t) = \frac{1}{2} \left[ (2 \rho_{--}^0 - 1) e^{-R_x(t)t} + 1 \right].$$  \hspace{1cm} (B.9)

On the other hand, the differential equation for the coherences takes the form

$$\frac{d}{dt} \left( \rho_{+-} - \rho_{-+} \right) = -\frac{1}{2} \left( \gamma_1(t) + \gamma_2(t) \int \left( \mu_1(t) - \mu_2(t) \right) \gamma_1(t) - \gamma_2(t) \right) \left( \rho_{+-} - \rho_{-+} \right)$$  \hspace{1cm} (B.10)

with the additional definitions (herein $R$ denotes the real and $I$ the imaginary part)

$$\gamma_2(t) = \int_0^t dt' \phi(t - t') R \left[ U(t) U^\dagger(t') \right], \quad R_y(t) = \frac{1}{t} \int_0^t dt' \gamma_2(t') dt'$$

$$\mu_1(t) = \int_0^t dt' \phi(t - t') I \left[ U(t) U^\dagger(t') \right], \quad \mu_2(t) = -\int_0^t dt' \phi(t - t') I \left[ U(t) U(t') \right].$$  \hspace{1cm} (B.11)

As will be seen later, the combination $\rho_{+-} - \rho_{-+}$ is responsible for the decay of coherences in the density matrix description. Moreover it is straightforward to show that the off-diagonal elements (the $\mu$-terms) are related to a coherent evolution whereas the diagonal elements describe the decay terms of the corresponding quantities. Since we are not interested in the coherent evolution it is possible to set those off-diagonal contributions to zero resulting in a description of the envelope decay of the quantities. Therefore one ends up with

$$(\rho_{+-} - \rho_{-+})(t) = e^{-1/2 \left( R_x(t) + R_y(t) \right)} \left( \rho_{+-} - \rho_{-+} \right)(0).$$  \hspace{1cm} (B.12)

Now consider the arbitrary phase state (B.2) that can be expressed in the $| \pm \rangle$ basis as (neglecting a global phase factor)

$$| \psi_\phi \rangle = \cos (\phi/2) | + \rangle + i \sin (\phi/2) | - \rangle, \quad \rho_0 = | \psi_\phi \rangle \langle \psi_\phi |.$$  \hspace{1cm} (B.13)

Using (B.9) and (B.12), the density matrix after a time evolution of $t$ follows to be

$$\rho(t) = | + \rangle \langle + | + \frac{1}{2} \left[ \cos \phi e^{-R_x(t)t} + 1 \right] + | - \rangle \langle - | + \frac{1}{2} \left[ - \cos \phi e^{-R_x(t)t} + 1 \right]$$

$$- (i/2) | + \rangle \langle - | + | + \rangle \langle - | + | - \rangle \langle + | \sin \phi e^{-1/2 \left( R_x(t) + R_y(t) \right)}.$$  \hspace{1cm} (B.14)

Knowing the density matrix time evolution it is straightforward to calculate the decay rate of the initial state $| \psi_\phi \rangle$ towards the completely mixed state $\rho_{\text{mixed}} = 1/2 ( | + \rangle \langle + | + | - \rangle \langle - |)$ and the probability for finding the system in the initial state after a time $t$. New J. Phys. 16 (2014) 093002 A Albrecht et al
\[
\text{tr} \left( \left| \psi_\phi \right\rangle \left\langle \psi_\phi \right| \rho(t) \right) = \left\langle \psi_\phi \right| \rho \left| \psi_\phi \right\rangle = \frac{1}{2} \left( 1 + \cos^2 \phi \ e^{-R_{r(t)}} + \sin^2 \phi \ e^{-1/2(R_{r(t)}+R_{r(t)})} \right) \quad \text{(B.15)}
\]

which corresponds exactly to the result given in (B.3).

B.3. Decay rates, filter functions and definitions

B.3.1. Decay rate and general filter function formula

\[
R_i(t) = \frac{1}{2} \frac{1}{t} \int_{-\infty}^{\infty} S(\omega) F_i^j(\omega) d\omega \quad \text{(B.16)}
\]

with

\[
S(\omega) = \int_{-\infty}^{\infty} e^{-\omega \tau} \langle b(t) b(t + \tau) \rangle \ d\tau \quad \text{(B.17)}
\]

and

\[
F_i^x(\omega) = \left| \int_0^t e^{-i \omega \tau} \cos \left( \int_0^t \tau \Omega(\tau) \right) d\tau' \right|^2 + \left| \int_0^t e^{-i \omega \tau} \sin \left( \int_0^t \tau \Omega(\tau) \right) d\tau' \right|^2
\]

\[
F_i^y(\omega) = \left| \int_0^t e^{-i \omega \tau} \cos \left( \int_0^t \tau \Omega(\tau) \right) d\tau' \right|^2 - \left| \int_0^t e^{-i \omega \tau} \sin \left( \int_0^t \tau \Omega(\tau) \right) d\tau' \right|^2 .
\]

B.3.2. Specific filter functions

- Free induction decay (\(\Omega = 0\))

\[
F_i^x(\omega) = F_i^y(\omega) = \frac{4 \sin^2 \left( \frac{\omega t}{2} \right)}{\omega^2} \quad \text{(B.18)}
\]

\[
\lim_{t \to \infty} F_i(\omega) / (2\pi t) = \delta(\omega), \quad \lim_{t \to \infty} R_i(t) = \lim_{t \to \infty} R_j(t) = \frac{1}{2} S(0) .
\]

- Continuous control field (\(\Omega = \text{const.}\))

\[
F_i^x(\omega) = \frac{1}{2} t^2 \left[ \text{sinc}^2 \left( \frac{\omega - \Omega}{2} t \right) + \text{sinc}^2 \left( \frac{\omega + \Omega}{2} t \right) \right] \quad \text{(B.19)}
\]

\[
F_i^y(\omega) = \frac{2 \cos (\Omega t) (\cos (\Omega t) - \cos (\omega t))}{\omega^2 - \Omega^2} . \quad \text{(B.20)}
\]

Markovian limit: \(t \gg \tau, \Omega t > 1\)

\[
\lim_{t \to \infty} F_i^x(\omega) / (2\pi t) = \frac{1}{2} \left[ \delta(\omega - \Omega) + \delta(\omega + \Omega) \right]
\]

\[
\lim_{t \to \infty} R_i(t) = \frac{1}{2} S(\Omega), \quad \lim_{t \to \infty} R_j(t) \approx 0 .
\]
B.3.3. Spectrum for the Ornstein Uhlenbeck process

\[ \langle b(t)b(0) \rangle = b^2 e^{-\frac{t}{\tau}}, \quad S(\omega) = \frac{2 b^2 \tau}{1 + \omega^2 \tau^2}. \quad (B.21) \]

B.4. Decay rate in the uncorrelated noise limit

Here we will briefly discuss the coherence and relaxation timescales in the uncorrelated noise limit \( t \gg \tau \), particularly relevant for the high frequency surface noise component. In that case the level transition rate, separated by an energy gap \( \omega_0 \) and induced by the noise component \( k \), is given by [22, 40]

\[ r = \frac{1}{4} S_k(\omega_0) \quad (B.22) \]

with \( S_k(\omega) \) the corresponding noise spectrum. Here \( k \) denotes a noise component capable of inducing transitions, i.e. for relaxation processes in the undressed system it can be either the \( x \) or \( y \) component. Different components can be added and the final decay rates be obtained by means of classical rate equations [28, 33]. This situation is illustrated in figure B3 (a) for the \( T_1 \) relaxation and in figure B3 (b) for the dressed state decay in a three level system as the NV-center ground state triplet. This latter case corresponds to the situation appearing in continuous dynamical decoupling.

![Figure B3. Relaxation and coherence time in the NV ground state triplet. (a) \( T_1 \) relaxation rates. (b) \( T_2^\Omega \) rotating frame relaxation for a resonant driving with Rabi frequency \( \Omega \). Here \( |+\rangle = 1/\sqrt{2} (|1\rangle + |-1\rangle) \) and \( |-\rangle = 1/\sqrt{2} (|1\rangle - |-1\rangle) \) correspond to the dressed states.](image)

For the configuration (b) this leads to a rate equation for the state populations of the form

\[
\frac{d}{dt} \begin{pmatrix} p_{|+\rangle} \\ p_{|-\rangle} \\ p_{|\text{dressed}\rangle} \end{pmatrix} = \begin{pmatrix} -\gamma - n_0 & \gamma & n_0 \\ \gamma & -\gamma - n_0 & n_0 \\ n_0 & n_0 & -2 n_0 \end{pmatrix} \begin{pmatrix} p_{|+\rangle} \\ p_{|-\rangle} \\ p_{|\text{dressed}\rangle} \end{pmatrix} \quad (B.23)
\]

with \( \gamma = n + n_0 \) the total transition rate between the dressed states induced by the noise \( z \) and \( y \)-component, respectively, \( n_0 = 1/4 S_z(\omega_0) = 1/4 S_y(\omega_0) \) and \( n = 1/4 S_z(\Omega) \). Here \( \omega_0 \) represents the transition frequency of the bare states and \( r_1 \) corresponds to the pure dephasing rate characterized by the spectral noise at the microwave Rabi frequency \( \Omega \). With \( p_{|+\rangle}(0) = 1 \) this
does lead to the solution
\[ p_{1+}(t) = \frac{1}{3} + \frac{1}{6} \left[ e^{-3n_0 t} + 3 e^{-(2\gamma + n_0) t} \right] \approx \frac{1}{2} \left[ 1 + e^{-(2\gamma + n_0) t} \right] \] (B.24)
wherein the last approximation is valid for short enough times based on the realistic assumption that \( n_0 \ll n \). This allows one to identify the (decoupled) coherence time \( T_2^\Omega \)
\[ T_2^\Omega = \left[ 2 \gamma + n_0 \right]^{-1} = \left[ 2 n + 3 n_0 \right]^{-1} \] (B.25)
leading to (5). Note that the two level analogue can be obtained by retaining only \( \gamma \) in the above equations. An analogue calculation can be performed for the \( T_1 \) relaxation illustrated in figure B3(a), which leads to
\[ T_1 = \left[ 6 n_0 \right]^{-1} \] (B.26)
(or \( T_1 = [4n_0]^{-1} \) for a two level configuration). Comparing (B.26) to (B.25), and noting that \( r_1 \) is suppressed with increasing decoupling amplitudes \( \Omega \), the maximally achievable coherence time in a decoupled system is given by \( T_2^\Omega \leq 2 T_1 \).
(B.27)

Appendix C. Hamiltonian, quantization axis adjustment and hyperfine structure influence

Let us consider a system of NV centers, namely the electron spin-1 ground state triplet manifold \( ^3A \) coupled by a dipolar interaction \( H = H_0 + H_{\text{dip}} \), with the zero-field and external magnetic field contribution \[ H_0 = \sum_i \vec{S}_i \cdot \vec{D}_i \vec{S}_i + \gamma_{\text{el}} \vec{B} \cdot \vec{S}_i , \quad \vec{D} = \text{diag} \left( -\frac{1}{3}D + E, -\frac{1}{3}D - E, \frac{2}{3}D \right) \] (C.1)
Herein \( \vec{D} \) denotes the orientation dependent zero-field splitting tensor given in the principal axis frame defined by the NV symmetry axis, with \( D = 2.87 \text{ GHz} \) and \( E \) a strain induced, for NDs with possible non-zero \( \left| 1 \right\rangle \)\left| 1 \right\rangle \) degeneracy. \( \vec{S}_i \) are spin-1 operators, \( \vec{B} \) denotes the external magnetic field and \( \gamma_{\text{el}} \) is the gyromagnetic ratio of the NV center electron spin. In the principal axis frame (denoted by the primed quantities) \( H_0 \) can be rewritten as
\[ H_0 = \sum_i D \left[ S_{i}^{x^2} - \frac{1}{3} S_{i}^{z^2} \right] + \gamma_{\text{el}} B' \cdot \vec{S}_i \] (C.2)
providing a good choice for either small magnetic fields or in cases where the magnetic field is parallel to the NV center symmetry axis.

The dipolar coupling term has the form \[ H_{\text{dip}} = \sum_{i<j} \frac{\mu_0 \gamma_{\text{el}}^2}{4\pi r_{ij}^3} \left[ \vec{S}_i \cdot \vec{S}_j - 3 \left( \vec{S}_i \cdot \vec{e}_{ij} \right) \left( \vec{S}_j \cdot \vec{e}_{ij} \right) \right] \] (C.3)
with \( \mu_0 \) the magnetic permeability and \( r_{ij} \) and \( \vec{e}_{ij} \) the distance and unit direction vector between NV centers \( i \) and \( j \), respectively. Assuming an equal quantization axis and imposing the secular approximation allows one to approximate (C.3) by
\[ H_{\text{dip}} \approx \sum_{i>j} \frac{1}{2} \left( \frac{\mu_0}{4\pi} \frac{\gamma_{el}^2 \hbar}{r_{ij}^3} \right) \left( 1 - 3 \cos^2 \theta_{ij} \right) \left[ 2 S_i^z S_j^z - \left( S_i^x S_j^x + S_i^y S_j^y \right) \right] \]  

(C.4)

with \( \theta_{ij} \) the angle between \( \vec{e}_{ij} \) and the quantization axis that is given by the external magnetic field direction for \( B \gg D \). Note that the dipolar coupling in the present situation is rather small, e.g. \( \mu_{\text{dip}} \equiv \mu_0 \gamma_{el}^2 \hbar/(4\pi r_{ij}^3) = 2\pi \times 52 \text{ kHz} \) for \( r_{ij} = 10 \text{ nm} \) and therefore small inhomogeneous broadening effects (e.g. different strain contributions) as well as different orientations of the NV-center symmetry axis as will be outlined below, essentially reduce (C.4) to

\[ H_{\text{dip}} \approx \sum_{i>j} \mu_{\text{dip}} \left( 1 - 3 \cos^2 \theta_{ij} \right) S_i^z S_j^z \approx \sum_{i>j} \frac{H_{\text{dip}}}{4} \left( 1 - 3 \cos^2 \theta_{ij} \right) \left( \sigma_i^- \sigma_j^- \mp \sigma_i^x \sigma_j^x \mp \sigma_i^y \sigma_j^y \right). \]  

(C.5)

In the last step a reduction to a two level system, namely to the two states that will be driven by a continuous microwave drive to reduce decoherence, has been performed, using that \( S_j^z \equiv 1 + 1 \rangle \langle 1 + 1 + 1/2(\sigma_j^- - 1_j) \rangle \) or \( S_j^z \equiv 1 - 1 \rangle \langle - 1 + 1/2(\sigma_j^- + 1_j) \rangle \). Note that the single local \( \sigma_z \) terms can be incorporated in the energy part of the Hamiltonian or will be suppressed anyway by adding a strong enough driving.

Creating an arrangement of NDs has the additional complication that the symmetry axis of the NV-center, the axis pointing along \( \text{NV field direction} \), is not controllable, i.e. there exists no common quantization axis in a laboratory frame, leading to a vast orientation dependent distribution of dipolar coupling frequencies. To solve that disadvantage an applied external magnetic field \( (\gamma_{el} B > D) \), sufficiently strong in the sense that its associated energy shift \( (\gamma_{el} B) \) outperforms that of the crystal-field \( D \), can redefine a new and common quantization axis. In the large field limit \( (\gamma_{el} B \gg D) \) the Hamiltonian can be rewritten as

\[ H \approx \sum_i \left( \frac{1}{4} S_i^2 - \frac{1}{3} \hat{s}^2 \right) \left[ D \left( 1 + 3 \cos (2\theta_i) \right) + 3 E \left( 1 - \cos (2\theta_i) \right) \right] + \gamma_{el} B S_z + H_{\text{dip}} \]  

(C.6)

with \( \theta_i \) the angle between the magnetic field direction \( z \) and the symmetry axis of NV-center \( i \) and \( H_{\text{dip}} \) given by (C.3–C.5) with \( \theta_{ij} \) the angle of the vector connecting \( i \) and \( j \) to the \( z \)-axis, i.e. the external magnetic field. Two important prerequisites are achieved that way: first, the quantization axis is now completely determined by the external magnetic field and not by the symmetry axis any more such that the dipolar coupling will be homogeneous and independent of the individual orientations (for equal \( \theta_{ij} \)). Second, it provides individual addressability as there exists an orientation dependent \( (\theta_i) \) distribution of transition frequencies differing in the 10–100 MHz range. Moreover this property of individual addressing is directly linked to the suppression of exchange flip-flop terms in the dipolar coupling, simplifying the dipolar coupling to the form (C.5).

Adding noise \( b(t) \) and an additional resonant continuous driving \( \Omega \) for decoupling, the total Hamiltonian in the two level basis and in a frame rotating with the microwave frequency can be written as (compare to (C.5) and (B.1))

\[ H' \approx \sum_i \frac{b_i(t)}{2} \sigma_i^x + \sum_i \frac{\Omega_i}{2} \sigma_i^z + \sum_{i>j} \frac{J_{ij}}{2} \sigma_i^x \sigma_j^x \text{ with } J_{ij} = 2 \xi_{ij} \left( \frac{\mu_0}{4\pi} \frac{\gamma_{el}^2 \hbar}{r_{ij}^3} \right). \]  

(C.7)

The transition frequency of the selected dressed states \( \omega_0^r \) will be \( \omega_0^r = (D + \gamma_{el} B)/2 \) for a zero and a magnetic field aligned with the NV symmetry axis or
In the limiting case of a strong magnetic field, or more generally for equal quantization axes of \( i \) and \( j \) the parameter \( \xi_{ij} \) is given by (C.5) \( \xi_{ij} = 1/4(1 - 3 \cos^2 \theta_{ij}) \), whereas for general magnetic field magnitudes the parameter ranges are plotted in figure 1(c) in the main text, showing that around \( B \gtrsim 0.5 T \) is required for providing an almost uniform coupling. Claiming that the interaction strength should be equal in all spatial directions the maximal dipolar coupling is achieved in a linear chain and in a 2D array when the magnetic field is parallel to the chain (\( \xi_{ij} = -1/2 \)) and orthogonal to the plane (\( \xi_{ij} = -1/4 \), respectively. As a last remark it should be noted that the combination of a strong magnetic field and the condition \( \cos \theta_{ij} = 1/\sqrt{3} \) could be used to decouple the system from the dipolar interaction.

**C.1. NV\(^{-}\)-center hyperfine-structure and its influence on the decoupled gate interaction**

An additional complication arises from the hyperfine structure associated with the nuclear spin of the nitrogen atom involved in the vacancy center (spin \( I = 1 \) for N-14 or spin \( I = 1/2 \) for the N-15 isotope). Other nuclear spins will be neglected in the description, assuming that they can be efficiently described in the spin bath decoherence framework. The ground state level structure in the principal axis frame (analogue to (C.2)) is then given by [59, 60]

\[
H_{gs} = H_0 + H_{\text{nucl}} + H_{\text{hyp}} \quad \text{with} \quad H_{\text{nucl}} = \sum \gamma_i I_i^2 - \sum \gamma_i \vec{B}_i \cdot \vec{I}_i^\prime, \quad H_{\text{hyp}} \approx A_{\parallel} S_\parallel I_\parallel^\prime \quad \text{(C.8)}
\]

with \( H_0 \) the pure electron spin-Hamiltonian given by (C.2) and \( H_{\text{nucl}} \), \( H_{\text{hyp}} \) the (nitrogen) nuclear spin part and the hyperfine coupling interaction, respectively. Herein the quadrupole splitting
\[ P = -4.95 \text{ MHz}, \ \text{the gyromagnetic ratio} \ \gamma_f \simeq 3.1 \text{ MHz T}^{-1} \ \text{and the coupling constant} \ \Lambda \simeq -2.16 \text{ MHz. For the regime of our proposal} \ (B = 0.5 \text{ T}), \ \text{this leads to a hyperfine-structure level scheme as depicted in figure C1. With the selection rule} \ \Delta m_I = 0 \ \text{it becomes clear that neighboring transitions between two different electron spin states differ by} \ \Delta \omega \sim 2.2 \text{ MHz. In order to avoid off-resonant microwave transitions that would lead to an imperfect decoupling and a different form of the effective dipolar coupling} \ H_{I,M_F} \ \text{as is most easily verified in the limit of large detunings, several strategies can be followed. (i) The most simple one consists of eliminating the hyperfine structure by sufficiently large microwave driving fields} \ \Omega \gg |\Lambda|. \ \text{That way, the hyperfine coupling is suppressed, or analogously all possible nuclear states are excited simultaneously in the strong field limit, and there is thus no need to distinguish between individual hyperfine states. (ii) A second option, though not optimal here due to its insufficient noise decoupling strength, would be the regime of weak microwave driving} \ \Omega \ll |\Lambda|, \ \text{in which only a single nuclear spin state transition is excited. (iii) A third possibility to achieve an effective two level system consists of polarizing the nuclear spin prior to the actual experiment. Together with the nuclear spin selection rules this results in a single possible transition and has been demonstrated as well at room [60–62] and at low temperatures [42, 63].}

\textbf{Appendix D. Noise spectrum and numerical noise simulation}

\textit{D.1. Noise spectrum for a fluorine terminated surface}

Here we will outline the calculation of the noise spectrum arising from a bath of surface spins, following the approach developed in [22, 64]. This allows one to identify the relevant noise parameters, namely the root mean square noise amplitude and the noise correlation time, that have been used in the discussion of section 3. We will focus on a fluorine (nuclear spin) terminated surface and briefly discuss the influence of potential electronic surface spins at the end of this appendix.

Terminating the ND surface by fluorine, oxygen or hydrogen / hydroxyl groups replaces the electron spins associated with the sp2-hybridized orbitals by much weaker nuclear spins [29] and therefore reduces the dipolar interaction strength (see table D1) between surface spins by a factor of \(10^{-6}\) (as given by the square ratio of the corresponding gyromagnetic ratios.) Additionally the coupling to the central spin, the electron spin of the NV center, reduces by a factor of \(10^{-3}\). Recalling that the pure dephasing noise responsible for the decoherence mechanism can be described by a fluctuating magnetic field and that the strength and fluctuation rate depends on the (hyperfine) coupling to the central spin and the surface spin flip-flop rate, respectively, a significant improvement can be obtained by terminating the surface purely by nuclear spins. As an illustrative example we will concentrate on the fluorine terminated surface

| Table D1. Magnitude for different coupling constants. |
|-----------------------------------------------------|
| Mutual electron spin coupling: | Electron spin—fluorine nuclear spin coupling: | Mutual nuclear spin fluorine coupling: |
| \(c_{el,el} = \left( \frac{\mu_0 \gamma_e^2 \hbar}{4\pi} \right)\) | \(c_{el,fl} = \left( \frac{\mu_0 \gamma_e \gamma_f \hbar}{4\pi} \right)\) | \(c_{fl,fl} = \left( \frac{\mu_0 \gamma_f^2 \hbar}{4\pi} \right)\) |
| 52 MHz (nm\(^3\)) | 74.4 kHz (nm\(^3\)) | 106.3 Hz (nm\(^3\)) |
(nuclear spin 1/2), having the additional advantage of not affecting the charge state of the NV-center and forming a lattice with nearest neighbor distance 2.5 Å [35].

Such a coupled system can be described by

\[ \hat{H} = H_{0}^{NV} + H_{0}^{sf} + H_{int}^{sf} + H_{hf} \]

with \( H_{0}^{NV} \) the NV-center energy Hamiltonian as given in (C.1), \( H_{0}^{sf} \) the magnetic field splitting of the surface nuclear spins, \( H_{int}^{sf} \) the dipolar coupling between surface nuclear spins and \( H_{hf} \) the hyperfine coupling of the surface spins to the central spin (the NV-center electron spin):

\[ H_{0}^{sf} = \sum_{i} \frac{\gamma_{i} B}{2} \sigma_{i}^{z} \]

\[ H_{int}^{sf} \approx \sum_{i>j} \left( \frac{\mu_{0} \gamma_{i} \gamma_{j}}{4 \pi r_{ij}^{3}} \right) \left( 3 \cos^{2} \theta_{ij} - 1 \right) \left( -\sigma_{i}^{z} \sigma_{j}^{z} + \frac{1}{2} \left[ \sigma_{i}^{x} \sigma_{j}^{x} + \sigma_{i}^{y} \sigma_{j}^{y} \right] \right) \]

\[ H_{hf} \approx \sum_{i} \left( \frac{\mu_{0} \gamma_{i} \gamma_{0}}{4 \pi r_{i}^{3}} \right) \left( 1 - 3 \cos^{2} \theta_{i} \right) S_{z} \sigma_{i}^{z} \]

Herein \( S \) denotes the spin-1 operator of the vacancy center, \( \sigma_{k} \) the spin 1/2 operators of the surface nuclear spins, \( r_{ij} \) the distance between spins \( i \) and \( j \), \( r_{i} \) that between surface spin \( i \) and the central spin and \( \theta_{ij} \) and \( \theta_{i} \) the angles between the vector connecting the two coupled spins involved and the external magnetic field. As discussed in appendix C we will assume that the quantization axis of the NV-center is essentially determined by the external magnetic field and not by the symmetry axis of the vacancy center. Alternatively one might assume that the external magnetic field is parallel to the NV symmetry axis. In the two level approximation, used for the driven system in appendix C, one can substitute \( \Delta \rightarrow 1/2(s_{z} \pm 1) \) with \( s_{z} \) the spin 1/2 operator of the quasi-spin. Herein only secular contributions have been retained, and second order nuclear spin flip-flop processes [65–67] are orders of magnitude smaller than the direct ones for the dense spin bath considered and therefore can be neglected.

Calculating the noise spectrum and the corresponding noise parameters is in general intractable for a large number of surface spins due to exponentially increasing computational resources. As early as in 1962 Klauder and Anderson showed by very general arguments that a Lorentzian noise distribution has to be expected in the case of dipolar couplings to a spin bath [68]. Since then various approaches, mean-field and exact approaches in certain limits, have been invented to infer the noise properties and to calculate the decoherence decay rate, ranging from the simple Ornstein–Uhlenbeck model [69] to cluster expansion methods [65, 67, 70, 71]. Here we used the mean-field method described in [22, 64] which corresponds to the lowest order of the cluster expansion methods, the so called pair-correlation approximation, corrected by a mean-field broadening using the method of moments [72]. In the pair-correlation approximation it is assumed that each of the flipping processes in the dipolar coupling (D.2) is independent of all other processes, i.e. the Hilbert-space is substituted by a pair Hilbert space \( (ij) \) wherein \( (H_{ij}) \) follows directly from out of (D.2)

\[ H_{int}^{sf} = \sum_{i>j} \tilde{H}_{ij} = \sum_{(ij)} \tilde{H}_{(ij)} \quad \text{with} \quad \left[ H_{ij}, H_{kl} \right] = 0 \quad \forall \ i, j, \ kl \]

This leads to a discrete spectrum of \( \delta \)-peaks at the different pair-induced transition frequencies and can be justified as long as correlations between those pairs can be neglected, that is as long
as the evolution time from an initial thermal state is short enough such that
\[ 1 - \exp(-q N_{\text{flip}}/N) \] is small [67] (with \( N_{\text{flip}} \) the number of flipped bath spins during the
considered time, \( q \) the number of nearest neighbors and \( N \) the total number of bath spins.)

Higher orders would lead to additional frequency peaks as well as couplings of the already
existing peaks, i.e. a finite lifetime broadening which is taken into account by using a mean-
field type approach based on the theory of moments. From (D.2) and (B.1) the operator for the
effective field on the NV-center follows to be

\[
\hat{b} = \sum_i \left( \frac{\mu_0}{4\pi} \frac{\gamma_i \gamma_n}{r_i^3} \right) (1 - 3 \cos^2 \theta_i) \sigma_i^z \tag{D.4}
\]

and the noise spectrum can be calculated by (see section B.1)

\[
S(\omega) = \int_{-\infty}^{\infty} dt \langle \hat{b}(t)\hat{b}(0) \rangle \exp^{i\omega t}, \tag{D.5}
\]

where in good approximation the initial bath states can be assumed to be uncorrelated with the
NV-center and at room temperature given by \( 1/2^{51} \) [69]. Following the calculation presented in
[22] this leads to

\[
S(\omega) = 2\pi \sum_{i<j} \frac{b_{ij}^2 \Delta_{ij}^2}{b_{ij}^2 + \Delta_{ij}^2} \frac{1}{2\pi \sigma_{ij}^2} \left[ \exp \left( -\frac{(\omega - E_{ij})^2}{2\sigma_{ij}^2} \right) + \exp \left( -\frac{(\omega + E_{ij})^2}{2\sigma_{ij}^2} \right) \right] \tag{D.6}
\]

with

\[
b_{ij} = \left( \frac{\mu_0}{4\pi} \frac{\gamma_i \gamma_n}{r_{ij}^3} \right) (3 \cos^2 \theta_{ij} - 1)
\]

\[
\Delta_{ij} \equiv \frac{1}{4} \left( A_i - A_j \right) \quad \text{with} \quad A_i = 2 \left( \frac{\mu_0}{4\pi} \frac{\gamma_i \gamma_n}{r_i^3} \right) (1 - 3 \cos^2 \theta_i) \tag{D.7}
\]

and \( E_{ij} = 2\sqrt{b_{ij}^2 + \Delta_{ij}^2} \) and \( \sigma_{ij} \) the mean-field broadening used in replacing the original delta-
peaks by Gaussian peaks leading to the same second moment as that obtained by the moment
theory

\[
\sigma_{ij}^2 = \frac{b_{ij}^2 + \Delta_{ij}^2}{4 \Delta_{ij}^2 b_{ij}^2} \sum_{k \neq i,j} \left( b_{ik}^2 A_i^2 + b_{jk}^2 A_j^2 \right). \tag{D.8}
\]

The spectrum (D.6) has been numerically evaluated by randomly distributing nuclear
surface spins on a sphere with equal inter-spin distance and placing the NV-center in the center
of the sphere, i.e. for a sphere radius \( r = 5 \text{ nm} \) a number of 5026 (which corresponds to a
distance of 2.5 \( \text{Å} \)) nuclear spins were distributed on the surface. Assuming an equal
quantization direction for both the NV-center and the nuclear spins (corresponding to a strong
magnetic field or to a magnetic field parallel to the NV symmetry axis) the noise spectrum was
calculated and subsequently fitted to a Lorentzian in order to obtain the noise amplitude \( b \) and
correlation time \( \tau \) defined in (B.21). Depending on the number of surface spins an average over
different random positions was performed.
We performed the same calculation as well for different numbers of electron surface spins (see figure D1) on diamond with radius 5 nm. In that case the decoherence parameters are very poor, e.g. \( T_\mu = 0.1 \, \text{s} \), \( \tau = 21.7 \, \text{ns} \), and \( b = 3.6 \, \text{MHz} \) for 30 surface spins and getting worse on further increasing the number of spins. For such a situation decoupling fields in the range \( \Omega \approx 1 \, \text{GHz} \) are required that, despite still allowing simple two qubit gates (provided the \( \Omega \) stability can be achieved), are intractable for multi-qubit applications that require a certain level of individual addressing. As the validity of the mean-field approach for fast flipping electron spins is debatable, we performed an exact numerical \( T_2 \)-calculation for smaller electron spin numbers (up to 10) showing that the mean-field values seem at least to be correct in their order of magnitude.

D.2. Numerical simulation of the noise process

Based on the noise parameters as obtained in section 3 and (B.21), the numerical simulations have been performed assuming an Ornstein–Uhlenbeck (Gaussian, Markovian and stationary) noise process [26] and its numerical implementation as described in [6, 73].

For such a process the evolution of the random field is governed by the Langevin equation

\[
\frac{db(t)}{dt} = -\frac{1}{\tau} b(t) + \sqrt{c} \, \Gamma(t) \quad (D.9)
\]

with \( \Gamma(t) \) a Gaussian zero-mean noise \([6]\) \((\langle \Gamma(t) \rangle = 0, \langle \Gamma(t) \Gamma(t') \rangle = \delta(t-t'))\). The parameter \( c \) appearing in (D.9) is related to the noise correlation time \( \tau \) and field variance \( b^2 \)
as defined in (1) by \( b^2 = c \tau / 2 \). Exact updating formulas can be obtained for the differential equation (D.9) \( \Delta \xi = - \Delta t = - \beta \) with \( \xi = b(t) \mu + \xi_n \) \( n_1 \) with \( \mu = \exp(-\Delta t / \tau), \quad \xi_n = (c \tau / 2)(1 - \mu^2) \), (D.10)

and \( n_1 \) a unit normal random number. Introducing (D.10) into the corresponding Hamiltonians directly allows for a numeric integration of the associated equations of motion, followed by an averaging process that reveals the correct influence of decoherence.

Appendix E. Systematic error compensation

E.1. Compensation cycle for the two qubit gate interaction

The two qubit gate interaction corresponds essentially to a single qubit rotation in a more complicated two qubit manifold \( \mathcal{M}_1 \) and \( \mathcal{M}_2 \), respectively. Introducing the (unknown) systematic error \( \epsilon \) this results, assuming \( \Omega \gg J \), in the following Hamiltonians

\[
H_{I, \mathcal{M}_k} \approx \frac{J}{2} (1 + \epsilon) S_{\mathcal{M}_k}^{1, 2}
\]

which can also be written as \( H_{I, \mathcal{M}_k} \approx (J/2)(1 + \epsilon)\sigma^{\mathcal{M}_k}_i \) with \( \sigma_{\mathcal{M}_k}^i \) the \( \sigma_i \) operation defined in the manifolds \( \{ l + - \}, \{ l - + \} \) and \( \{ l++ \}, \{ l-- \} \) for \( k = 1 \) and \( k = 2 \), respectively (see figure 3(a) in the main text).

References [44, 74] provide a method to remove the systematic error contribution based on noting that multiples of \( 2 \pi \) pulses with respect to the ideal error-less gate end up with pure \( \epsilon \) contributions which can, together with the property \( \sigma_{\phi}^{\mathcal{M}_k} \sigma_{-\phi}^{\mathcal{M}_k} = 2 \cos \phi \sigma_0^{\mathcal{M}_k} (\sigma_{\phi}^{\mathcal{M}_k} := \cos \phi \sigma_{x}^{\mathcal{M}_k} + \sin \phi \sigma_{y}^{\mathcal{M}_k}) \), be used to create a compensation cycle by means of a Suzuki–Trotter time addition. A compensated gate is then obtained by the sequence (herein the
compensation sequence is marked by the square brackets, figure E1 (b))
\[
\left[ M^{[e]}_\phi (\pi) M^{[e]}_\phi (2 \pi) M^{[e]}_\phi (\pi) \right] M^{[e]}_\phi (\theta) = M^{(e=0)}_\phi (\theta) + \mathcal{O}(\epsilon^3)
\]
(E.2)
with
\[
M^{[e]}_\phi (\theta) = \exp \left( -i(\theta/2)(1 + \epsilon) \sigma^z_\phi \right) \exp \left( -i H_{1, M_i} \theta / J \right), \quad 2 \pi \cos \phi = -\theta / 2
\]
(E.3)
and
\[
M^{[e]}_\phi (\theta) = T_\phi M^{[1]}_\phi (\theta) \overline{T}_\phi \quad \text{with} \quad T_\phi = \exp \left( -i\phi / 2 \sigma^z_\phi \right).
\]
Note that
\[
\sigma^z_{M_i} \overline{M}_i = \left\{ 1 / 2 (\sigma^1_\phi + \sigma^2_\phi), \sigma^1_\phi, \sigma^2_\phi \right\}
\]
(E.4)
with the upper and lower sign referring to \( M_1 \) and \( M_2 \), respectively, and the last two options having additional contributions that however do not affect the gate manifold.

\textbf{E.2. Compensated } \sigma_z \otimes \sigma_z \text{ interaction for multiple qubits}

Assuming systematic errors \( \epsilon_{ij} \) in the dipolar coupling term resulting in the Hamiltonian
\[
H^{[c]}_{zz} = \frac{J}{2} \sum_{i \neq j} (1 + \epsilon_{ij}) \sigma^z_i \sigma^z_j
\]
(E.5)
leads, besides the desired contribution, to additional \( \epsilon_{ij} \) dependent terms in the defective evolution operator
\[
M^{[c]}_\phi (\theta) = \prod_{(i,j)} M^{[c]}_{i,j} \quad \text{with} \quad M^{[c]}_{ij} (\theta) = \exp \left( -i \frac{\theta}{2} \sigma^z_i \sigma^z_j \right) \exp \left( -i \frac{\theta}{2} \epsilon_{ij} \sigma^1_i \sigma^1_j \right).
\]
(E.6)
A (compensation) contribution only involving the systematic error part can be obtained by any multiple of \( 2 \pi \)-pulses \( M^{[c]}_{ij} (n 2 \pi) = (-1)^n \exp \left( -i n \pi \epsilon_{ij} \sigma^1_i \sigma^1_j \right) \) with \( n \in \mathbb{Z} \). This property forms the basis for creating a compensation sequence provided that the relatively fixed phase, limited by the \( 2 \pi \) condition, can be controlled. This latter prerequisite is achieved using that
\[
\left( \sigma^z_\phi + \sigma^z_{-\phi} \right) \sigma^z_i = T_\phi \left( \sigma^z_i \sigma^z_j \right) T^\dagger_\phi + T_{-\phi} \left( \sigma^z_i \sigma^z_j \right) T^\dagger_{-\phi} = 2 \cos \phi \sigma^1_i \sigma^1_j
\]
(E.7)
with \( T_\phi = \exp (-i \phi / 2 \sigma^1_i) \) and \( \sigma_{-\phi} = \cos \phi \sigma_z - \sin \phi \sigma_i \). Performing a Suzuki–Trotter addition of the two components \( \sigma_\phi \) and \( \sigma_{-\phi} \) therefore allows for the construction of a compensated sequence
\[
\left[ M^{[c]}_{ij, \phi} (n 2 \pi) M^{[c]}_{ij, -\phi} (n 4 \pi) M^{[c]}_{ij, \phi} (n 2 \pi) \right] M^{[c]}_{ij} (\theta) = \exp \left( -i \frac{\theta}{2} \epsilon_{ij} \sigma^1_i \sigma^1_j \right) + \mathcal{O}(\epsilon_{ij}^3)
\]
(E.8)
with \( 4 n \pi \cos \phi = -\theta / 2 \) and \( M^{[c]}_{ij, \phi} (\theta) = T_\phi M^{[c]}_{ij} (\theta) T^\dagger_\phi \). Taking into account that the error scales as \( \mathcal{O}(n \epsilon_{ij}^2) \) the parameter \( n \) should be as small as possible, leading to the obvious choice \( n = 1 \). This can then be straightforwardly extended to the total evolution \( M^{[e]}_\phi \) as defined in (E.6), exhibiting the same form as (E.8) and \( T_\phi = \exp \left( -i \phi / 2 \sum_{i \neq j} \mathcal{N} \sigma^1_i \right) \) and \( \mathcal{N} \) the space of non-neighboring qubits. As an example the method is illustrated for the creation of a four qubit cluster state in figure E1(a), showing that high decoupling fields are required in the presence of decoherence in order to benefit from the compensation despite the significant increased gate time that is problematic in terms of decoherence.

As outlined above, smaller values for \( n \) lead to an improved scaling of the compensation method, i.e. to a smaller remaining error contribution and in the case when decoherence is
relevant, to a significant reduction of the compensated gate time. Favorably, the single and two particle case allows for the construction of a compensation sequence with \( n = 1/2 \) (E.2), which is beyond the \( n \pi \) analysis outlined above in that the \( \epsilon \) independent contributions survive in the first stage. However this concept cannot be extended to multiple particles; a detailed analysis shows that for such a \( n = 1/2 \) sequence to be valid, the rotation operator \( T_\phi \) has to commute with the remaining \( \epsilon \)-independent contribution involving \( \phi \to -\phi \), which is valid for an odd but not for an even commutation, the latter case relevant for the multiparticle situation

\[
\begin{align*}
\sigma_{\phi_{i2}} \leftrightarrow e^{-i\pi/2} = e^{-i\phi/2} e^{-i\pi/2} = e^{-i\phi/2} e^{-i\pi/2} \left[ \sigma_{i1} \sigma_{i2} \sigma_{j1} \sigma_{j2} \right]. (E.9)
\end{align*}
\]

E.3. Non-next nearest neighbor couplings in the compensation sequence

The Hamiltonians (E.1) and (E.5) used to describe the compensation mechanism have been defined up to next-nearest neighbors, i.e. higher order contributions were neglected so far. However, whereas those contributions give only a small correction for simple \( \pi/2 \) multiqubit pulses, as can be seen from the numerical results in the main text, they are crucial in the compensation sequence due to the prolonged pulse time. One has to distinguish between two types of higher order couplings: even couplings defined as next-nearest neighbor and third, fifth, ...nearest neighbor couplings and odd couplings as second, fourth, ...nearest and diagonal couplings. Whereas the first ones have always the form of a \( \sigma_i \otimes \sigma_i \) coupling and are automatically compensated for by the next-nearest neighbor based compensation sequence, the second class consists just of the reduced manifold \( M_k \) couplings and is not removed by the compensation sequence. This failure for odd couplings originates both from the fact that the compensation pulse acts on both qubits involved such that (E.7) is not fulfilled any more, and from the fact that the manifold interaction does not commute with the \( \sigma_i \sigma_i \) type contributions such that a splitting of the evolution in a perfect and defective part as in (E.6) is not possible any more.

A solution to that problem consists of eliminating odd order couplings from the beginning by adding different contributions in time. Examples for that are given for a two qubit state in

![Figure E2. Removing second nearest neighbor interactions for a linear four qubit configuration. Each of the blocks removes second nearest neighbor couplings; however both blocks are needed to restore the proper next nearest neighbor interaction. Blue lines denote \( \sigma_\uparrow \sigma_\uparrow \) and red lines \( M_\uparrow \) interactions, while dashed lines denote a negative sign of the corresponding interaction. Red marked qubits denote that the interaction is embedded between a \( U \) and \( U^\dagger \) pulse with \( U = \exp(-i\pi/2\sigma_z) \). Couplings higher than second order are neglected in the illustration.](image)
figure 4(b) in the main text and in figure E2 for second nearest neighbor couplings. With the evolutions obtained that way as a starting point higher orders can be removed in a concatenated way benefiting from the different evolution timescales dependent on the qubit distance. For the multiqubit compensation sequence (E.8) it is sufficient to remove odd order couplings up to the second order (e.g. up to couplings of qubit one to five), because higher order effects are too weak to make significant contributions.

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